SORPTION AND DESORPTION BEHAVIOUR OF CHROMIUM (VI) IN SOILS

Thesis

Submitted to the Punjab Agricultural University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE
in
SOIL SCIENCE
(Minor Subject: Chemistry)

By

Satnam Kaur
(L-2016-A-149-M)

Department of Soil Science
College of Agriculture
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CERTIFICATE - I

This is to certify that the thesis entitled, **"Sorption and desorption behaviour of chromium (VI) in soils"** submitted for the degree of **M.Sc.** in the subject of **Soil Science** (Minor subject: **Chemistry**) of the Punjab Agricultural University, Ludhiana, is a bonafide research work carried out by **Ms. Satnam Kaur (L-2016-A-149-M)** under my supervision and that no part of this thesis has been submitted for any other degree.

The assistance and help received during the course of investigation have been fully acknowledged.

(Dr. Dhanwinder Singh)
Major Advisor
Senior Soil Chemist
Department of Soil Science
Punjab Agricultural University
Ludhiana-141004, India

CERTIFICATE – II

This is to certify that the thesis entitled, **"Sorption and desorption behaviour of chromium (VI) in soils"** submitted by **Ms. Satnam Kaur** (Admn. No. **L-2016-A-149-M**) to the Punjab Agricultural University, Ludhiana, in partial fulfillment of the requirements for the degree of **M.Sc.,** in the subject of **Soil Science** (Minor subject: **Chemistry**) has been approved by the Student's Advisory Committee after an oral examination on the same.

(Dr. Dhanwinder Singh)
Major Advisor

(Dr. Vishal Goyal
External Examiner
Assistant Soil Chemist
Deptt. of Soil Science
CCS HAU, Hissar

(Dr. O.P. Chaudhary)
Head of the Department

(Dr. Gurinder Kaur Sangha)
Dean Postgraduate Studies

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Date:

Satnam Kaur

Place:

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ABSTRACT

Sorption and desorption of chromium (VI) were examined on twenty eight surface and sub-surface soil samples collected from four different locations viz Ludhiana, Jalandhar, Malerkotla and Mandi Gobindgarh. Sorption of Cr was carried in presence of background electrolyte 0.01 M $Ca(NO_3)_2$ solution. Sorbed Cr was desorbed back by resuspending the same soil samples in fresh Cr-free 0.01 M $Ca(NO_3)_2$ and giving five repeated washings sequentially. Chromium sorption was observed to be significantly and negatively correlated with pH both in surface (r = -0.764) and sub-surface samples (r = -0.757). Simple linear regression model for different soil variables showed that 58% and 57% of the variation in Cr sorption in the surface and sub-surface soils under study, respectively, was explained by soil pH. The stepwise multiple regression model showed that other factors, like total Cr and EC could marginally increase the variability to 68% in surface soils and OC to 61% in sub-surface soils. The amounts and patterns of chromium desorbed varied among the soils. Chromium desorption was significantly and positively correlated with soil pH both in surface (r = 0.635) and sub-surface (r = 0.438) soil samples. Among polluted samples, 51% variability was explained by pH in surface samples and 80% variability in sub-surface samples by pH, EC and clay content. In non-polluted soils, CEC, $CaCO_3$, DTPA extractable Cr and total Cr together explained 91% variability in Cr desorption in surface samples and OC, CEC and DTPA extractable Cr explained 66% variation in sub-surface samples. The Cr sorption data of the three selected soil samples were very well described by Langmuir adsorption isotherm (R^2=0.959 to 0.994), Freundlich adsorption isotherms (R^2= 0.985 to 0.994) and Dubinin–Radushkevich (D-R) adsorption isotherm (R^2=0.926 to 0.973). The Cr desorption data of the soils well fitted to Langmuir desorption isotherm (R^2= 0.967 to 0.992). Effect of pH on Cr sorption-desorption was also studied by adjusting the pH of each of three selected surface soil samples in the range of 6-8 in the laboratory. The sorption of chromium decreased with the increase in soil pH from 6 to 8. Chromium sorption data fitted well in Langmuir (R^2= 0.924 to 0.995), Freundlich (R^2= 0.977 to 0.995) and (D-R) (R^2= 0.954 to 0.981) adsorption isotherm equations at all pH levels. Percent chromium desorbed increased with the increase in pH from 6 to 8.

Key words: Chromium, Sorption, Desorption, pH, Isotherms

Signature of Major Advisor **Signature of the Student**

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ਸਾਰ

ਪੰਜਾਬ ਦੇ ਚਾਰ ਸ਼ਹਿਰਾਂ, ਲੁਧਿਆਣਾ, ਜਲੰਧਰ, ਮਲੇਰਕੋਟਲਾ ਅਤੇ ਮੰਡੀ ਗੋਬਿੰਦਗੜ੍ਹ ਵਿੱਚੋਂ 28 ਵੱਖ-ਵੱਖ ਜਗ੍ਹਾ ਤੋਂ ਸਤਹ ਅਤੇ ਹੇਠਲੀ ਮਿੱਟੀ ਦੇ ਨਮੂਨੇ ਲਏ ਗਏ। ਇਕੱਤਰ ਕੀਤੇ ਗਏ ਨਮੂਨਿਆਂ ਵਿੱਚ ਕ੍ਰੋਮੀਅਮ ਦੀ ਸੋਰਪਸ਼ਨ ਅਤੇ ਡੀਸੋਪਰਸ਼ਨ ਵਿਵਹਾਰ ਦੇਖਿਆ ਗਿਆ। ਕ੍ਰੋਮੀਅਮ ਦੀ ਸੋਰਪਰਸ਼ਨ ਇਲੈਕਟ੍ਰੋਲਾਈਨ 0.01 M $Ca(NO_3)_2$ ਘੋਲ ਦੀ ਮੌਜੂਦਗੀ ਵਿਚ ਕੀਤੀ ਗਈ। ਮਿੱਟੀ ਤੇ ਸੋਰਬ ਹੋਏ ਕ੍ਰੋਮੀਅਮ ਨੂੰ ਕ੍ਰੋਮੀਅਮ ਮੁਕਤ 0.01 $Ca(NO_3)_2$ ਘੋਲ ਵਿਚ ਦੁਬਾਰਾ ਰੱਖ ਡੀਸੋਰਬ ਕੀਤਾ ਗਿਆ। ਡੀਸੋਰਪਸ਼ਨ ਦੀ ਇਹ ਪ੍ਰੀਕਿਰਿਆ ਪੰਜ ਵਾਰ ਦੋਹਰਾਈ ਗਈ। ਦੋਨੋਂ ਹੀ ਤਰ੍ਹਾਂ ਦੇ ਨਮੂਨਿਆਂ ਅੰਦਰ ਖਾਰੀ ਅੰਗ ਸੋਰਬ ਹੋਏ ਕ੍ਰੋਮੀਅਮ ਨਾਲ ਨਾਕਾਰਾਤਮਕ ਤੌਰ ਤੇ ਸੰਬੰਧਿਤ ਸੀ। ਸਾਧਾਰਨ ਰੇਖਾਤਮਕ ਰਿਗਰੈਸ਼ਨ ਮਾਡਲ ਦੀ ਵਰਤੋਂ ਕਰਨ ਤੇ ਦੇਖਿਆ ਗਿਆ ਕਿ ਖਾਰੀ ਅੰਗ ਨੇ ਸਤਹ ਅਤੇ ਹੇਠਲੀ ਮਿੱਟੀ ਦੇ ਨਮੂਨਿਆਂ ਅੰਦਰ ਕ੍ਰੋਮੀਅਮ ਦੀ ਸੋਰਪਸ਼ਨ ਵਿਚ 58% ਅਤੇ 57% ਤੱਕ ਭਿੰਨਤਾ ਦਰਸਾਈ। ਪੜਾਅਵਾਰ ਰਿਗਰੈਸ਼ਨ ਮਾਡਲ ਦਰਸਾਉਂਦਾ ਹੈ ਕਿ ਹੋਰ ਕਾਰਨ ਜਿਵੇਂ ਕੁੱਲ ਕ੍ਰੋਮੀਅਮ ਅਤੇ ਚਾਲਕਤਾ ਸਤਹ ਮਿੱਟੀ ਦੇ ਨਮੂਨਿਆਂ ਵਿੱਚ 68% ਅਤੇ ਹੇਠਲੀ ਮਿੱਟੀ ਦੇ ਨਮੂਨਿਆਂ ਵਿੱਚ ਜੈਵਿਕ ਕਾਰਬਨ 61% ਤੱਕ ਬਦਲਾਅ ਲਿਆ ਸਕਦੇ ਹਨ। ਮਿੱਟੀ ਦੇ ਨਮੂਨਿਆਂ ਵਿਚਕਾਰ ਕੁੱਲ ਡੀਸੋਰਬ ਹੋਇਆ ਕ੍ਰੋਮੀਅਮ ਖਾਰੀ ਅੰਗ ਨਾਲ ਅਰਥਪੂਰਨ ਅਤੇ ਸਕਾਰਾਤਮਕ ਤੌਰ ਤੇ ਸਬੰਧਿਤ ਸੀ। ਪ੍ਰਦੂਸ਼ਿਤ ਸਤਹ ਮਿੱਟੀ ਦੇ ਨਮੂਨਿਆਂ ਵਿਚ ਸੋਰਬ ਹੋਏ ਕ੍ਰੋਮੀਅਮ ਵਿੱਚ 51% ਤੱਕ ਭਿੰਨਤਾ ਖਾਰੀ ਅੰਗ ਦੁਆਰਾ ਦਰਸਾਈ ਗਈ ਅਤੇ ਹੇਠਲੀ ਮਿੱਟੀ ਵਿਚ 80% ਤੱਕ ਭਿੰਨਤਾ ਖਾਰੀ ਅੰਗ, ਚਾਲਕਤਾ ਅਤੇ ਕਲੇਅ ਮਾਤਰਾ ਦੁਆਰਾ ਦਰਸਾਈ ਗਈ। ਗ਼ੈਰ ਪ੍ਰਦੂਸ਼ਿਤ ਸਤਹ ਅਤੇ ਹੇਠਲੀ ਮਿੱਟੀ ਦੇ ਨਮੂਨਿਆਂ ਵਿਚਕਾਰ 91% ਭਿੰਨਤਾ ਕਟਾਇਨ ਅਕਸੇਜ ਕੇਪੇਸਟੀ, ਕੈਲਸ਼ੀਅਮ ਕਾਰਬੋਨੇਟ ਮਾਤਰਾ, ਡੀ.ਟੀ.ਪੀ.ਏ. ਅਕਸਟਰੈਕਟੇਬਲ ਕ੍ਰੋਮੀਅਮ ਅਤੇ ਕੁੱਲ ਕ੍ਰੋਮੀਅਮ ਦੁਆਰਾ ਅਤੇ 66% ਭਿੰਨਤਾ ਜੈਵਿਕ ਕਾਰਬਨ, ਕਟਾਇਨ ਅਕਸੇਜ ਕੇਪੇਸਟੀ ਅਤੇ ਡੀ.ਟੀ.ਪੀ.ਏ. ਅਕਸਟਰੈਕਟੇਬਲ ਕ੍ਰੋਮੀਅਮ ਮਾਤਰਾ ਦੁਆਰਾ ਦਰਸਾਈ ਗਈ। ਤਿੰਨ ਚੁਣੇ ਗਏ ਨਮੂਨਿਆਂ ਦਾ ਸੋਰਪਰਸ਼ਨ ਡਾਟਾ ਲੈਂਗਮੁਅਰ (R^2=0.959 ਤੋਂ 0.994), ਫਰੈਂਡਲਿਚ (R^2=0.985 ਤੋਂ 0.994) ਅਤੇ ਡੂਬਿਨਨ-ਰਾਧੂਕੇਵਿਚ (R^2=0.926 ਤੋਂ 0.973), ਐਡਸੋਰਪਸ਼ਨ ਆਇਸੋਥਰਮ ਵਿਚ ਸਹੀ ਫਿਟ ਆਉਂਦਾ ਹੈ। ਕ੍ਰੋਮੀਅਮ ਡੀਸੋਰਪਸ਼ਨ ਡਾਟਾ ਲੈਂਗਮੁਅਰ ਡੀਸੋਰਪਸ਼ਨ ਆਇਸੋਥਰਮ ਵਿਚ ਸਹੀ ਫਿਟ ਬੈਠਦਾ ਹੈ। ਇਸ ਤੋਂ ਇਲਾਵਾ ਮਿੱਟੀ ਦੇ ਖਾਰੀ ਅੰਗ ਦਾ ਪ੍ਰਭਾਵ ਕ੍ਰੋਮੀਅਮ ਦੀ ਸੋਰਪਸ਼ਨ ਉੱਪਰ ਦੇਖਣ ਲਈ ਤਿੰਨ ਮਿੱਟੀ ਦੇ ਨਮੂਨੇ ਚੁਣੇ ਗਏ। ਕ੍ਰੋਮੀਅਮ ਸੋਰਪਸ਼ਨ ਮਿੱਟੀ ਦੇ ਖਾਰੀ ਅੰਗ 6-8 ਤੱਕ ਵੱਧਣ ਨਾਲ ਘਟੀ ਪਾਈ ਗਈ। ਕ੍ਰੋਮੀਅਮ ਸੋਰਪਸ਼ਨ ਡਾਟਾ ਲੈਂਗਮੁਅਰ (R^2=0.924 ਤੋਂ 0.995); ਫਰੈਂਡਲਿਚ (R^2=0.977 ਤੋਂ 0.995) ਅਤੇ ਡੂਬਿਨਨ-ਰਾਧੂਕੇਵਿਚ (R^2=0.954 ਤੋਂ 0.981) ਐਂਡਸੋਰਪਸ਼ਨ ਆਇਸੋਥਰਮ ਵਿਚ ਸਹੀ ਫਿੱਟ ਬੈਠਿਆ ਪਾਇਆ ਗਿਆ ।

ਮੁੱਖ ਸ਼ਬਦ: ਕ੍ਰੋਮੀਅਮ, ਸੋਰਪਸ਼ਨ, ਡੀਸੋਰਪਸ਼ਨ, ਖਾਰੀ ਅੰਗ, ਆਇਸੋਥਰਮ

ਮੁੱਖ ਸਲਾਹਕਾਰ ਦੇ ਹਸਤਾਖਰ

ਵਿੱਦਿਆਰਥੀ ਦੇ ਹਸਤਾਖਰ

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CHAPTER-I

INTRODUCTION

Chromium (Cr) is a transitional metal with atomic number 24. It belongs to group VI of the periodic table. The electronic configuration of chromium is $[Ar]3d^5 4s^1$.

Two stable oxidation states of chromium are Cr (III) and Cr (VI) though it can exist in several oxidation states from 0 to VI. Among the two, Cr (VI) is the more toxic form of chromium due to its high mobility and water solubility. Cr (VI) is 100 times more toxic and more mobile than Cr (III) (Sang *et al* 2002). On the other hand Cr (III) is immobile and insoluble as it can be strongly adsorbed on to soil minerals, and soil organic matter and form mineral precipitates (Palmer and Wittbrodt 1991; Losi *et al* 1994). Sorption and desorption of Cr (III) are important determinants of the availability of soluble forms of Cr and for further oxidation to toxic Cr (VI) in soils. Chromate ion (CrO_4^{2-}) and dichromate ion ($Cr_2O_7^{2-}$) are most soluble and toxic forms of hexavalent chromium. Chromium distribution is also controlled by redox processes. The main oxidants in soils, which can oxidize Cr (III) to Cr (VI) are Mn oxides (Kim *et al* 2002). On the other hand, ferrous iron (Fe^{2+}) (Buerge and Hug 1997), organic matter (Wittbrodt and Palmer 1995), and reduced sulfur (S^{2-}) (Patterson *et al* 1997) can reduce Cr (VI) to Cr (III). When high amount of organic matter and Fe (II) are present in soil, Cr (VI) is reduced to Cr (III) (Richard 1991). Chromium (Cr) is known to be widespread chemical contaminant of soil and hence considered to be threat to the environment. Untreated waste, municipal sewage sludges, fertilizers etc. all can contribute to Cr accumulation in soils. The concentration range of Cr in soil ranges between 5 and 1500 mg kg^{-1}. Maximum permissible limit of total chromium in soils is less than 75 mg kg^{-1}.Chromium contamination is a major concern in agricultural land near the industrial areas. Chromium is used on a large scale for electroplating, paper and pulp production, wood preservation, production of paints and pigments, tannery and chromium chemical production. Chromium is also used for producing stainless steel as it has high corrosion resistance. Disposal of industrial waste on to the land and water bodies results in the increase in concentration of Cr in soil and this increased concentration posses hazards to plant growth. An increase in the Cr content of the soil has been observed when sewage sludge is used as a soil amendment in the agricultural fields. Beside being a source of essential nutrients, sewage water also adds a significant amount of heavy metal, which can effect the plant growth badly. So, irrigating with sewage effluents increases heavy metals such as Cr in soil (Rattan *et al* 2005). Elevated levels of different heavy metals in soils regularly irrigated with sewage water than ground water have also been found (Aghabarati *et al* 2008).

Ludhiana is one of the big industrial city of Punjab. Untreated waste from electroplating, dyeing, chemical and dairy industries is released into Budda Nala and farmers use this contaminated water to irrigate the crops. Maximum permissible limit of Cr for irrigation water is 0.1mg L^{-1} but concentration of Cr in Budda Nala sewage water was reported to be 0.40 mg L^{-1} (Hira *et al* 2006) which can proves toxic to plants when sewage water is used for irrigation for long time. Ludhiana city sewage has been reported to be contaminated with high amounts of toxic elements such as chromium (Cr), cadmium (Cd), nickel (Ni), lead (Pb) and it has potential to pollute soil and water and eventually enter the food chain (Singh and Kansal 1985, Arora *et al* 1985; Gupta *et al* 1986). Azad *et al* (1987) observed that when agricultural fields are irrigated with contaminated water, the physical and chemical properties of soil were affected. Potato plants in the field irrigated with sewage water contaminated with leather industry effluents reported very high level of Cr (Brar *et al* 2000).

Chromium containing industrial effluents can be absorbed by the plants in the form of Cr (III) and Cr (VI). Under normal conditions, concentration of Cr in plants is less than 1µg g^{-1}. Chromium affect positively on plant growth by influencing the levels of plant growth hormones like cytokinin and its interaction with nucleic acids (Alloway *et al* 2013), however Cr toxicity can also occur in plants if absorbed in high concentration.

The bioavailability of Cr in soil depends on its concentration in soil solution and the ability of the soil to release it from the solid surfaces. Chromium is sorbed on a wide range of soil constituents such as iron and aluminium oxides, clay minerals and organic matter. Chromium applied to soil may undergoes several reactions with different soil constituents which ultimately affect its mobility and hence availability to plants. Sorption and desorption processes are important to understand fate and transport of chromium in environment. The level of Cr in soil solution is controlled by sorption and desorption reactions. The Cr ions in soil solution are always in equilibrium with the Cr ions adsorbed on solid phase. Sorption of Cr depends upon factors like soil pH, clay content, competing effect of other cations, inorganic and organic ligands, cation exchange capacity of soil (Steward *et al* 2003). Soil containing more colloidal, organic matter and mineral materials can sorb Cr to a greater extent than soils poor in these reactive materials. Soil pH and redox potential are important factors that regulate the sorption/desorption of chromium. Cr (VI) adsorption decreases as pH increases and the adsorption of Cr (III) increases as pH increases (Griffen *et al* 1977). Sorption of Cr is also influenced by presence of other heavy metal cations in soil. Sorption of Cr increases with the presence of heavy metals like Cd, Pb, Zn, Ni. This is due to increase in the number of reactive surface groups having ability to complex with chromate ions (Adhikari 2010). The pH of the soil act as an important factor which affects the desorption of Cr. Desorption of chromium increased with increase in pH of the soil. The cumulative amount of Cr desorbed was higher in alkaline surface soils (pH 7.9) as compared to acidic sub-surface soils (Avudainayagam *et al* 2001).

Objectives

The present study was designed keeping in view the following objectives:

1. To study the sorption and desorption of chromium from range a of Punjab soils in relation to soil properties.
2. To characterize the Cr behaviour in soil and influence of pH as described by sorption / desorption isotherms.

CHAPTER-II

REVIEW OF LITERATURE

Literature pertinent to present investigation was reviewed under the following heads.

2.1 Chromium in environment and its speciation

2.2 Sorption and desorption of chromium in soils

2.3 Factors affecting sorption/desorption of chromium

2.1 Chromium in environment and its speciation

2.1.1 Chromium in rocks and minerals

Oze *et al* (2004) found that serpentine soils containing higher concentration of Cr and other toxic elements like Ni, Co, and Mn were formed by weathering of ultramafic rocks and serpentinites in the Franciscan Complex of California. Concentration of chromium in serpentine soil profiles varied between 1,725 to 4,760 mg kg^{-1} related directly to the weathering of chromite and Cr-magnetite. Chromium-bearing igneous and metamorphic silicates in the protolith and Cr-bearing clay minerals in the soil were observed to be the sources of chemically mobile and bioavailable Cr.

Alexakis and Gamvroula (2014) quantified the potentially toxic elements (As, Mo, Ni, Cr, Hg and U) in rocks and sediments of the Oropos-Kalamos basin, Greece. The concentration of As, Mo, Ni, Cr, Hg and U were high in lignite as compared to crustal element averages. The ultramafic rock bodies surrounding the basin were drained by rivers and streams into the lignite deposition which resulted in high concentration of chromium.
High chromium contents present in Oropos-Kalamos lignite (212.3mg kg^{-1}), chromiferous iron ore (256.6mg kg^{-1}) and alluvial deposits (212.5mg kg^{-1}) resulted in contamination of Oropos-Kalamos groundwater.

Shen *et al* (2015) studied the Cr isotope composition of 27 metamorphic mafic rocks from different metamorphic zones of the Dabie orogen to investigate the Cr isotope behavior during continental crust subduction. They found that BSE (Bulk silicate earth)-like Cr isotope largely retained by subducted continental crust despite of undergoing metamorphic dehydration and subsequent exhumation. The increase in Cr isotope compositions of cogenetic Luobusa chromitites and peridotites was in the following sequence: chromite-free peridotites<chromite-bearing peridotite.

2.1.2 Chromium in groundwater

Naturally occurring Cr (VI) had been reported by Oze *et al* (2007) in surface and ground waters of New Caledonia. Rock strata rich in Cr (III)-bearing minerals, in particular chromite, were universally found in the areas that occur near convergent plate margins. They reported accelerated dissolution of chromite and subsequent oxidation of Cr (III) to aqueous

Cr (VI) in the presence of birnessite, a common manganese mineral that explained the generation of Cr (VI) by a Cr (III)-bearing mineral considered geochemically inert. The results demonstrated that Cr (III) within ultramafic- and serpentinited derived soils/sediments could be oxidized and dissolved through natural processes, leading to hazardous levels of aqueous Cr (VI) in surface and groundwater.

Fantoni *et al* (2002) observed that thirty out of the 58 groundwaters sampled in Italy had undetectable Cr (III) contents and equal concentrations of total dissolved Cr and Cr (VI). The dissolved Cr was present as Cr (VI) with its concentrations of 5–73 µg L^{-1}which was above the maximum permissible level for drinking waters. Local ophiolites rocks such as serpentinites and ultramafites were rich in chromium and represented as a source for groundwater contamination. Chromium was present as Cr (III) in rock-forming minerals. The oxidation of Cr (III) to Cr (VI) was performed by different electron acceptors such as Mn oxides, gaseous O_2 and H_2O_2. The oxidation of trivalent form of chromium was required for its release to the aqueous solution. Higher Cr (VI) concentrations measured in the waters of the study area were attributed to natural pollution.

Kazakis *et al* (2017) observed the hexavalent chromium as a major contaminent of groundwater quality of the Sarigkiol hydrological basin, Greece. They carried out detailed geochemical, mineralogical, geophysical, hydrogeological and hydro-chemical studies on the rocks, soils, sediments and water resources of the basin. In different aquifers, the Cr (VI) concentrations ranged widely with its highest concentration (up to 120 µg L^{-1}) recorded in the groundwater of the unconfined porous aquifer situated near the temporary fly ash disposal site. The presence of high concentration of Cr (VI) in the groundwater of this area could be due to both weathering of the ophiolitic rocks in the soils and the local leaching of Cr (VI) from the diffused fly ash located in the area surrounding the lignite power plant.

2.1.3 Chromium in soil

Mapanda *et al* (2005) studied the level of contamination and annual loadings of soils with heavy metals such as Cu, Zn, Cd, Ni, Cr and Pb at three sites in Harare (Zimbabwe), where waste water was used for irrigating the vegetable gardens for last ten years. They reported that concentrations of heavy metals in sandy and sandy–clay soils ranged from 7.0 to 145 mg kg^{-1} for Cu, 14 to 228 mg kg^{-1} for Zn, 0.5 to 3.4 mg kg^{-1} for Cd, <0.01 to 21 mg kg^{-1} for Ni, 33 to 225 mg kg^{-1} for Cr and 4 to 59 mg kg^{-1} for Pb up to 20 cm soil depth. From annual heavy metal loading rates, it was observed that all studied heavy-metals exceeded their permissible limits in soils, depending on the site.

Dheri *et al* (2007) conducted a study on concentration of heavy metals such as lead (Pb), chromium (Cr), cadmium (Cd), and nickel (Ni) in contaminated sewage water in unlined channels and their impact on underground water, soil and crop plants in alluvial soils of northwestern India. The mean concentrations of Pb, Cr, Cd, and Ni in crop plants growing on soils irrigated with sewage-contaminated water were 4.88, 4.20, 0.29, and 3.99 mg kg^{-1}, that were 1.2, 2.1, 8.7, and 1.9 times higher than in plants irrigated with tubewell water.

They finally concluded that long term use of sewage contaminated water for irrigation results in the heavy metal accumulation in soil as well as plants and also resulted in contamination of groundwater due to leaching of mobile metals.

Chen *et al* (2009) analyzed the total concentrations of heavy metals like Cd, Cr, Cu, Zn and Ni in sewage irrigated soils of Beijing, China. They observed a remarkable increase in the concentration of Cd, Cr, Zn and Cu in sewage irrigated top soils as compared to the reference topsoils. Heavy metals such as Cd, Cr, Ni, Zn and Cu were dominated by residual fractions in sewage irrigated soils. Chromium in sewage-irrigated soils present as in the order residual > organic > Fe-Mn oxide > carbonate > exchangeable forms.

Brar *et al* (2000) studied the effects of discharged effluents from a leather complex of Jalandhar on the concentrations of toxic elements (Cu, Fe, Mn, Zn, Al, As, Cr and Ni) in sewage water and the effect of this applied contaminated sewage irrigation water on the growth of potato (*Solanum tuberosum* L.). The addition of leather complex effluents in the sewage water resulted in increase in concentrations of all the toxic elements, with the biggest increase in the concentration of Cr (from 2.7 mg to 14.0 mg Cr L^{-1}). Increased concentrations of toxic elements (Cu, Fe, Mn, Zn, Al, As, Cr and Ni) in potato leaves and tubers were observed and the increase was generally higher in leaves than in tubers.

2.1.4 Impact of chromium on plants

Sundaramoorthy *et al* (2010) conducted a field experiment on irrigation of paddy (*Oryza sativa*) with water containing different concentrations of chromium (0, 2.5, 5, 10, 25, 50, 75, 100 and 200 mg L^{-1}) and observed the gradual decrease in the growth of shoot, root, total leaf area, fresh weight, dry weight and yield of the paddy with the increase in Cr concentration. A gradual decrease in uptake of macronutrients (N, P, K) and micronutrients (Mn, Cu, Zn, Fe) was also observed. However, the accumulation of chromium in paddy increased with the increase in concentrations of added chromium.

Fozia *et al* (2008) evaluated the effect of increased levels of chromium on growth attributes of sunflower (*Helianthus annuus* L.) by conducting a pot experiment. Three different levels 20, 40, and 60 mg Cr kg^{-1} soil were applied to three different varieties of sunflower (G-3, G-9, and G-59). The germination of sunflower decreased with the increase in Cr concentrations. Also the morphological parameters like root fresh and dry weights, shoot fresh and dry weights and plant height decreased with the increase in Cr levels. Significant reduction in yield parameters as achenes/capitulum, achenes/plant and 100 achenes weight was observed in three varieties.

Datta *et al* (2011) determined the phytotoxic effect of chromium on seed germination and seedling growth of wheat cultivars (*Triticum aestivum* L.). The seeds of five wheat varieties (HD2956, HD2932, DBW14, KO512, WH775) were treated with 25, 50, 75, 100 and 125 mg L^{-1} of Cr (VI) concentrations. Increased levels of Cr (VI) concentrations resulted in inhibition of seed germination and other growth parameters in all wheat cultivars. Phytotoxicity in all wheat cultivars increased with gradual increase in Cr (VI) concentration with its major effect on root growth. The total chlorophyll content was highest in controlled conditions and the decrease in total chlorophyll content was observed with increased levels of Cr (VI) solutions in all the five varieties.

Neeraj (2017) conducted a glass house experiment to study the effect of increased levels of applied chromium (0, 40, 80, 160 and 320 mg Cr kg^{-1} soil) on the growth of maize crop in a tubewell water irrigated soil in the presence and absence of two amendments (lime @ 1% and FYM @ 1%). Significant reduction in dry matter yield of maize was observed with increased levels of applied chromium in the soil in the absence of amendments. The adverse effect of added Cr was greater at highest level of its application. The Cr uptake by maize plants decreased with application of amendments and its dry matter production also increases. The addition of FYM @ 1 % decreased the Cr content in maize at any level of applied Cr in comparison to where no amendment was applied whereas application of lime @ 1% decreased the shoot Cr content up to 160 mg kg^{-1} of applied Cr.

2.2 Sorption and desorption of Cr in soils

2.2.1 Sorption of chromium in soils

Alumaa *et al* (2002) studied the capacity of four different soils of Eostonia to sorb toxic heavy metals like chromium, copper, cadmium and lead. The adsorption data of different heavy metals was obtained by batch study and data was fitted into Langmuir isotherm. Different soils show different behaviour towards adsorption of heavy metals and distribution coefficient (K_d) that determines the adsorption capacity varied from 57 to 63000 L kg^{-1}. The general sequence of affinity of metals for the four experimental soils was Pb > Cr> Cu > Cd.

Adhikari (2010) studied the influence of the presence of different heavy metals such as Cd, Ni, Zn and Pb on the sorption of chromium (VI) in inceptisols of Delhi and Hisar. He found that both the experimental soils varied in their ability to sorb Cr (VI). The sorption of Cr (VI) increased in presence of other heavy metal cations and its sorption in soils depended on the heavy metals concentration in the following order Pb > Cd >Ni >Zn.

Covelo *et al* (2007) studied the simultaneous sorption and desorption of Pb, Zn, Cu, Ni, Cd and Cr in acidic soils by conducting batch experiments. They revealed that Pb was sorbed to highest extent than any other metal. Chromium sorption was little greater than Cd, Ni, and Zn and its retention depended on type of clay mineral present in soil. Adsorption and retention of Cr was highly influenced by properties of the soil rather than properties of metallic ion.

Yolcubal and Akyol (2007) studied the retention and transport of hexavalent chromium in calcareous and alkaline surface soil. Batch sorption studies and column experiments were conducted to evaluate sorption/desorption and transport of Cr (VI) in alkaline soil. The study revealed that sorption of Cr (VI) was relatively low and reversible. Cr (VI) species were very mobile and its bioavailability was high in highly calcareous soil condition.

Kwikima *et al* (2017) conducted a batch experiment to evaluate the effect of soil pH, solute concentration and ionic strength on the sorption of Cr (VI). It was observed that Cr (VI) removal from soil solution increased with increasing solute concentration, with decreasing pH and with decreasing ionic strength.

Amfalk *et al* (1996) examined the Cd, Hg, Pb, Cr (III) and Cr (VI) retention in 14 different minerals based on pH dependency and other physico-chemical parameters. Metal uptake was found to be controlled by geochemical parameters of soils such as organic carbon content, type of clay mineral, presence of complexing ions and redox potential. Retention of Cd, Cr (VI), Hg and Pb strongly depended upon organic carbon content of the materials studied. Highest uptake of Cd, Cr (III) and Pb in montmorillonite (in bentonite and smectite) while lower uptake in illite and kaolinite among all the minerals, was observed.

Irha *et al* (2009) evaluated the capacity of five Estonian soils to sorb heavy metals like Cd, Pb, Cu and Cr. The experimental sorption data fitted well to the Freundlich adsorption isotherm. The results obtained indicated that the content of quartz and carbonates affected the metal sorption capacity of subsoil. The sequence of sorption affinity of metals toward subsoils was in the order: Pb > Cr > Cu > Cd for Podzoluvisol, Cr > Pb > Cu > Cd for Podzol, Pb > Cu > Cr > Cd for Podzolic Gleysols, Pb > Cu, Cd >Cr for Rendzic Leptosol. Highly significant and positive correlation was observed between Cr adsorption and quartz content which implied that Cr had high affinity to subsoil.

2.2.2 Desorption of chromium.

Barrow *et al* (2012) compared the rates of desorption of heavy metals (Cr, Mn, Co, Ni, Cu, Zn, Cd and Pb) from goethite for better understanding the mechanisms of their sorption and desorption. Samples of goethite were reacted with salt solutions of heavy metals for 2 hours and for 8 weeks. Desorption was then induced by successive treatments with 0.7 M HNO_3. After sorption period of 2 hours, a large proportion of the sorbed metals were desorbed back on treatment (15 minutes) with HNO_3. This suggests that the metals were mainly sorbed on or close to the external goethite surfaces. After longer sorption peroid of 8 weeks of extraction with 0.7 M HNO_3, all of the sorbed metals didnot recover back. This suggests that the eight heavy metals had penetrated deep into the goethite particles. The observed desorption was often faster than predicted. This discrepancy was marked for Ni, Cr and Co as large portions of these metals were incorporated into the goethite structure through lattice diffusion.

Marchi *et al* (2009) compared the desorption rates of heavy metals (Zn, Cd, Ni, Cr, Cu) from sewage sludge-amended soil by using seven extractants: four organic acid mixtures and three routine extractants (DTPA, Mehlich-I, and ammonium acetate). They performed single pass extractions, in which the extractable metal contents were determined by simply extracting the soil a single time and also 15 successive extractions, in which the solid residues of the first extraction was successively extracted 14 additional times was done. The extractability of heavy metals in a single pass extraction follows the order: Mehlich-I > DTPA > organic acids > NH_4OAc. The rate of extraction in 15 successive extractions followed the general order: DTPA > Mehlich-I > organic acids > NH4OAc. Among the studied extractants, Mehlich-I extracted the highest amount of heavy metals.

2.3 Factors affecting bioavailability of chromium

2.3.1 pH

Richard *et al* (1991) studied the geochemistry of chromium and found that Cr (III) and Cr (VI) are most stable oxidation states of chromium. Cr (III) exhibits a typical cationic behaviour in soil and its adsorption increases with pH. On the other hand Cr (VI) exhibits anionic sorption behaviour and its adsorption decreases with increase in pH. The mobility of chromium depends on sorption/desorption, dissolution/precipitation and redox reactions.

Lee *et al* (1999) studied the dependence of Cr (VI) sorption on physico-chemical properties such as pH, organic matter content and concentration of metal oxides in 15 Taiwan soils. The adsorption of Cr (VI) followed the langmuir relation and decreased with increase in pH from 2.5 and 9.5. At constant pH, soils with greater organic matter content sorb more Cr.

Lukhman *et al* (2013) studied the competitive adsorption of heavy metal ions (Cd, Cr, Pb and Zn) on natural clay to understand the influence of initial pH on the adsorptive capacity of clay mineral. Batch experiments were performed at six different pH values (2, 4, 6, 8, 10) and the amount of heavy metal removed at eqillibrium in single and multi-component adsorption scenarios were analyzed. The adsorption selectivity sequence for single and multi –component scenarios follows the order: Cr>Pb>Cu>Cd>Zn and Cr>Cu>Pb>Cd>Zn. The pH played significant role in competitive adsorption and desorption of heavy metal onto clay mineral. Adsorption of chromium was highest at pH 4, maximum upto pH 6 and then decreased at higher pH values.

Wang *et al* (2009) reported that in the presence of humic acid, the pH value significantly affected the reduction of Cr (VI) in a sandy soil. The removal rate of Cr (VI) was reduced with the increase in the pH due to reduction of Cr (VI) to Cr (III). Humic acid present in soil get dissolved in alkaline conditions and get oxidised by loosing H^+. Hexavalent Cr present in soil solution accepts H^+ and get reduced. The reduced form of Chromium i.e Cr^{3+}get adsorbed onto humic acid. Thus, there was a decline in the proportion of soluble chromium ions resulting in increase in the proportion of organic bound chromium.

Aide and Cummings (1997) proposed an outer sphere complex of Cr (VI) adsorption on boehmite. They found that adsorption of Cr (VI) on bohemite depended upon pH and this pH is strongly related to protonation of CrO_4^{2-} to form $HCrO_4^-$. Ortho-phosphates suppressed Cr (VI) adsorption by competing for similar sorption sites.

Bavaresco *et al* (2017) conducted an experiment to assess the maximum Cr adsorption capacity of four sub tropical soils differing in their mineralogy. The samples were supplied with Cr (III) nitrate solutions at pH 4.5 and 5.5. The results of Cr (III) adsorption fitted to a Freundlich equation and the adsorption capacity was positively correlated with soil organic matter and iron oxide contents. With an increase in soil pH, the Cr (III) adsorption capacity increased due to more charges on adsorbing surfaces. Finally, they concluded that the soils rich in organic matter and iron oxides and having a pH above 4.5 are suitable for disposal of Cr (III)-loaded industrial wastes.

Tzou *et al* (1998) investigated the Cr (VI) sorption and its reduction rate in alkaline and acidic soils. They observed that Cr (VI) sorption was high in the presence of 0.01 M $Ca(NO_3)_2$ as compared to 0.001 M $Ca(NO_3)_2$ solution. Non-specific anions also influenced the Cr (VI) sorption by the acidic soils in the order: $Cl^- < ClO_4^- < SO_4^{2-}$. In alkaline soils, these three electrolyte solutions showed slight difference in Cr (VI) sorption. The amount of Cr (VI) desorbed by phosphate increased with increasing Cr (VI) concentrations due to the competition for the sorption sites and decreased with increase in equilibration time in acidic soils but there was no effect of equilibration time on Cr(VI) desorption in alkaline soils.

2.3.2 Oxidation- Reduction Reactions

Kozuh *et al* (2000) studied the parameters influencing the reduction and oxidation of soluble chromium in various soils (peat, clay, sand and luvi -chromic cambisols). They revealed that reduction and oxidation of soluble chromium depend on soil structure and oxidation/reduction conditions in a particular soil. Oxidation and reduction of Cr depends on the content of organic matter and pH of the soil. Oxidation of soluble chromium was observed in soils low in organic matter and high in manganese oxides. No oxidation of added soluble chromium occurred in peat soil due to its high organic matter content.

Trebien *et al* (2011) carried out incubation experiments to examine influence of soil moisture content and organic matter addition on soil Cr (VI) formation and they concluded that amount of Cr (III) oxidation depend upon concentration of easily reducible Mn oxides.

Bolan *et al* (2003) investigated the effects of organic amendments on the reduction of Cr (VI) in mineral soils by applying eight treatments i.e. soil, soil+biosolid, soil+FYM, soil+fish manure, soil+horse manure, soil+spent mushroom, soil+pig manure and soil+poultry manure. They found that rate of reduction of Cr (VI) increased with the increased levels of easily oxidisable carbon. Linear relationship was found between Cr (VI) and organic carbon.

Stepniewska *et al* (2004) examined two aspects of Cr (III) oxidation in soils i.e. the soil oxidation potential and sorption of Cr (III) in four soils of Poland that differ in organic matter content (0.72% to 3.72% of organic carbon) and total and easily reducible Mn. Experiments were carried out in batches with initial Cr (III) concentration 52 ppm. Sorption capacities for chromium (III) were similar for each soil and ranged from 9.72 $x10^{-4}$ to 9.95 $x10^{-4}$ mol Cr (III)/100 g of soil. For examination of Cr (III) oxidation by MnO_2, the oxidant was added in three amounts: 0.065, 0.13 and 0.26 g/100 g soil. The oxidation of Cr (III) by MnO_2 progressed with a maximum conversion of 2.66% for the highest dose of oxidant (0.26 g). The sorption of Cr (III) on soil decreased in presence of manganese oxide due to oxidation of Cr (III) to Cr (VI).

2.3.3 Organic matter

Leita *et al* (2009) studied the interaction between Cr (VI) as K_2CrO_4 and standard humic acid in bulk solution using three methods i.e UV-visible spectroscopy, X-ray adsorption spectroscopy and differential pulse stripping voltammetry. They concluded that humic acid did not induce reduction of Cr (VI) to Cr (III) rather it leads to formation of Cr(VI)-humic acid micelles with the result that Cr (VI) persist in soil.

Abollino *et al* (2003) studied the sorption of seven metals (Cd, Cr, Cu, Mn, Ni, Pb and Zn) on Na-montmorillonite as a function of pH and in the presence of organic ligands, forming complexes of different stability. Complex formation with different organic ligands such as oxalic acid, citric acid, tartaric acid, succinic acid decreased the sorption of metals (Cd, Cr, Cu, Mn, Ni, Pb and Zn) on the clay. Chromium sorption was highly influenced by complex formation. Complex formation hindered the sorption of metals on the clay with increasing influence in the order $Mn \leq Pb \leq Cd \leq Zn < Ni < Cu < Cr$.

Jardine *et al* (1999) conducted a study to investigate the impact of coupled hydrologic and geochemical processes on the fate and transport of Cr (VI) in undisturbed soil cores obtained from acidic inceptisol. They observed that the mobility of Cr (VI) decreased significantly with increased loading of the solid phase organic matter. The reduction of Cr (VI) to Cr (III) was more significant in soils having higher levels of surface bound natural organic matter (NOM). This indicated that organic matter acts as a suitable reductant even in the presence of potentially competing geochemical oxidation reactions involving Cr. The redox reaction was catalyzed by the presence of soil mineral surfaces and the reduced product Cr(III) get immobilized.

Luo *et al* (2010) observed the influence of pH (2-12), ionic strength (0.005-1.0 M) and concentration of sorbate (1-10 mg/L) on the extent of sorption in following organic complexes: chromium (III) ascorbate, chromium (III) cysteine, chromium (III) histidine, chromium (III) mandelate, chromium (III) glutamate, chromium (III) citrate, chromium (III) serine, chromium (III) pyruvate and chromium (III) oxalate. Ionic strength between 0.005 and

0.01 M KNO_3 did not influence the Cr sorption. Sorption and desorption data obtained at pH 7, 0.01 M KNO_3 and 1-10 mg/L for each chromium (III) organic complex were analyzed using Freundlich and Langmuir models. Sorption data for chromium (III) oxalate, chromium (III) glutamate, chromium (III) cysteine, chromium (III) pyruvate, chromium (III) ascorbate and chromium (III) citrate were described well by the Langmuir model. Estimates for the saturated sorption capacities were 141, 70.9, 36.5, 35.5, 28.6 and 4.4 µg/g, respectively. It was not possible to desorb significant amounts of the previously sorbed chromium (III) organic complexes. At the same pH, ionic strength and solid:liquid ratio, the order of the observed sorption to the Matawan soil from highest to lowest was chromium (III) mandelate > chromium (III) glutamate > chromium (III) histidine > chromium (III) cysteine > chromium (III) serine > chromium(III) pyruvate > chromium (III) oxalate > chromium (III) ascorbate > chromium (III) citrate.

Han *et al* (2004) investigated the solid-phase distribution, transformation and bioavailability of Cr in Cr (III) and Cr (VI) contaminated soils. They observed that Cr in both Cr (III) and Cr (VI) contaminated soils was mainly present in organic matter bound fraction. Transformation between Cr (III) and Cr (VI) took place in both contaminated soils. Chromium in Cr (III) contaminated soils mainly present as Cr (III) while in Cr (VI) treated soils get transformed into Cr (III) due to its reduction carried out by organic matter present in soil. They concluded that addition of organic matter to Cr (III) or Cr (VI) contaminated soils would be a cost-effective remediation method for stabilization of Cr and to lower its ability and mobility in the contaminated soils.

Steward *et al* (2003) observed the influence of soil geochemical and physical properties on the sorption and bioaccesibility of Cr (III) in soils and revealed that soil having high quantity of clay, inorganic carbon, high pH and high CEC sorb more Cr (III).

2.3.4 Fe and Mn oxides

Hsia *et al* (1993) studied specific adsorption of chromate on hydrous iron oxide. For characterizing Cr (VI) adsorption sites on hydrous iron oxide, chemical and spectroscopic analysis (EDAX, Energy Dispersive Analysis of X-ray) was used. It was concluded that specific adsorption of Cr anions occured at iron oxide surface.

Landrot *et al* (2010) conducted an experiment to study kinetics of Cr (III) oxidation by manganese oxides using quick scanning X-ray absorption fine structure spectroscopy. The rate of Cr (III) oxidation on manganese oxide were measured at three different pH 2.5, 3 & 3.5 and it was found that rate of Cr (III) oxidation by manganese oxides depended on temperature, Cr (III) concentration and pH.

Brigatti *et al* (2000) studied the reduction of hexavalent chromium species in aqueous solution by interaction with Fe (II) bearing solid surface (chlorite, corrensite and montmorillonite) using 0.96×10^{-3} M Cr (VI) solution. Fe (II) - bearing phyllosilicates (chlorite, corrensite and montmorillonite) reduced aqueous Cr (VI) ions at acidic pH. The rapid reduction of Cr (VI) found to occur at the surface of chlorite and corrensite as compared to montomorillonite due to high Fe (II)/ Fe (III) ratio at its surface. After reduction, Cr was sorbed or precipitated as Cr (III) in octahedral coordination.

Jung and Lee (2005) investigated the kinetics and chemical stiochiometry for homogeneous and heterogenous Cr (VI) reduction by soluble Fe (II) and Fe (II) bearing soil minerals (magnetite) in batch studies. The kinetics rate constants for Cr (VI) reductions ranged between 2.81-49.90 hr^{-1}. The rate for the reduction of Cr (VI) depended upon the initial Cr (VI) concentration and Fe (II) contents in homogenous solution and heteogenous suspension. The soluble Fe (II) in homogenous solution was more reactive than surface Fe (II) on magnetite in heterogenous suspension. A significant conversion of Fe (II) to Fe (III) was observed, verifying that Cr (VI) was transformed to Cr(III) coupled with oxidations of Fe (II) bearing soil minerals.

Pantsar- Kallio *et al* (2001) examined reactions of Cr (III) and Cr (VI) with $Fe(OH)_3$, MnO_2, $CaCO_3$, kaolinite and natural organic matter by conducting batch experiments. They found that the ability of the pure components was different to that in mixture in order to change speciation of Cr (III) and Cr (VI). The order of pure components to convert Cr (III) was $Fe(OH)_3$= Kaolinite= $CaCO_3$ >NOM>MnO_2 whereas in mixture the order was : $Fe(OH)_3$> $CaCO_3$ > Kaolinite> MnO_2> NOM. On the other hand, the order of pure components to convert Cr (VI) was $Fe(OH)_3$ >NOM >Kaolinite> $CaCO_3$ >MnO_2 and in mixture was NOM> $Fe(OH)_3$>Kaolinite> MnO_2> $CaCO_3$.

Kim and Dixon (2002) reported that oxidation rate of Cr increased with increased content of reactive maganese oxides and decreasing pH of the soil. Chromium oxidation rate in soil samples collected from four Texas soil series (Silcawa, Boonville, Burleson and Pledger) followed the order: Pledger > Silawa> Boonville≅ Burleson. They concluded that soil with low content of Mn oxides and high pH was best for safe land disposal of waste containing Cr.

Franco *et al* (2009) studied chemical reduction of the hexavalent chromium Cr (VI) using different reductants [ferrous sulphate (Fe(II))], sodium bisulphite, sucrose, ascorbic acid and zerovalent iron (ZVI)] to evaluate the influence of the reductant on the redox process in the contaminated soil. The experiment was conducted in batches using different molar ratios of Cr (VI) and reductant which discovered that only Fe(II) and ZVI species could promote both reduction of Cr (VI) as well as immobilisation of Cr(III) (formation of an insoluble hydroxide compound). It was verified that 1.0 g of ZVI was capable to convert 104 mg of Cr (VI) to Cr (III).

CHAPTER-III

MATERIAL AND METHODS

3.1 COLLECTION OF SOIL SAMPLES

Twenty eight soil samples both surface (0-15 cm) and sub-surface (15-30 cm) were collected from different locations of Ludhiana, Jalandhar, Malerkotla and Mandi Gobindgarh. The soil samples were processed before passing them through a 2 mm stainless steel sieve and then analysed for different physico-chemical characteristics.

3.2 PHYSICAL AND CHEMICAL ANALYSIS OF SOIL

3.2.1 Soil Reaction

Ten g each of the air dried soil sample was equilibrated with 20 ml of distilled water. The pH of suspension after stirring the mixture, was then determined using pH meter.

3.2.2 Electrical Conductivity

The electrical conductivity of 1:2 soil water supernatent solution was measured using EC meter after leaving the samples for overnight to attain an equillibrium.

3.2.3 Organic Carbon

To determine organic carbon content, rapid titration method proposed by Walkley and Black's (1934) method was used.

3.2.4 Particle Size Distribution

Particle size distribution of the soils was carried out as per international pipette method (Day 1965). The textural classes were determined using USDA system of soil classification.

3.2.5 Cation Exchange Capacity

Cation exchange capacity of the soil samples were determined by using 1N sodium acetate solution (Richard 1954). The soil was saturated with Na^+ followed by leaching with absolute alcohol. Adsorbed Na^+ was then replaced with NH_4^+ using normal ammonium acetate. The leachate was collected and concentration of Na^+ in it was determined by flame photometer.

3.2.6 Calcium Carbonate Content

Calcium carbonate content was determined by using Puri's method (1949). The soil was heated to boiling after it was treated with 0.1 N $AlCl_3$ solution in presence of calcium sulphate, bromothymol blue and bromocresol green indicators. The contents were titrated against 0.5 N H_2SO_4 to get the end point.

3.2.7 DTPA- Extractable Chromium

The DTPA (0.005 M) solution is used to extract Cr from the soil. Ten g of soil is shaken with 20 ml of the extractant for 2 hours at 25°C (Lindsay and Norvell 1978). The concentration of chromium in filterate was determined using Inductively coupled plamsa – atomic emission spectrophotometer (ICP-

3.2.8 Total Soil Chromium

For total chromium analysis 1g of finely ground soil sample was taken in teflon beakers followed by addition of 5ml of HCl: HNO_3 (Aqua regia) and 5 ml HF. After that these beakers were heated on hot plate at 110°C till 1-2 ml of the volume is left. Procedure was repeated with further addition of 5 ml of each acid. Further 0.1 M $AlCl_3$ (10 ml) solution was added and kept on water bath for 5 minutes at 60°C. After the cooling of the suspension, 50 ml of the final volume was made. Contents were filtered, collected and analysed for Cr using ICP-AES.

3.3 Sorption/Desorption Studies

A preliminary study was conducted to find out the equilibration period required to attain equilibrium between the added Cr in solution and Cr sorbed on solid phase of the soil.

For this 3g soil was taken in eight polypropylene bottles and 30 ml of 40 µg ml^{-1}Cr was added using $K_2Cr_2O_7$ and kept overnight. Next day, these were allowed to shake for 1 hr, 2 hrs, 4 hrs and 8 hrs. Then the samples were centrifuged, filtered and supernatent was analysed for Cr concentration by ICP-AES. It was found that shaking of soil and solution mixture for 2 hrs after keeping overnight was sufficient to attain equillibrium (Table 1)

Table 1. Equilibrium Cr conc. in the soil solution after shaking for different time periods

Time of shaking (Hrs.)	Initial Cr Conc. (µg ml^{-1})	Equilibrium Cr Conc. (µg ml^{-1})
1	40	2.016
2	40	2.543
4	40	2.516
8	40	2.519

3.3.1 Sorption and desorption of chromium in soils under study in relation to their physical and chemical characteristics.

The sorption of added chromium in different soils was determined after equilibration of 3 g of soil samples with 30 ml of equilibrating solution (in triplicate) *viz.*0.01 M $Ca(NO_3)_2$ containing 40µg Cr ml^{-1} (equivalent to 400µg Cr g^{-1}) in polypropylene centrifuge tubes. The samples were allowed to equilibrate for 24 hrs followed by shaking of 2 hrs on reciprocating shaker. After the centrifugation of the samples, the supernatent was collected for analysis of Cr by ICP-AES. The amount of chromium sorbed by the soil was computed by substracting the amount of Cr retained in equilibrium solution from the amount of initially added Cr.

The desorption of chromium from the soil samples was carried out sequentially. After decanting and collecting the supernatent, the same soil samples were re-suspended in fresh Cr free 0.01 M calcium nitrate [$Ca(NO_3)_2$] and were equilibrated by shaking for two hours on reciprocating shaker. After that, the centrifugation was done and supernatent was collected and analyzed for Cr by ICP-AES. This process was repeated for five times. Corrections factor was used to access the actual amount of desorbed chromium (by weighing the centrifuge tubes containing soil and calcium nitrate solution before and after decanting the supernatent solution). Cumulative chromium desorbed was calculated from chromium concentrations obtained in five successive desorptions. Relationship was worked out between amounts of Cr sorbed/desorbed and various soil physico-chemical properties like pH, EC, texture, $CaCO_3$, organic carbon and CEC using correlation, linear and multiple regression analysis.

3.3.2 Behaviour of chromium as described by sorption and desorption isotherms

The chromium behaviour in soils was studied by sorption and desorption isotherms, three soil samples from different location viz Kumbarh (near drain pull) Mandi gobindgarh; Bhamian road, Ludhiana and Opposite bridge, chamiara, Jalandhar were selected and Cr sorption-desorption were carried out in the same way as described in the section 3.3.1 However in this experiment, five different solutions of Cr concentrations i.e. 5μg Cr ml^{-1},10μg Cr ml^{-1}, 30μg Cr ml^{-1}, 60μg Cr ml^{-1} and 90μg Cr ml^{-1}.were used to study sorption of chromium on soils before the same was be desorbed with Cr free 0.01 M $Ca(NO_3)_2$ sequentially for five times. The data for amount of Cr adsorption by per unit mass of soil under Cr concentrations was fitted to Frendlich adsorption, Langmuir adsorption isotherm and Dubinin Raduhkevitch (D-R) adsorption isotherm.

Langmuir adsorption isotherm: Langmuir adsorption equation was used to calculate the adsorption parameters, adsorption maxima 'b' and bonding energy coefficient 'K'

The linear equation can be written as:

$$C/(x/m) = 1/Kb + C/b$$

Where,

C is the equilibrium Cr concentration (μg ml^{-1})

x/m is the amount of Cr adsorbed by soil (μg g^{-1})

'b' and 'K' are Langmuir Constants

' K' is the bonding energy of the adsorbent for the Cr (ml $μg^{-1}$). The plot between C/x/m and C is a straight line. The 'b' and 'K' coefficients for the Langmuir equation were derived from Langmuir isotherm using following relation.

b = 1/slope K= slope /intercept

Freundlich adsorption isotherm : Linearised Freundlich equation used is described below:

$$Log(x/m) = \log K_f + n \log c$$

Where, c denotes the equilibrium Cr concentration (μg ml^{-1} soil)

x/m is amount of Cr absorbed by the soil (μg g^{-1} soil)

'K_f' and 'n' are emperical constants

A linear plot between log(x/m) and log c gives the value of ‘ K_f’ (intercept) and ‘ n’ (slope), respectively.

Dubinin Raduhkevitch (D-R) adsorption isotherm: It helps to distinguish between the chemical adsorption and physical adsorption. The D-R equation in linear form is written as:

$$\ln Q_e = \ln Q_m - \beta \varepsilon^2$$

where

Q_e = amount of Cr adsorbed per unit weight of soil (mgg^{-1})

C_e = equilibrium concentration of Cr in solution after adsorption (mgL^{-1})

β = activity coefficient

ε = polanyi potential (KJ^2mol^{-2})

ε can be obtained from following relation :

$$\varepsilon = RT(1 + 1/C_e)$$

where R is the gas constants and T is the temperature. The experimental data was evaluated by plotting $\ln Q_e$ against ε^2 to obtain value of Qm and β from intercept and slope respectively.

3.3.3 Sorption-desorption of chromium as affected by pH

The effect of pH on sorption/desorption of Cr in three soils (in triplicates) from Malerkotla, Jalandhar and Mandi Gobindgarh were studied by adjusting the pH between 6.0 to 8.0 range and comparing the sorption-desorption with that at original pH values of the soils. The pH of each soil was altered by adding 0.1 N NaOH and 0.1 N HCl. The amount of 0.1N NaOH and 0.1N HCl required to change the pH was calculated from preliminary equilibrium curves plotted for each individual soil. The soils were incubated at 25ºC at field capacity until the pH of the soil samples become constant. Three soil samples were initially taken after one month and then after every 15 days. Once the pH was stabilized, the soils were processed before passing through 2 mm sieve and then used for Cr sorption and desorption as described in section 3.3.2.

The Cr sorption data at different pH were fitted in the Freundlich equation, Langmuir equation and Dubinin Raduhkevitch equation. Adsorption parameters were calculated. Cumulative desorption isotherms were drawn.

CHAPTER IV

RESULTS AND DISCUSSION

Results and discussion has been divided in two headings as follows

4.1 To study the sorption and desorption of chromium from a range of Punjab soils in relation to soil properties.

4.2 To characterize the Cr behaviour in soil and influence of pH as described by sorption / desorption isotherms.

4.1 To study the sorption and desorption of chromium from a range of Punjab soils in relation to soil properties.

4.1.1 Soil Properties

Twenty eight surface (0-15 cm) and sub-surface (15-30 cm) soils varying in their physical and chemical properties were selected. The pH of sewage irrigated surface soils and tubewell irrigated surface soils varied from 6.16 to 8.39 and 6.62 to 8.44, electrical conductivity from 0.21 to 0.71 dSm^{-1}and 0.16 to 2.22 dSm^{-1}, organic carbon content from 0.45 to 1.94% and 0.49 to 1.45%, calcium carbonate content from 0 to 1.47% and 0 to 0.92%, cation exchange capacity from 5.44 to 32.98 cmol (p^{+}) kg^{-1} and 6.20 to 22.94 cmol (p^{+}) kg^{-1} and clay content from 7.9 to 21.5% and 10.1 to 19.8%, respectively (Table 2 and 3).

In sub-surface samples, pH varied from 6.24 to 8.47 and 6.45 to 8.89, electrical conductivity from 0.21 to 0.48 dSm^{-1}and 0.17 to 1.81 dSm^{-1}, organic carbon content from 0.19 to 1.43% and 0.35 to 0.76%, calcium carbonate content from 0 to 3.40% and 0 to 0.95%, cation exchange capacity from 3.53 to 28.22 cmol (p^{+}) kg^{-1} and 4.96 to 21.66 cmol (p^{+}) kg^{-1} and clay content from 5.4 to 21% and 8.2 to 18% in sewage irrigated and tubewell irrigated soils (Table 4 and 5).

4.1.2 DTPA extractable Chromium

DTPA extractable chromium ranged between 0.102 to 0.464 µg g^{-1}and 0.139 to 0.798 µg g^{-1} in sewage and tubewell irrigated surface soils (Tables 2 and 3). But in sub-surface sewage and tubewell irrigated samples, it varied from 0.134 to 2.880 µg g^{-1} and 0.090 to 0.736 µg g^{-1}(Tables 4 and 5). Papafilippaki *et al* (2007) found significant correlations between the total concentration and the DTPA extractable fraction of chromium. They also found linear relationship between the total and bio available forms of Cr in the investigated soils of Keritis, Greece.

4.1.3 Total Chromium

The total chromium concentration varied from 2.52 to 71.70 µg g^{-1} and 2.7 to 53.75 µg g^{-1} in sewage and tubewell irrigated surface soils (Tables 2 and 3) whereas in sub-surface sewage and tubewell irrigated soils, it ranged between 2.30 to 113.9 µg g^{-1} and 13.10 to 41.20 µg g^{-1} (Tables 4 and 5). Mohamed *et al* 2012 found significant difference in the total chromium content was found in the three analysed dumpsite soils of Nigeria. The results

Table 2. Physico-chemical characteristics of sewage irrigated surface soils under study

Sample No.	Location/ Area	pH	EC (dS m^{-1})	Organic Carbon (%)	$CaCO_3$ (%)	CEC Cmol (p$^+$)/Kg)	Sand (%)	Silt (%)	Clay (%)	DTPA Cr (µg g^{-1})	Total Cr (µg g^{-1})
Sewage Water Irrigated											
1	Chauni mohalla, Luhdiana	6.59	0.35	1.10	1.00	15.58	76.2	10.5	13.3	0.146	53.65
2	Salem Tabri, Ludhiana	6.60	0.55	0.45	0.25	10.04	70.5	11.2	18.3	0.112	52.60
3	Vijay Nagar, Ludhiana	7.30	0.34	0.68	1.47	10.80	70.2	9.8	20.0	0.286	37.80
7	Opposite Leather complex, Jalandhar	6.52	0.38	1.06	Absent	10.80	75.4	9.2	15.4	0.102	2.52
8	Near Gatta Factory Nahalon, Jalandhar	6.16	0.71	0.60	Absent	5.44	73.8	14.7	11.5	0.184	17.70
9	Opposite Bridge Chamiara, Jalandhar	6.64	0.22	0.74	Absent	6.38	70.2	12.4	17.4	0.332	37.75
10	Bhudu Pinder ,Jalandhar	6.67	0.26	0.45	Absent	7.10	78.5	13.6	7.9	0.124	20.80
15	Ahmedgarh, Malerkotla	7.64	0.57	1.10	0.18	15.73	67.3	17.2	15.5	0.153	44.40
16	Opposite Modern Public school, Malerkotla	7.99	0.49	0.94	0.55	12.86	70.5	15.6	13.9	0.172	41.8
17	Jarg road near modern college, Malerkotla	8.39	0.49	0.70	0.55	12.43	63.7	17.8	18.5	0.136	71.7
18	Amar colony, Malerkotla	7.93	0.29	0.62	Absent	10.94	79.1	12.0	8.9	0.207	51.65
22	Kumbarh, Mandi Gobingarh	7.18	0.31	1.12	1.10	20.80	62.5	21.6	15.9	0.301	23.15
23	Kumbarh near Drain pull 1 Mandi Gobingarh	7.12	0.21	1.94	Absent	32.98	65.3	21.2	13.5	0.188	35.40
24	Badali I, Mandi Gobingarh	7.11	0.32	1.51	Absent	28.12	65.0	13.5	21.5	0.194	23.90
25	Badali II, Mandi Gobingarh	7.14	0.37	1.67	0.45	20.19	78.7	7.0	14.3	0.464	48.80

Table 3. Physico-chemical characteristics of tubewell irrigated surface soils under study

Sample No.	Location/ Area	pH	EC (dS m^{-1})	Organic Carbon (%)	$CaCO_3$ (%)	CEC Cmol (p^+)/Kg)	Sand (%)	Silt (%)	Clay (%)	DTPA Cr (µg g^{-1})	Total Cr (µg g^{-1})
Tubewell Water Irrigated											
4	Bhamian road, Ludhiana	7.18	0.32	1.12	0.77	11.74	67.6	19.3	13.1	0.230	2.70
5	Talwara, Ludhiana	7.25	0.33	0.82	0.65	11.27	70.8	13.7	15.5	0.268	40.35
6	Noorpur Bait, Ludhiana	7.32	0.40	1.21	0.90	10.84	77.6	9.3	13.1	0.798	24.6
11	Opposite Bajwa and Ghuman Dairy Farm,Jalandhar	6.69	0.20	0.70	Absent	6.20	63.3	21.5	15.2	0.336	35.15
12	Chamiara, Jalandhar	6.66	0.28	1.06	Absent	7.72	73.7	15.1	11.2	0.384	18.55
13	Athola, Jalandhar	6.62	0.27	0.78	Absent	8.99	69.1	20.2	10.7	0.336	13.90
14	Kohala, Jalandhar	6.72	0.21	1.35	Absent	7.36	63.3	20.8	15.9	0.312	14.65
19	Ahmedgarh ,Malerkotla	7.96	0.53	0.49	0.60	14.86	64.8	15.4	19.8	0.163	53.75
20	Chippar, Malerkotla	8.21	0.37	0.74	0.92	13.05	68.4	19.8	11.8	0.139	38.20
21	Amar colony, Malerkotla	8.04	0.16	1.45	0.15	13.05	67.4	20.1	12.5	0.186	38.60
26	Kumbarh near Drain pull 2, Mandi Gobindgarh	7.60	2.22	0.84	Absent	22.94	67.0	15.1	17.9	0.684	11.90
27	Fatehpur I, Mandi Gobindgarh	8.20	0.37	1.23	Absent	18.16	72.5	11.2	16.3	0.458	40.05
28	Fatehpur II (1 Km Ahead), Mandi Gobindgarh	8.44	0.21	1.45	Absent	15.11	75.2	14.7	10.1	0.514	20.05

Table 4. Physico-chemical characteristics of sewage irrigated sub-surface soils under study

Sample No.	Location/ Area	pH	EC (dS m^{-1})	Organic Carbon (%)	$CaCO_3$ (%)	CEC Cmol (p^{+})/Kg)	Sand (%)	Silt (%)	Clay (%)	DTPA Cr (µg g^{-1})	Total Cr (µg g^{-1})
Sewage Water Irrigated											
1	Chauni mohalla, Luhdiana	6.24	0.35	0.88	2.90	13.18	76.0	12.0	12.0	0.192	49.85
2	Salem Tabri, Ludhiana	6.97	0.48	0.35	3.40	8.12	70.6	13.4	16.0	0.138	113.90
3	Vijay Nagar, Ludhiana	7.29	0.28	0.33	0.67	7.59	72.2	9.8	18.0	0.194	2.30
7	Opposite Leather complex, Jalandhar	6.66	0.22	1.08	Absent	9.30	76.4	11.2	12.4	0.186	41.40
8	Near Gatta Factory Nahalon, Jalandhar	6.54	0.25	0.23	Absent	3.53	72.4	19.6	8.0	2.880	18.60
9	Opposite Bridge Chamiara, Jalandhar	6.36	0.42	0.64	Absent	6.21	68.8	16.8	14.4	0.406	98.75
10	Bhudu Pinder ,Jalandhar	6.60	0.25	0.19	Absent	5.02	75.6	19.0	5.4	0.146	26.65
15	Ahmedgarh, Malerkotla	7.55	0.45	0.72	0.37	13.56	67.6	18.4	14.0	0.163	40.95
16	Opposite Modern Public school, Malerkotla	8.16	0.43	0.68	0.52	10.64	67.8	20.2	12.0	0.139	43.15
17	Jarg road near modern college, Malerkotla	8.47	0.43	0.47	Absent	10.32	61.6	22.4	16.0	0.134	44.30
18	Amar colony, Malerkotla	7.83	0.29	0.31	0.40	7.54	79.8	12.0	8.2	0.173	35.85
22	Kumbarh, Mandi Gobingarh	7.13	0.30	0.86	0.42	16.11	61.4	24.6	14.0	0.265	31.75
23	Kumbarh near Drain pull 1 Mandi Gobingarh	7.18	0.21	0.78	Absent	28.22	63.8	24.4	11.8	0.180	36.65
24	Badali I, Mandi Gobingarh	7.16	0.30	1.43	Absent	24.62	62.6	16.4	21.0	0.206	23.55
25	Badali II, Mandi Gobingarh	7.21	0.34	1.35	0.25	19.23	77.6	8.4	14.0	0.446	21.50

Table 5. Physico-chemical characteristics of tubewell irrigated sub-surface soils under study

Sample No.	Location/ Area	pH	EC (dS m^{-1})	Organic Carbon (%)	$CaCO_3$ (%)	CEC Cmol (p^+)/Kg)	Sand (%)	Silt (%)	Clay (%)	DTPA Cr (µg g^{-1})	Total Cr (µg g^{-1})
Tubewell Water Irrigated											
4	Bhamian road, Ludhiana	7.32	0.30	0.56	0.95	9.48	65.0	21.4	13.6	0.202	36.15
5	Talwara, Ludhiana	7.30	0.30	0.56	0.87	11.01	71.0	14.2	14.8	0.206	41.20
6	Noorpur Bait, Ludhiana	7.38	0.40	0.74	0.72	8.83	73.4	14.8	11.8	0.090	40.20
11	Opposite Bajwa and Ghuman Dairy Farm,Jalandhar	6.45	0.27	0.35	Absent	4.96	61.0	24.6	14.4	0.338	13.10
12	Chamiara, Jalandhar	6.75	0.26	0.47	Absent	6.25	74.6	17.2	8.2	0.226	16.89
13	Athola, Jalandhar	6.77	0.18	0.45	Absent	8.13	68.0	23.0	9.0	0.232	24.45
14	Kohala, Jalandhar	6.56	0.34	0.56	Absent	6.92	62.8	21.80	15.4	0.222	13.95
19	Ahmedgarh ,Malerkotla	8.19	0.24	0.47	Absent	14.12	64.4	17.6	18.0	0.191	40.05
20	Chippar, Malerkotla	8.25	0.43	0.47	0.50	12.53	67.0	21.0	12.0	0.138	30.55
21	Amar colony, Malerkotla	8.03	0.17	0.37	0.35	11.82	66.1	21.9	12.0	0.196	25.35
26	Kumbarh near Drain pull 2, Mandi Gobindgarh	7.44	1.81	0.76	Absent	21.66	67.0	17.0	16.0	0.736	24.65
27	Fatehpur I, Mandi Gobindgarh	8.42	0.35	0.55	Absent	17.82	70.6	15.4	14.0	0.468	21.55
28	Fatehpur II (1 Km Ahead), Mandi Gobindgarh	8.89	0.22	0.58	Absent	13.95	74.4	15.0	10.6	0.450	20.75

Table 6. Coefficients of correlation 'r' between DTPA - Cr, Total – Cr, added Cr sorbed- desorbed and soil properties of surface soil samples

Cr Fraction	pH	EC	Organic carbon	$CaCO_3$	CEC	Clay
DTPA - Cr	0.111	0.348	0.262	-0.020	0.094	-0.024
Total - Cr	0.404*	-0.166	-0.183	0.312	0.060	0.258
Cr sorbed	-0.764**	-0.199	0.129	-0.141	-0.116	-0.118
Cr desorbed (Cumulative)	0.635**	0.352	-0.065	0.374	0.386*	0.201
Percent Cr desorbed	0.714**	0.400*	0.101	0.165	0.330	0.147

**Significant at both 1% and 5% level of significance

Table 7. Coefficients of correlation 'r' between DTPA - Cr, Total – Cr, added Cr sorbed- desorbed and soil properties of sub-surface soil samples

Cr Fraction	pH	EC	Organic carbon	$CaCO_3$	CEC	Clay
DTPA - Cr	-0.190	0.095	-0.185	-0.178	-0.169	-0.242
Total - Cr	-0.133	0.072	-0.001	0.575**	-0.105	0.132
Cr sorbed	-0.757**	-0.125	-0.272	-0.088	-0.124	-0.059
Cr desorbed (Cumulative)	0.438*	0.069	-0.109	-0.054	0.025	-0.023
Percent Cr desorbed	0.789**	0.282	-0.168	0.059	0.329	-0.002

**Significant at both 1% and 5% level of significance

showed that the metal was distributed between oxides, carbonate and carbonate/organically bound fractions.

4.1.4 Correlation between physico-chemical properties of experimental soils and Cr sorption and desorption

The relationship between different physico-chemical properties and Cr sorption and desorption were analyzed by Pearson's correlation coefficient. The correlation analysis is a bivariant method which is applied to describe the relation between two different parameters. The high correlation co-efficient (near +1 or -1) means a good relation between two variables, and its concentration around zero means no relationship between them at a significant level of 5% level.

4.1.5 Sorption of added chromium

The concentration of Cr sorbed by the soils ranged from 0 to 97 µg g^{-1} for surface samples and 0 to 84 µg $g^{-1}$for sub-surface samples for sewage and tubewell irrigated soils (Table 8 and 9). The highest Cr sorption (24.3 %) was observed in surface soil sample collected from Bhudu pinder, Jalandhar (97.06 µg Cr g^{-1} out of added 400 µg Cr g^{-1}) and lowest sorption (2.9 %) was in surface soil of Fatehpur I, Mandi Gobindgarh (11.66 µg Cr g^{-1} out of added 400 µg Cr g^{-1}) (Table 8). In the sub-surface samples, highest Cr sorption (21.1 %) was observed in Kohala, Jalandhar (84.2 µg Cr g^{-1} out of added 400 µg Cr g^{-1}) and lowest sorption (4%) was in Fatehpur II, Mandi Gobindgarh (15.96 µg Cr g^{-1} out of added 400 µg Cr g^{-1}) (Table 9).

No Cr sorption occurred in Malerkotla soils, both surface and sub-surface samples. The reason for this could be the high pH of the soil. With the increase in pH of the soil, the net negative charge on soil surface could be increased that restricted the Cr sorption. Also very low Cr sorption was observed in tubewell irrigated surface soils of Mandi Gobindgarh soils relatively due to high pH and high cation exchange capacity of soils. Highly significant and negative correlation was observed between chromium sorbed and pH of both in surface (r = -0.764) as well as subsurface soils (r = -0.757) (Tables 6 and 7).

Adhikari (2010) observed that sorption of Cr (VI) in soils having high pH (pH >7.0) is negligible due to negative surface charge on the soil and chromate as a negative ion would not be sorbed by soil. He also observed that Cr (VI) sorption occurred in presence of heavy metal cations though the pH was high. The reason for this was sorption of heavy metal cations resulted in neutralization of the negative charge of soil and increased in the number of reactive surface groups which can be able to complex chromate ions.

Tzou *et al* (2003) reported that the increase in positive charges with pH dropping on pH-dependent sites contributed to Cr (VI) sorption. Lee *et al* (1999) observed that the amount of Cr (VI) adsorbed on the soils decreased sharply with pH, upto pH 5 to 6 and reached a minimum at pH 8.0 with only marginal decrease between pH 6 and 8 for Tacha silty loam and Lichochen sand. The Cr (VI) sorption was highly dependent on pH as it affects the surface charge of the adsorbent and the degree of ionization and the speciation of adsorbate.

Otero *et al* (2015) observed significant correlation between the amount of Cr (VI) sorbed (mg kg^{-1}) and pH. They found that the pyritic material had the highest Cr (VI) sorption capacity due to its low pH (2.97) and the granitic material had the lowest Cr (VI) sorption. Correlations between adsorbed Cr (VI) and pH of the solution were positive for shell-amended granitic material (r = 0.770) whereas correlations were negative for pyritic material (r = -0.424). The highest Cr retention was observed at very acid pH value.

No significant correlation was observed between soil $CaCO_3$ and Cr sorbed both in surface (Table 6) as well as sub-surface soil samples (Table 7). The reason for non-significant correlation between Cr sorption and $CaCO_3$ is the low $CaCO_3$ content in experimental soils under study (0 to1.47 % in surface sewage irrigated soils and 0 to 0.92% in surface tubewell irrigated soils) (Tables 2 and 3) and (0 to 3.40% in sub-surface sewage irrrigated soils and 0 to 0.95% in sub-surface tubewell irrigated soils) (Tables 4 and 5). More than 50 % soil samples (both surface and subsurface) were non-calcareous.

Table 8. Chromium sorbed, cumulative Cr desorbed and per cent chromium desorbed in different surface soils

Soils	Cr Sorbed ($\mu g\ g^{-1}$soil)	Cr Desorbed ($\mu g\ g^{-1}$soil)	Per cent Cr Desorbed/Sorbed*100
Sewage Water Irrigated			
Chauni mohalla, Ludhiana	29.61	24.67	83.3
Salem Tabri, Ludhiana	37.56	29.36	78.2
Vijay Nagar, Ludhiana	53.97	27.73	51.4
Opposite Leather complex, Jalandhar	77.09	17.12	22.2
Near Gatta Factory Nahalon, Jalandhar	66.64	13.64	20.5
Opposite Bridge Chamiara, Jalandhar	37.00	13.06	35.3
Bhudu Pinder , Jalandhar	97.06	21.57	22.2
Ahmedgarh, Malerkotla	0	37.68	0
Opposite Modern Public school, Malerkotla	0	31.62	0
Jarg road near modern college, Malerkotla	0	33.13	0
Amar colony, Malerkotla	0	24.30	0
Kumbarh, Mandi Gobingarh	54.3	21.68	39.9
Kumbarh near Drain pull 1 Mandi Gobingarh	57.26	25.07	43.8
Badali I, Mandi Gobingarh	53.2	22.82	42.9
Badali II, Mandi Gobingarh	69.76	25.75	36.9
Tubewell Water Irrigated			
Bhamian road, Ludhiana	37.06	26.54	71.4
Talwara, Ludhiana	59.03	26.46	44.8
Noorpur Bait, Ludhiana	30.41	19.10	63.8
Opposite Bajwa and Ghuman Dairy Farm,Jalandhar	17.62	7.22	41.0
Chamiara, Jalandhar	76.15	18.48	24.3
Athola, Jalandhar	58.95	20.76	35.2
Kohala, Jalandhar	83.43	16.02	19.2
Ahmedgarh ,Malerkotla	0	32.05	0
Chippar, Malerkotla	0	37.33	0
Amar colony, Malerkotla	0	23.56	0
Kumbarh near Drain pull 2, Mandi Gobindgarh	14.83	32.68	100
Fatehpur I, Mandi Gobindgarh	11.66	25.65	100
Fatehpur I (1 Km Ahead), Mandi Gobindgarh	15.73	22.34	100

Table 9. Chromium sorbed, cumulative Cr desorbed and per cent chromium desorbed in different sub-surface soils

Soils	Cr Sorbed (μg g^{-1}soil)	Cr Desorbed (μg g^{-1}soil)	Per cent Cr Desorbed/Sorbed * 100
Sewage Water Irrigated			
Chauni mohalla, Ludhiana	35.23	14.08	39.9
Salem Tabri, Ludhiana	39.97	16.03	40.1
Vijay Nagar, Ludhiana	35.11	14.42	41.0
Opposite Leather complex, Jalandhar	59.46	10.79	18.1
Near Gatta Factory Nahalon, Jalandhar	78.58	11.10	14.1
Opposite Bridge Chamiara, Jalandhar	63.62	11.71	18.4
Bhudu Pinder ,Jalandhar	54.95	17.98	32.7
Ahmedgarh, Malerkotla	0	40.46	0
Opposite Modern Public school, Malerkotla	0	38.01	0
Jarg road near modern college, Malerkotla	0	31.86	0
Amar colony, Malerkotla	0	30.34	0
Kumbarh, Mandi Gobingarh	31.03	11.32	36.5
Kumbarh near Drain pull 1 Mandi Gobingarh	41.23	17.71	42.9
Badali I, Mandi Gobingarh	70.66	14.88	21.1
Badali II, Mandi Gobingarh	76.76	16.32	21.3
Tubewell Water Irrigated			
Bhamian road, Ludhiana	42.22	15.06	35.7
Talwara, Ludhiana	36.87	13.10	35.6
Noorpur Bait, Ludhiana	24.39	9.89	40.6
Opposite Bajwa and Ghuman Dairy Farm,Jalandhar	38.65	13.54	35.0
Chamiara, Jalandhar	78.44	13.88	17.7
Athola, Jalandhar	42.44	19.88	46.8
Kohala, Jalandhar	84.21	15.44	18.3
Ahmedgarh ,Malerkotla	0	22.94	0
Chippar, Malerkotla	0	25.93	0
Amar colony, Malerkotla	0	24.71	0
Kumbarh near Drain pull 2, Mandi Gobindgarh	25.4	15.65	61.6
Fatehpu Ir, Mandi Gobindgarh	19.07	13.19	69.2
Fatehpur II (1 Km Ahead), Mandi Gobindgarh	15.96	13.54	84.8

The experimental soils studied for Cr sorption showed non-significant relation with clay content both in surface as well as subsurface samples (Tables 6 and 7). Lee *et al* (1999) statistically analyzed the variation of Cr (VI) adsorption with measured soil properties and found that clay content showed poor relationship with adsorption. Battacharyya and Tenuv (2017) found that the coarse textured soils were least effective in retaining the anions in comparison to fine textured soil. The soils under study were mostly coarse textured soils that is why no significant correlation was observed between adsorption and clay content.

The soils under study showed non- significant relation of CEC with Cr sorption both in surface and sub-surface soils. Chopala *et al* (2013) also observed no significant effect of CEC on the adsorption of Cr (VI) in twelve Australian soils.

Simple linear regression for the soil variables (pH, EC, OC, $CaCO_{3,}$ and CEC) with Cr sorption were calculated. The simple linear regressions explained at the best upto 58 per cent of the total variation in chromium sorption among surface soil samples (Table 10) and upto 57 % among subsurface soil samples (Table 11). The pH was observed to be the most important factor on which the Cr sorption in the selected soils depends upon.

The stepwise multiple regression equations both for surface and sub-surface samples were calculated. It was observed 64% of influence on the variability in Cr sorbed was explained by pH and total Cr in the soil (Equation 1) but with the inclusion of electric conductivity, the variability explained increased to 68% (Equation 2) in surface soil samples. In case of sub-surface samples, pH and organic carbon had 61 % influence on the variability of Cr sorbed (Equation 4). In both surface and sub-surface samples the pH largely contributes to the variability of Cr adsorbed i.e 58 % in surface samples and 57 % in sub-surface samples.

Surface soil samples

Cr sorbed = 275.052 – 30.073pH – 0.557 Total Cr ($R^2 = 0.647$) ....Equation 1

Cr sorbed = 272.482 – 28.361 pH – 0.652 Total Cr - 15.831 EC ($R^2 = 0.684$) ....Equation 2

Sub-surface soil samples

Cr sorbed = 248.378 – 29.061 pH ($R^2 = 0.573$) ....Equation 3

Cr sorbed = 231.651 – 28.356 pH + 18.836 OC ($R^2 = 0.615$) ....Equation 4

Salmasi and Salmasi (2007) observed that chromium sorption varied from 0.736 to 0.817 g/kg by the twenty selected soils of Iran whose pH varied from 1.3 to 7.4. Cr sorption by the soils was strongly correlated with the soil properties (soil pH, total inorganic carbon, clay and CEC) ($R^2= 0.794$). Nearly 80 % variability in Cr (III) sorption could be described by soil pH, TIC, clay, and CEC.

Cr(III) (mg/kg on soil)= -12666.3 + 113.8 clay + 364.6 CEC + 1743.2 TIC + 1916.7 pH

Jiang *et al* (2008) observed the increase in system pH in the range 3.5 to 6 of three variable charge soil of China. Increase in pH of the soils tested decreased sorption of chromate. The decrease in the adsorption corresponding to an increase of pH by one unit was 4.0, 1.8, 2.2 mmol kg^{-1} in three experimental soils. The increase in soil pH can cause rise in negative charge and consequently repels the Cr (VI) ions from surface of soils. Ajouyed *et al* (2016) found that Cr (VI) has high sorption affinity in acidic medium and the sorption of Cr (VI) depends strongly on the pH. Similarly, low Cr (VI) sorption was noticed in chromate ore processing residue soils, because of their high pH (Matern and Mansfeldt, 2016).

Similar results were observed by Jardine *et al* (2013) that Cr sorption increased with increasing soil total organic carbon (TOC) and decreasing soil pH. The stepwise linear regression indicated that a combination of % soil TOC and soil pH described 67% of the variability in Cr (VI) sorption. The relationship describing Cr (VI) sorption was:

Cr (VI) sorption = 704.5 + 65.7 TOC - 88.4 pH, $R^2 = 0.67$

The reason could be more positive charge present on soil TOC and amphoteric mineral surfaces (e.g Fe oxides) due to low pH which enhances Cr (VI) sorption via inner and outer sphere complexes.

Choppala *et al* (2013) examined the relationship between various soil properties and Cr (III) and Cr (VI) sorption in 12 Australian soils by step-up linear multiple regression. Chromium (III) sorption was strongly correlated to the soil properties such that 93 % of variability of sorption of Cr (III) could be described by negative charge and cation

Table10. Single parameter regression equations for describing sorption and desorption of 28 surface soils

Regression equation	**R^2**
Cr sorbed (µg g^{-1} soils)	
Cr sorbed = 293.5 – 35.22 pH	0.583
Cr sorbed = 43.77 – 15.98 EC	0.039
Cr sorbed = 26.96 + 10.14 OC	0.016
Cr sorbed = 44.34 – 0.533 CEC	0.013
Cr sorbed = 40.42 – 9.816 $CaCO_3$	0.019
Cumulative Cr desorbed (µg g^{-1} soils)	
Cr desorbed = -26.73+ 6.994 pH	0.403
Cr desorbed = 21.36 + 6.760 EC	0.124
Cr desorbed = 25.41 – 1.225 OC	0.004
Cr desorbed = 18.42 + 0.423 CEC	0.148
Cr desorbed = 22.07 + 0.232 $CaCO_3$	0.140
Percent Cr desorbed (µgg^{-1})	
% Cr desorbed = - 196.3+ 35.19 pH	0.510
% Cr desorbed = 40.55 + 25.39 EC	0.159
% Cr desorbed = 43.96 + 6.960 OC	0.010
% Cr desorbed = 34.90 + 1.187 CEC	0.108
% Cr desorbed = 48.20 + 9.606 $CaCO_3$	0.027

exchange capacity (CEC) whereas 87% variability in the sorption of Cr (VI) was significantly explained by the positive charge (PC) of soil.

Table 11. Single parameter regression equations for describing adsorption and desorption of 28 sub-surface soils

Regression equation	R^2
Cr sorbed (μg g^{-1} soils)	
Cr sorbed = 248.3 – 29.06 pH	0.572
Cr sorbed = 39.78 – 11.67 EC	0.015
Cr sorbed = 20.24 + 24.86 OC	0.073
Cr sorbed = 42.20 – 0.567 CEC	0.015
Cr sorbed = 36.80 – 2.938 $CaCO_3$	0.007
Cumulative Cr desorbed (μg g^{-1} soils)	
Cr desorbed = -22.49+ 5.576 pH	0.241
Cr desorbed = 18.02 + 0.874 EC	0.001
Cr desorbed = 20.91 – 4.171 OC	0.023
Cr desorbed = 17.94 + 0.034 CEC	0.000
Cr desorbed = 18.61 – 0.594 $CaCO_3$	0.003
Percent Cr desorbed (μgg^{-1})	
% Cr desorbed = -120.6 + 22.24 pH	0.622
% Cr desorbed = 31.08 + 15.18 EC	0.072
% Cr desorbed = 42.73 – 9.177 OC	0.028
% Cr desorbed = 26.47 + 0.862 CEC	0.108
% Cr desorbed = 36.19 + 1.139 $CaCO_3$	0.003

4.1.6 Desorption of added chromium

The cumulative added chromium desorbed (from an initial application of 400 μg Cr g^{-1} soil) after five consecutive desorptions, varied from 7.22 μg Cr g^{-1} to 37.68 μg Cr g^{-1}in surface samples (Table 8) and 9.89 μg Cr g^{-1} to 40.46 μg Cr g^{-1} in sub-surface samples (Table 9) for sewage and tubewell irrigated soils, respectively. It was observed that, in most of the Ludhiana soils more than 70 % of the sorbed chromium desorbed back from the soil solid phase into soil solution. In Malerkotla soils, the amount of Cr desorbed was very high and varied from 23.56 μg Cr g^{-1} to 37.68 μg Cr g^{-1} in surface and from 22.94 μg Cr g^{-1} to 40.46 μg Cr g^{-1} in sub-surface soil samples. In these soils, the initially added chromium for sorption desorbed back alongwith some amount of native chromium into equilibrium solution. This desorbed amount of native chromium was taken as first desorption and so total six desorptions were carried out in Malerkotla soils. Higher Cr desorption could be due to the higher pH of the Malerkotla soils. The pH of the soils collected from Jalandhar was relatively lower and the per cent desorption was lowest in Jalandhar soils among all the samples. The variations between cumulative chromium desorption from 28 experimental soils (both surface and sub-surface) were illustrated in fig 1a-1g.

The amount of cumulative chromium desorbed from the experimental soils was significantly correlated with pH (positively) in both surface and sub-surface samples (Table 6 and 7). Simple linear regressions for variables (pH, EC, OC, CEC and $CaCO_3$) with cumulative chromium desorbed were calculated. The pH itself has 40% influence on chromium desorption in surface samples (Table 10) and 24% influence in sub-surface samples (Table 11).

Since the amount of chromium sorbed varied between the experimental soils so a term per cent chromium desorbed was calculated. Per cent chromium desorbed was found to be significantly correlated with pH (excluding seven samples from Malerkola as no sorption occurs in these samples). Positive correlation was obtained between the chromium desorbed as well as percent chromium desorbed and pH of the experimental soils both surface and sub-surface which depicts that with the increase in pH, chromium desorption increases. Avudainayagam *et al* (2001) observed that the cumulative Cr desorption was higher in alkaline surface soils (pH = 7.9) and was comparatively low in acidic subsurface soils (pH = 3.9). The chromium desorbed from alkaline surface soil was present as Cr (VI) but Cr present in acidic soils was present as Cr (III). Chokor and Augustine (2017) observed that nearly 66.78 % of the adsorbed chromium was desorbed from the sandy-loam Soil of Nigeria soil in six successive extractions indicated that most of adsorbed Cr was bioavailable within a short time of adsorption.

Stepwise multiple regression was worked out between Cr desorption and soil variables with 28 samples which depicts that in both surface and sub-surface samples, pH was major factor explaining the variability in chromium desorption. In surface soils, pH and EC together explain 49 % variability in chromium desorption and inclusion of DTPA extractable Cr improved the variability to 64 % and with further inclusion of $CaCO_3$, variation increased to 73 % (Equation 5,6 and 7). To explain better the chromium desorption dependence on soil variables (pH, EC, CEC, $CaCO_3$ and clay), the multiple regression model were worked separately for polluted and non polluted soil samples. It was found that in surface samples of polluted soils, pH itself contributes to 51 % variability in chromium desorption (Equation 9). The pH is the important factor on which desorption of chromium depends. In case of polluted sub-surface soil samples, pH and EC together improved the variability to 68% and inclusion of clay increases the variability to 80 % in chromium desorption (Equations 10 and 11).

Surface soils

Cr desorbed = -26.959 + 6.698 pH + 5.702 EC (R^2 = 0.491) ....Equation 5

Cr desorbed = -25.833 + 7.071 pH + 8.458 EC – 17.678 DTPA-Cr (R^2 = 0.646) ...Equation 6

Cr desorbed = -23.270 + 6.448 pH + 9.030 EC – 17.601 DTPA-Cr + 5.019 $CaCO_3$ (R^2 = 0.733)........Equation 7

Sub-surface soils

Cr desorbed = -18.371 + 4.953 pH (R^2 = 0.192) ....Equation 8

Polluted Surface Soils

Cr desorbed = -30.591+ 7.740 pH (R^2 = 0.510) ....Equation 9

Polluted Sub-surface soils

Cr desorbed = -68.748 + 10.908 pH + 31.512 EC (R^2 = 0.686) ....Equation 10

Cr desorbed = -65.191 + 11.484 pH + 46.237 EC -0.957 Clay content (R^2 = 0.807) ....Equation 11

Non polluted Surface soils

Cr desorbed = 5.723 + 1.207 CEC + 9.805 $CaCO_3$ (R^2 = 0.729) ....Equation 12

Cr desorbed = 9.239 + 1.414 CEC – 8.577 $CaCO_3$ – 15.399 DTPA-Cr (R^2 = 0.862) ....Equation 13

Cr desorbed = 14.515 + 1.549 CEC + 10.599 $CaCO_3$ – 21.861 DTPA-Cr – 0.180 Total Cr (R^2 = 0.911) ....Equation 14

Non-Polluted Sub-surface Soils

Cr desorbed = 27.261 – 31.459 OC + 0.537 CEC (R^2 = 0.470) ....Equation 15

Cr desorbed = 26.649 - 30.052 OC + 0.962CEC -17.447 DTPA-Cr (R^2 = 0.662)....Equation 16

A multiple regression model including terms CEC and $CaCO_3$ together improved the variability in chromium desorption to 72% and including DTPA extactable chromium in the model improved variability to 86% (Equations 12 and 13) . With further addition of total Cr in the model, the variation in Chromium desorption increased to 91 % (Equations 14) in surface samples of non polluted soils. In non-polluted sub-surface samples, two variables OC and CEC improves the variability in chromium desorption to 47% and inclusion of DTPA extractable Cr in the model improved variability in chromium desorption to 66% (Equation 15 and 16).

A total 60% of the variation in percent chromium desorbed among 21 soils (excluding seven Malerkotla soils) was explained by multiple regression model including terms pH and EC (Equation 17) whereas 72% variability could be explained including the terms pH, EC and total chromium in surface samples (Equation 18). In the sub-surface samples, pH and organic carbon together improved the variability to 67% and with inclusion of CEC the variability increases to72 % (Equations 19 and 20).

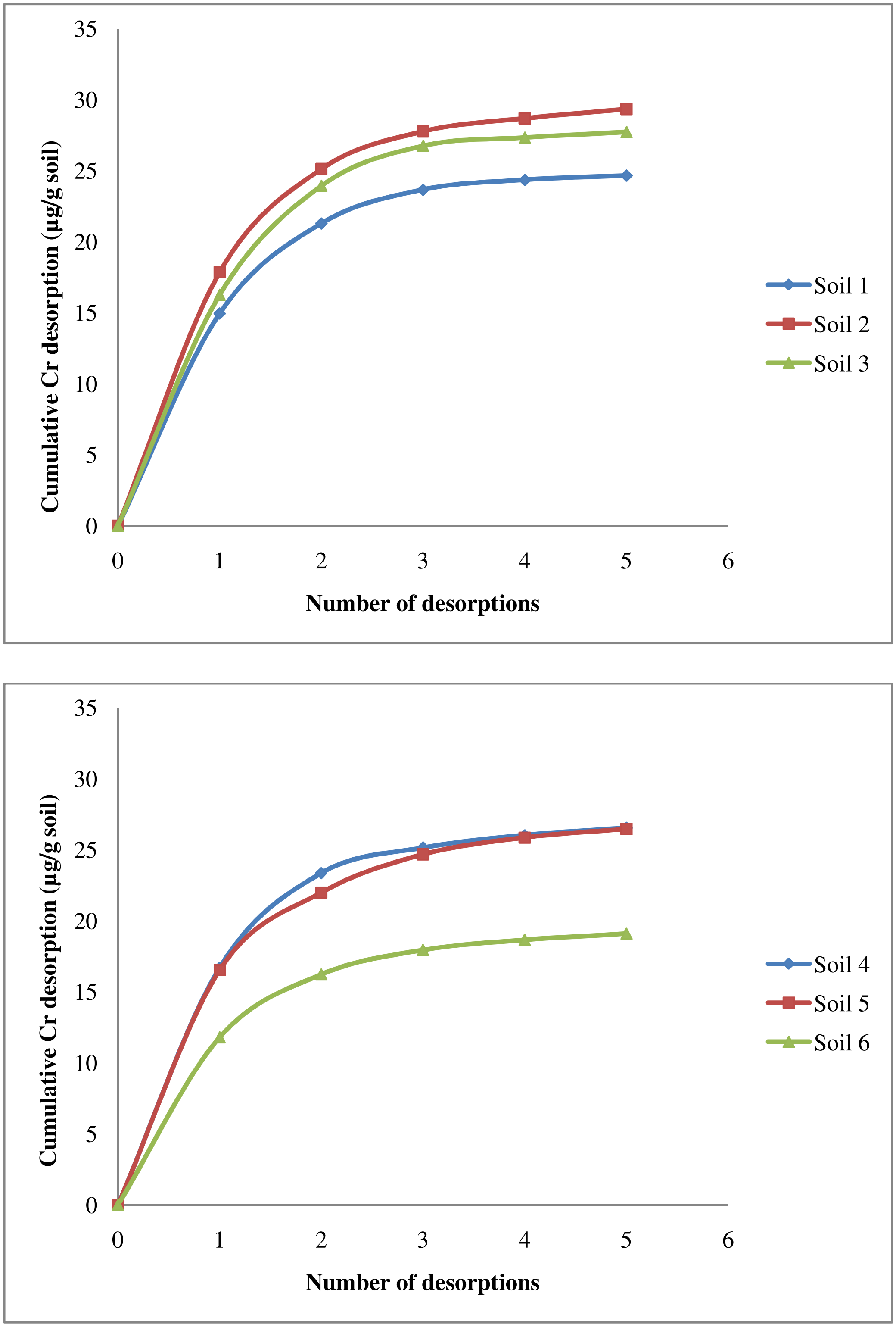


Figure 1a. Cumulative Desorption of Chromium from surface soil samples of Ludhiana

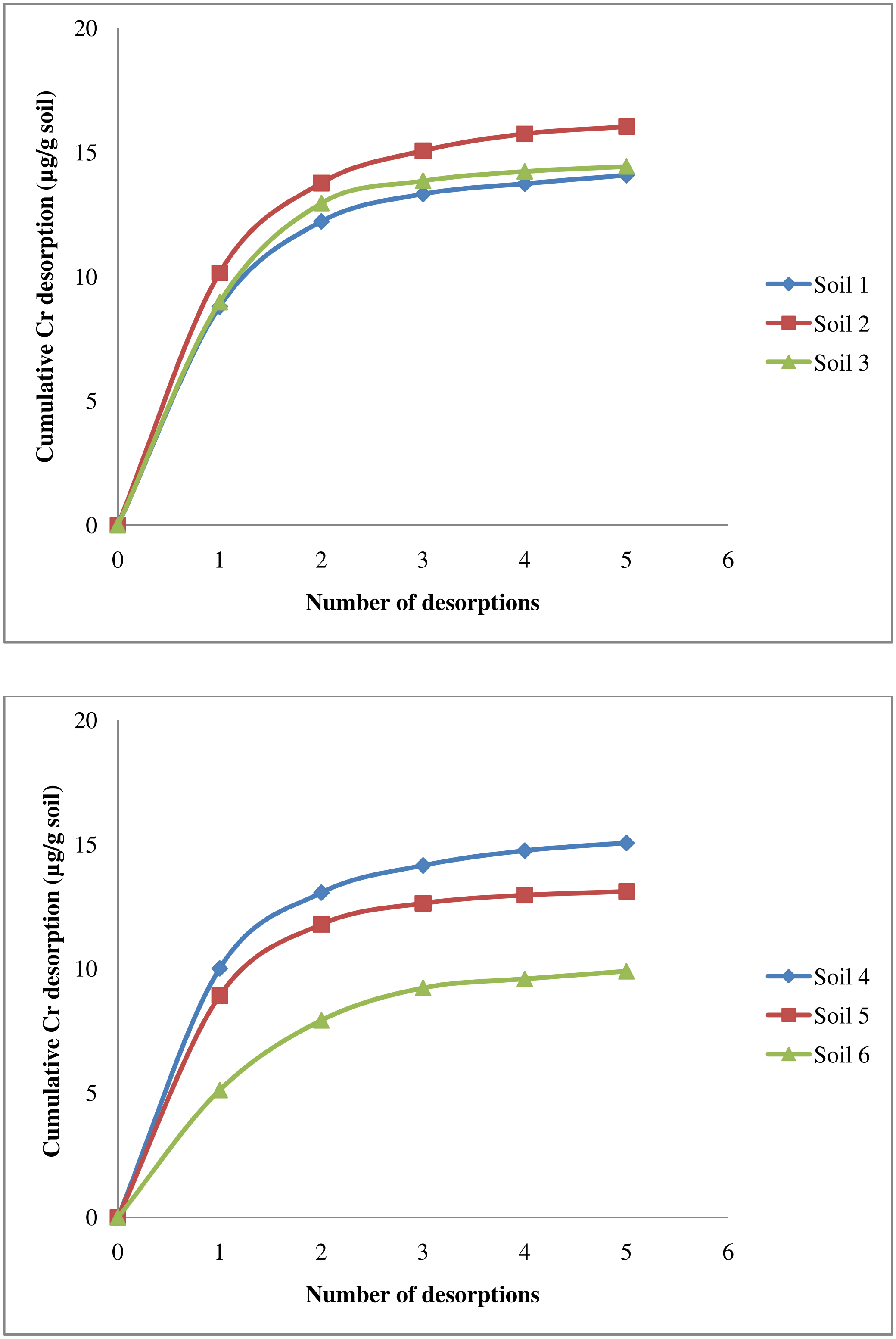


Figure 1b. Cumulative Desorption of Chromium from sub-surface soil samples of Ludhiana

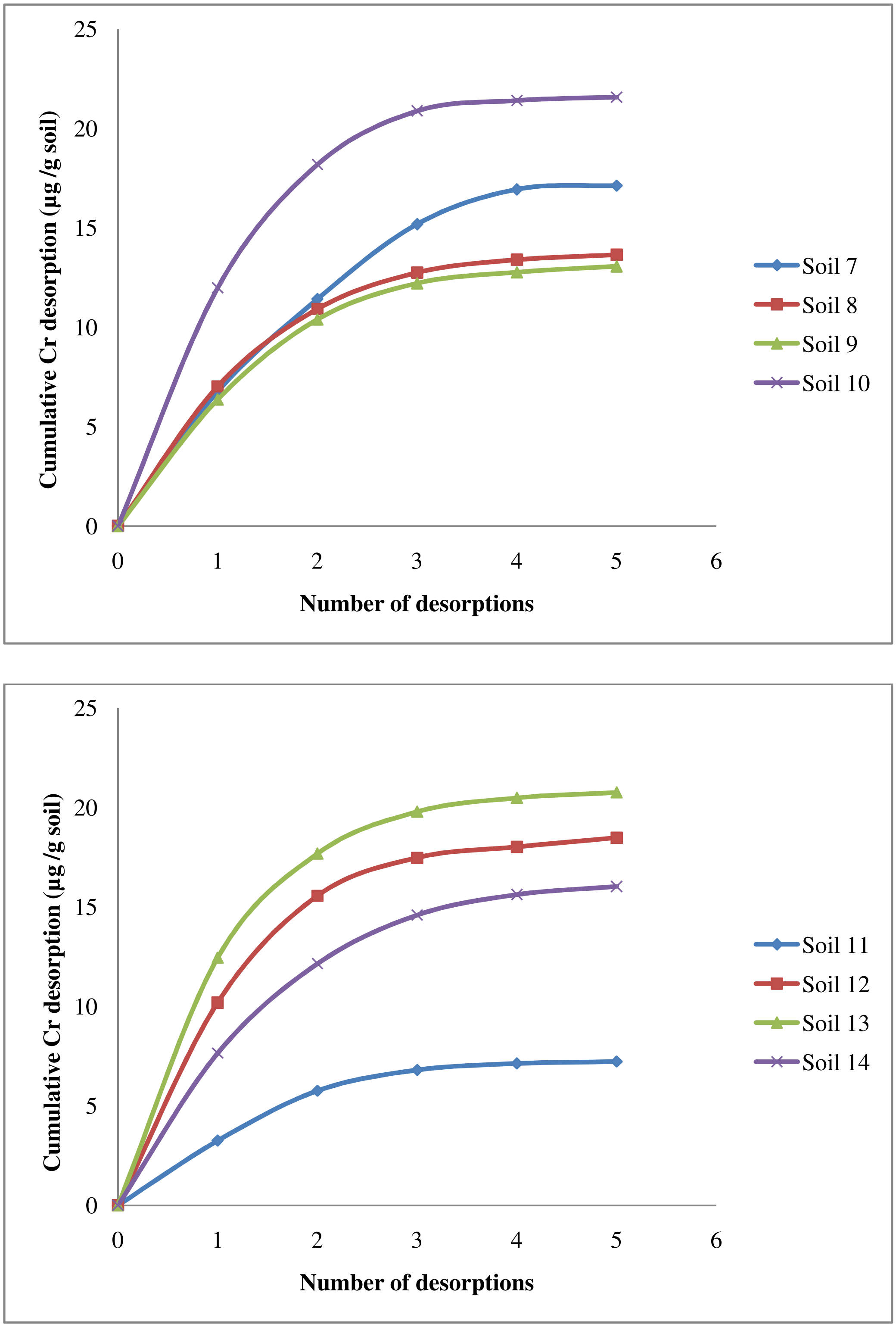
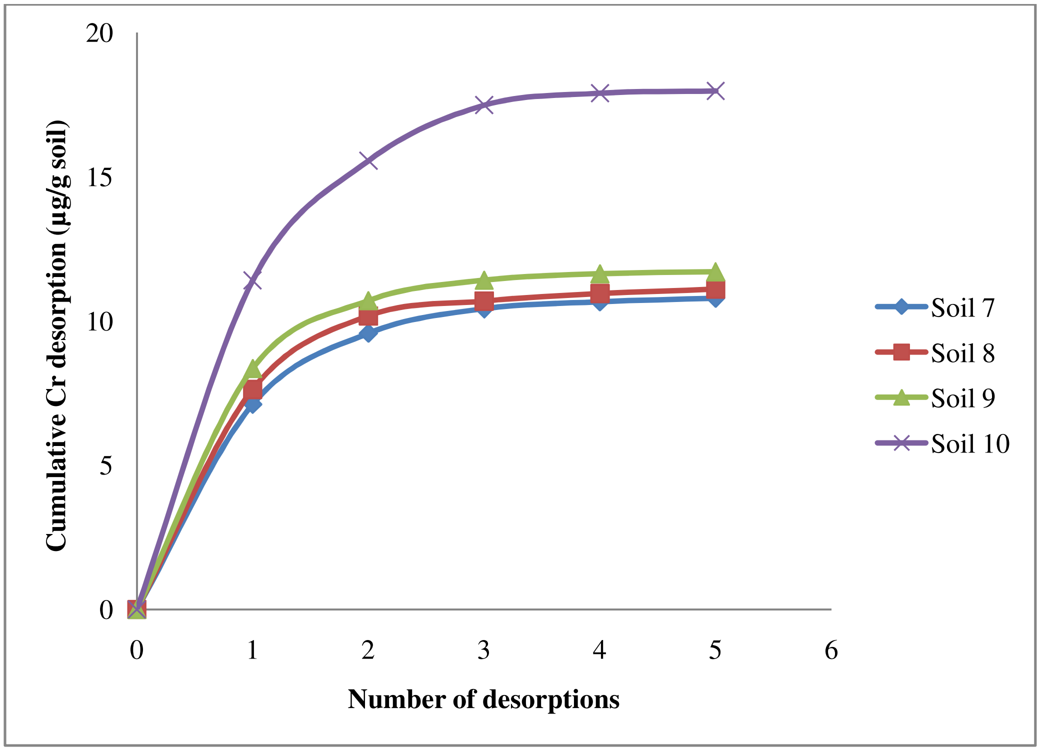


Figure 1c. Cumulative Desorption of Chromium from surface soil samples of Jalandhar



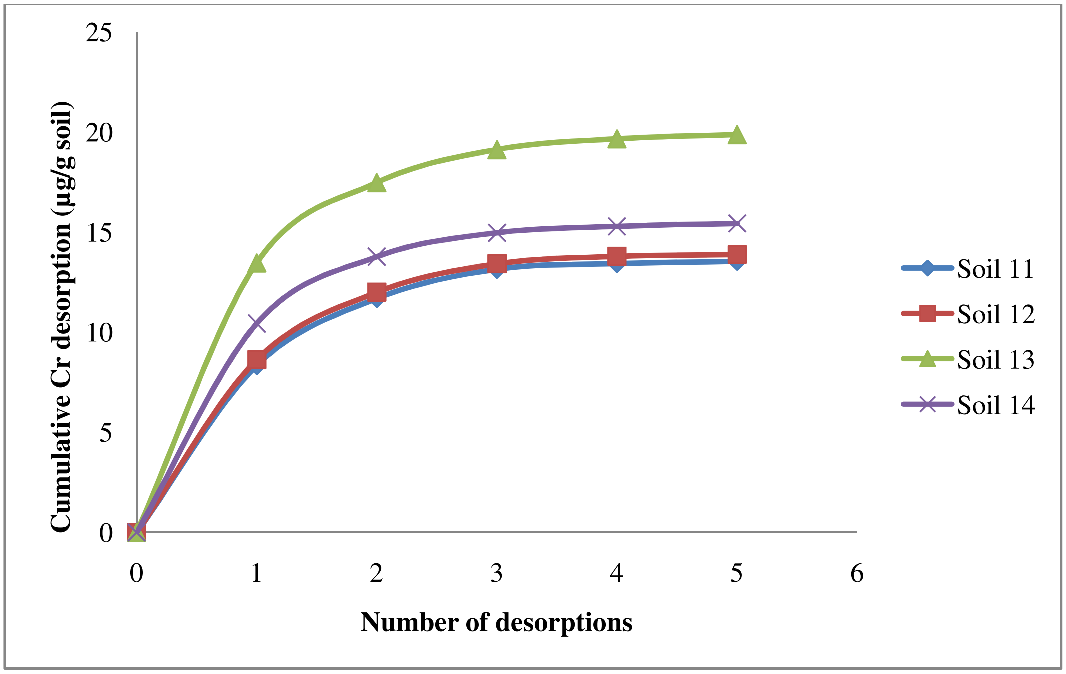


Figure 1d. **Cumulative Desorption of Chromium from sub-surface soil samples of Jalandhar**

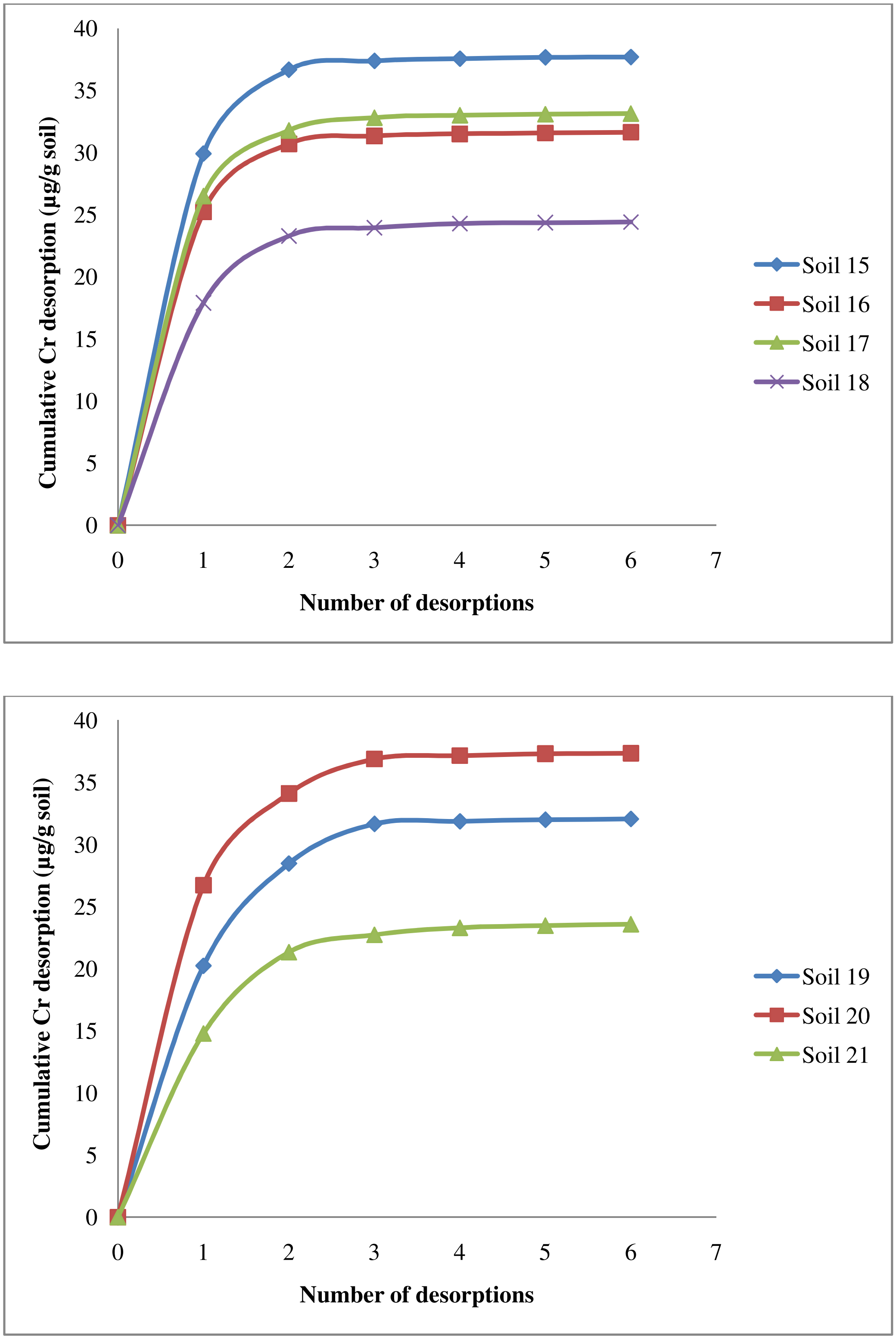


Figure 1e. Cumulative Desorption of Chromium from surface soil samples of Malerkotla

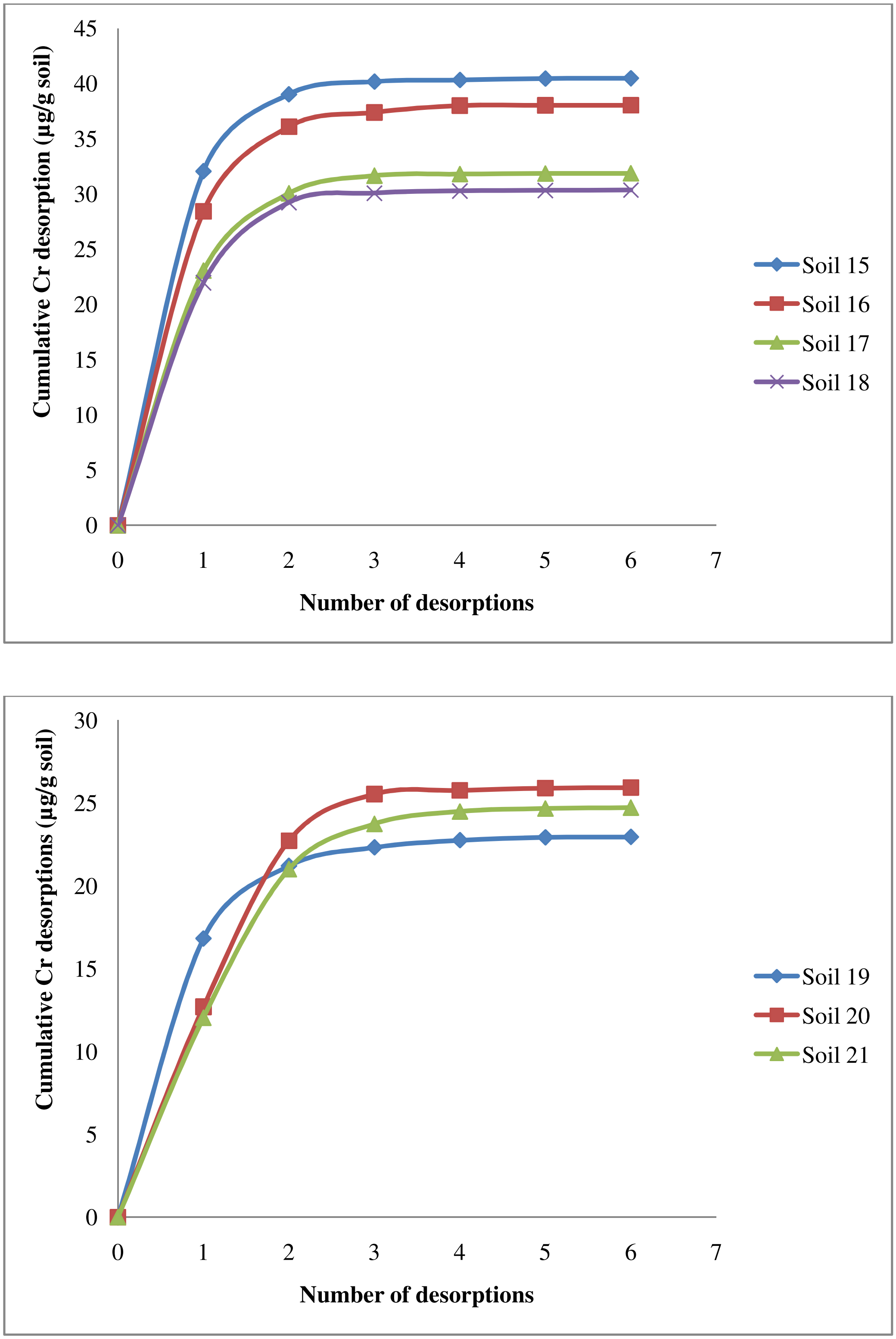
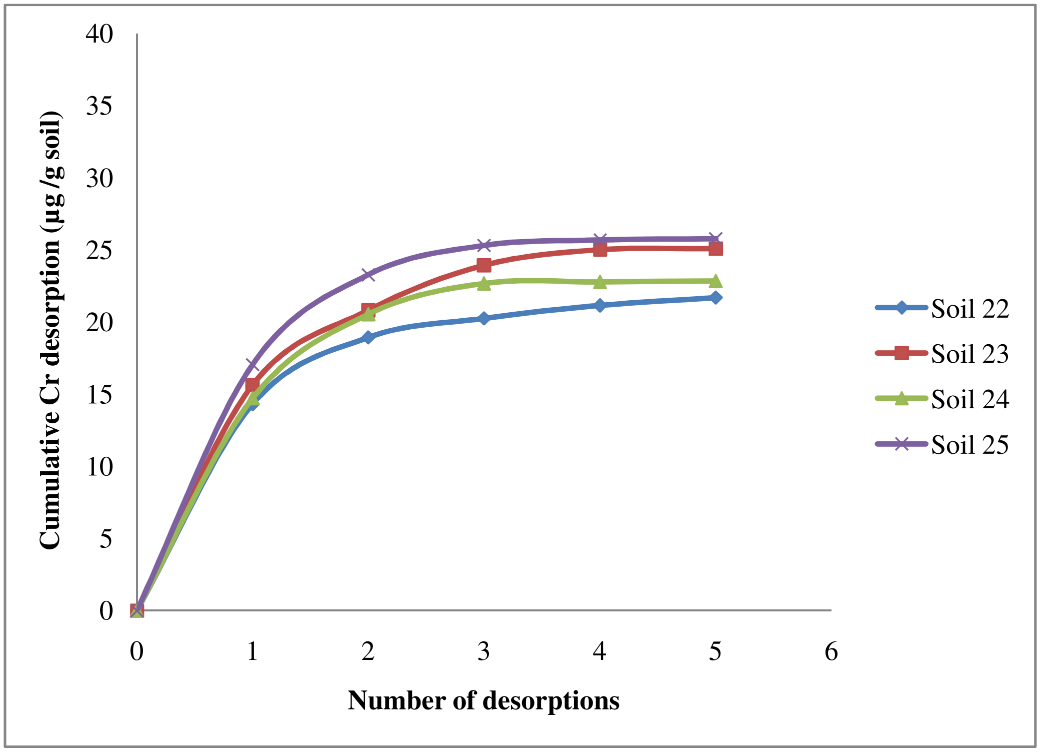


Figure 1f. **Cumulative Desorption of Chromium from sub-surface soil samples of Malerkotla**



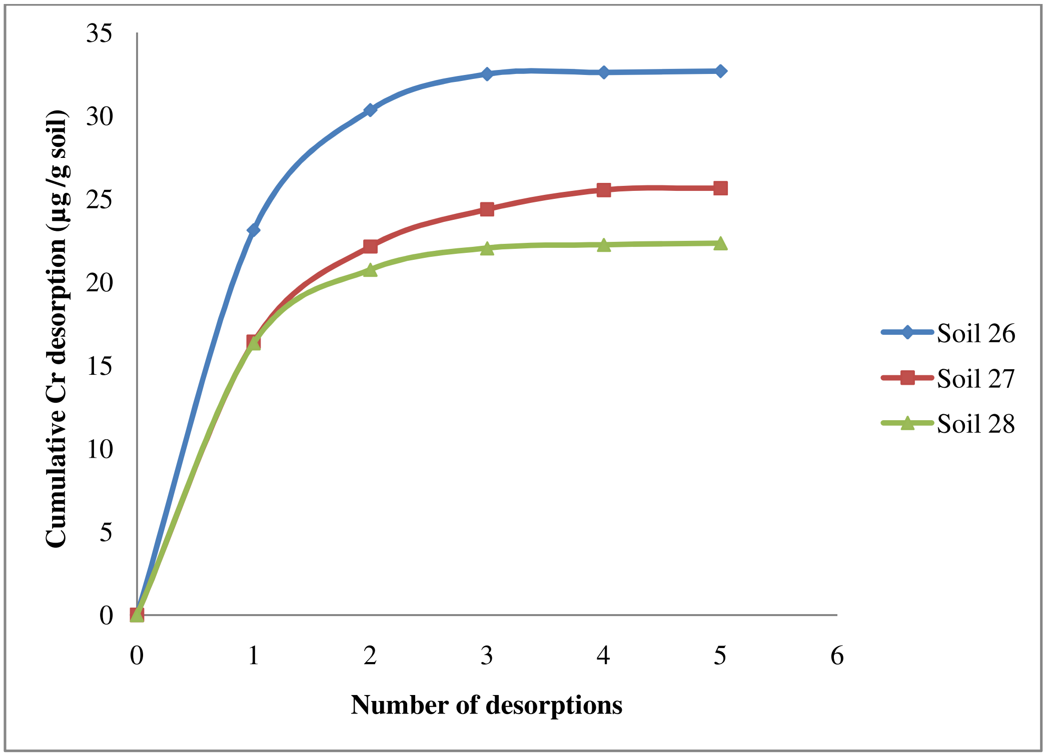
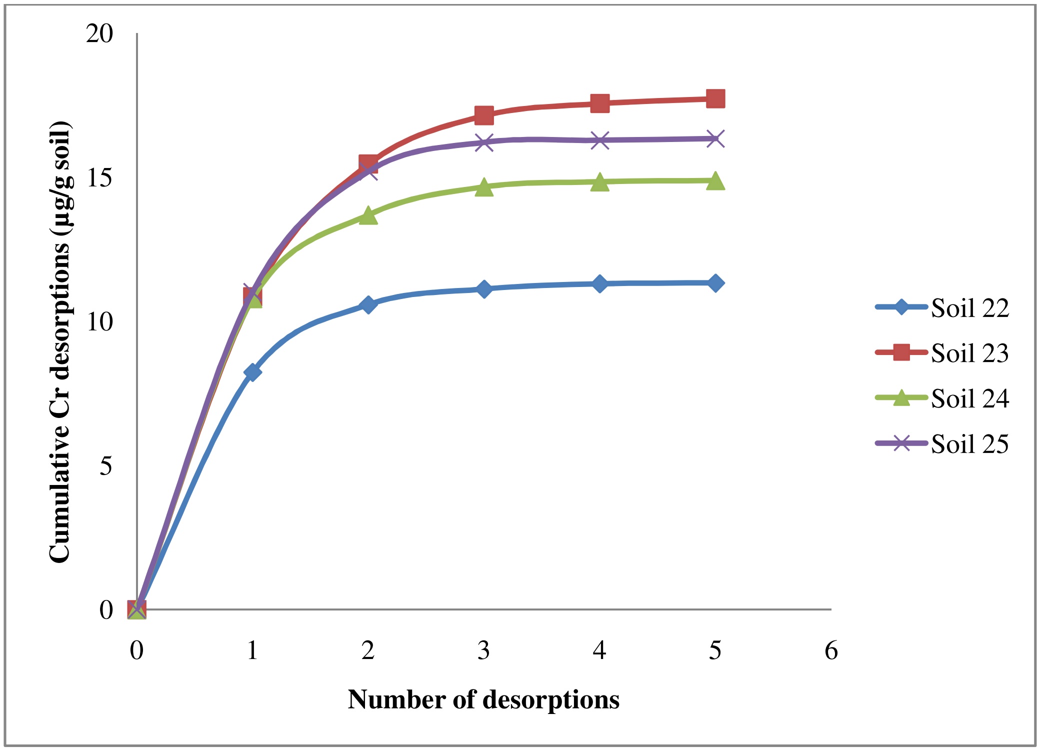


Figure 1g. **Cumulative Desorption of Chromium from surface soil samples of Mandi Gobindgarh**



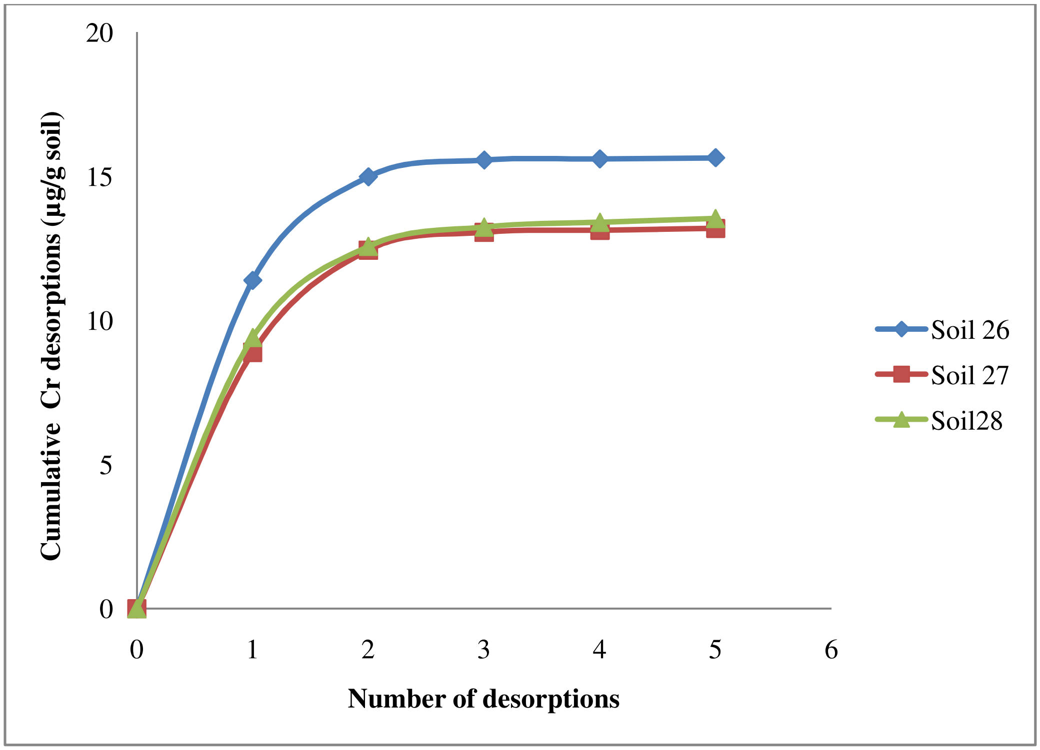


Figure 1h. **Cumulative Desorption of Chromium from sub-surface soil samples of Mandi Gobindgarh**

Surface soil samples

Percent Cr desorbed = - 189.422 + 33.061 pH + 19.324 EC (R^2 = 0.601).........Equation 17

Percent Cr desorbed = -210.153 + 32.372 pH +25.494 EC + 0.783 Total Cr

(R^2 = 0.728) ....Equation 18

Sub-surface soil samples

Percent Cr desorbed = -116.100 + 22.773pH – 12.755 OC (R^2 = 0.677) ......Equation 19

Percent Cr desorbed = -92.614 + 19.059 pH - 24.968 OC + 0.904 CEC

(R^2 = 0.724) ......Equation 20

4.2 To characterize the Cr behaviour in soil and influence of pH as described by sorption / desorption isotherms

4.2.1 Behaviour of chromium as described by sorption and desorption isotherms

Three surface soils (Jalandhar, Ludhiana and Mandi Gobindgarh) which significantly differ in their physico-chemical characteristics, expected to influence chromium sorption-desorption behaviour were selected for this study. The pH of soils selected for this study ranged from 6.64 to 7.18, electrical conductivity from 0.21 to 0.32 dSm^{-1}, CEC from 6.38 to 32.98 cmol (p$^+$) per kg soil, clay content 13.1 to 17.4 % and organic carbon from 0.74 to1.94 %. Total chromium content of soils ranged from 2.70 to 37.75 µg g^{-1} soil and DTPA Cr content ranged from 0.188 to 0.332 µg g^{-1} soil (Table 12).

Table12. Physico-chemical characteristics of surface soils selected for experiment 2

Sample No.	**pH**	**EC (dS m^{-1})**	**Organic Carbon (%)**	**CaCO$_3$ (%)**	**CEC Cmol (p$^+$)/Kg)**	**Clay (%)**	**DTPA Cr (µg g^{-1})**	**Total Cr (µg g^{-1})**
Soil 9	6.64	0.22	0.74	Absent	6.38	17.4	0.332	37.75
Soil 4	7.18	0.32	1.12	0.77	11.74	13.1	0.230	2.70
Soil 23	7.12	0.21	1.94	Absent	32.98	13.5	0.188	35.40

Soil 9: Opposite Bridge Chamiara, Jalandhar

Soil 4: Bhamian road, Ludhiana

Soil 23: Kumbarh near Drain pull 1 Mandi Gobingarh

Table13. Chromium sorbed (µg g^{-1}) at different levels of its addition by various soils

Location	Chromium sorbed (µg g^{-1}) after initial application				
	50	**100**	**300**	**600**	**900**
Jalandhar	6.92	12.06	29.12	46.10	53.52
	(13.8)	(12.1)	(9.7)	(7.7)	(5.9)
Ludhiana	6.31	11.81	29.86	46.53	52.51
	(12.6)	(11.8)	(9.9)	(7.8)	(5.8)
Mandi Gobindgarh	12.44	19.17	47.08	81.25	95.35
	(24.9)	(19.2)	(15.7)	(13.5)	(10.6)

(Figures in parenthesis denote per cent Cr sorbed)

4.2.1.1 Chromium sorption isotherms

The amount of chromium sorbed by the three experimental soils under study that were initially applied with varying concentrations of chromium (50, 100, 300, 600, 900 µg g^{-1} soil) are shown in table 13. It was observed that amount of chromium sorbed by each of three soils increased with increase in initially added concentration of chromium. This is due to the reason that with increase in added chromium concentration, more chromium became available for sorption on to soil colloids. Increase in added concentration of chromium resulted in the increase in occupied sorption sites. But the per cent Cr sorption decreased with increase in Cr concentration. The reason behind this could be less availability of more readily available sorption sites due to their saturation with higher levels of chromium addition.

With the increase in added concentration from 50 µg g^{-1} to 900 µg g^{-1} , the chromium sorbed increased from 6.92 to 53.52 µg g^{-1} for Jalandhar soil, 6.31 to 52.51 µg g^{-1} for Ludhiana soil and 12.44 to 95.35 µg g^{-1} for Mandi Gobindgarh soil (Table13). With initial application of higher concentrations of chromium, the percent chromium sorbed decreased from to 13.8 to 5.9, 12.6 to 5.8 and 24.9 to 10.6 in Jalandhar, Ludhiana and Mandi Gobindgarh soils, respectively. It was observed that among polluted Jalandhar and Mandi gobindgarh soils, the later has high sorption capacity though the pH of Jalandhar soil (6.64) is less than Mandi Gobindgarh soil (7.12). It implies that sorption of chromium also depends on physico-chemical factors other than pH. Mandi gobindgarh soils have high organic carbon content which may have reduced the added hexavalent chromium to its trivalent form and this trivalent form get adsorbed onto soil colloids. Our results are consistent with the findings of Bolan *et al* (2003) examined the fate of Cr (III) and Cr (VI) with and without organic matter and observed that adsorption of Cr (VI) was found to be negligible in absence of organic matter but in the presence of added organic matter, adsorption of Cr (VI) increased inferring that Cr (VI) was reduced to Cr (III) by the organic matter and then get adsorbed in trivalent form. Jardine *et al* (2013) also observed an increase in Cr (VI) sorption with the increase in soil total organic carbon (TOC) and decrease in pH by multiple linear regression analysis. They explained this increase was due to the reduction of Cr (VI) to Cr (III), prevalent in experimental soils and the redox transformation of Cr (VI) increased with increase in soil TOC. Earlier, Han *et al* (2004) reported that addition of organic amendments increases the rate of reduction of Cr (VI) to Cr (III) in soils and the extent of Cr (VI) reduction was positively correlated with the amount of dissolved organic carbon in the soil. The transformed trivalent form get adsorbed on soils that enhances the adsorption.

With the application of higher levels of initially added chromium to soils, the percent chromium sorbed decreased. The chromium sorption decreased from 13.8 to 5.94%, 12.6 to 5.8% and 24.9 to 10.6% in Jalandhar, Ludhiana and Mandi Gobindgarh soils. The decrease in percent sorption was comparatively more in Jalandhar and Ludhiana soils than Mandi

Gobindgarh soil. This implies that Mandi Gobindgarh soil has higher sorption capacity as compared to other two soils.

The sorption data was well described by Langmuir adsorption isotherm with high values of R^2 (0.959 to 0.994) derived from data pairs of C/(x/m) and C_e of three soils (Table 14; Fig 2a-c). Kwikima and Lema (2017) found that the adsorption isotherm of Cr (VI) for the experimental soil conforms well to the Langmuir isotherm at constant pH. Two adsorption parameters: the maximum sorption capacity (Q_o) and Langmuir adsorption constant (K_l), for Cr (VI) were determined as 1.013×10^{-4} mol/g and 0.062 mg/L. Sunil and Faziludeen (2015) observed that greater adsorption capacity in lateritic soil blended with 30% bentonite described by Langmuir model with adsorption capacity 71.43 mg/kg than lateritic soil blended with marine clay and black cotton soil for low concentrations of Cr (VI) solutions due to large surface area of bentonite clay.

Table 14. Langmuir equations and Langmuir parameters for various soils

Location	Linear equation	R^2	b_{max} (µg g^{-1})	K (ml µg $^{-1}$)
Jalandhar	y = 0.011x + 0.601	0.994	90.909	0.018
Ludhiana	y = 0.011x + 0.626	0.989	90.909	0.017
Mandi Gobindgarh	y = 0.006x + 0.334	0.959	166.66	0.017

In the three experimental soils, maximum Cr (VI) sorption occured in Mandi Gobindgarh as compared to other two soils, probably due to higher organic carbon content which enhanced reduction of added hexavalent chromium to its trivalent form. This trivalent form then get adsorbed onto soil. The trend of maximum amount of Cr sorption was in order of Mandi Gobindgarh > Jalandhar > Ludhiana.

Chromium sorption data was also well explained by Freundlich adsorption isotherm as indicated by high R^2 values (0.985 to 0.994) (Table15, Fig 3a-c).

The value of adsorption capacity ‘ K_f’ (relative affinity of adsorbent for adsorbate) was high in Mandi Gobindgarh soil. As discussed earlier also, higher organic carbon content could be responsible for its higher retention than other two soils. The higher organic carbon may have enhanced the rate of reduction of Cr (VI) to Cr (III) in soils and the extent of Cr (VI) reduction has been observed to be positively correlated with the amount of dissolved organic carbon in the soil (Han *et al* 2004). The Cr (VI) sorption capacity of the soils followed the order Mandi Gobindgarh > Jalandhar > Ludhiana. Jalandhar soil has high

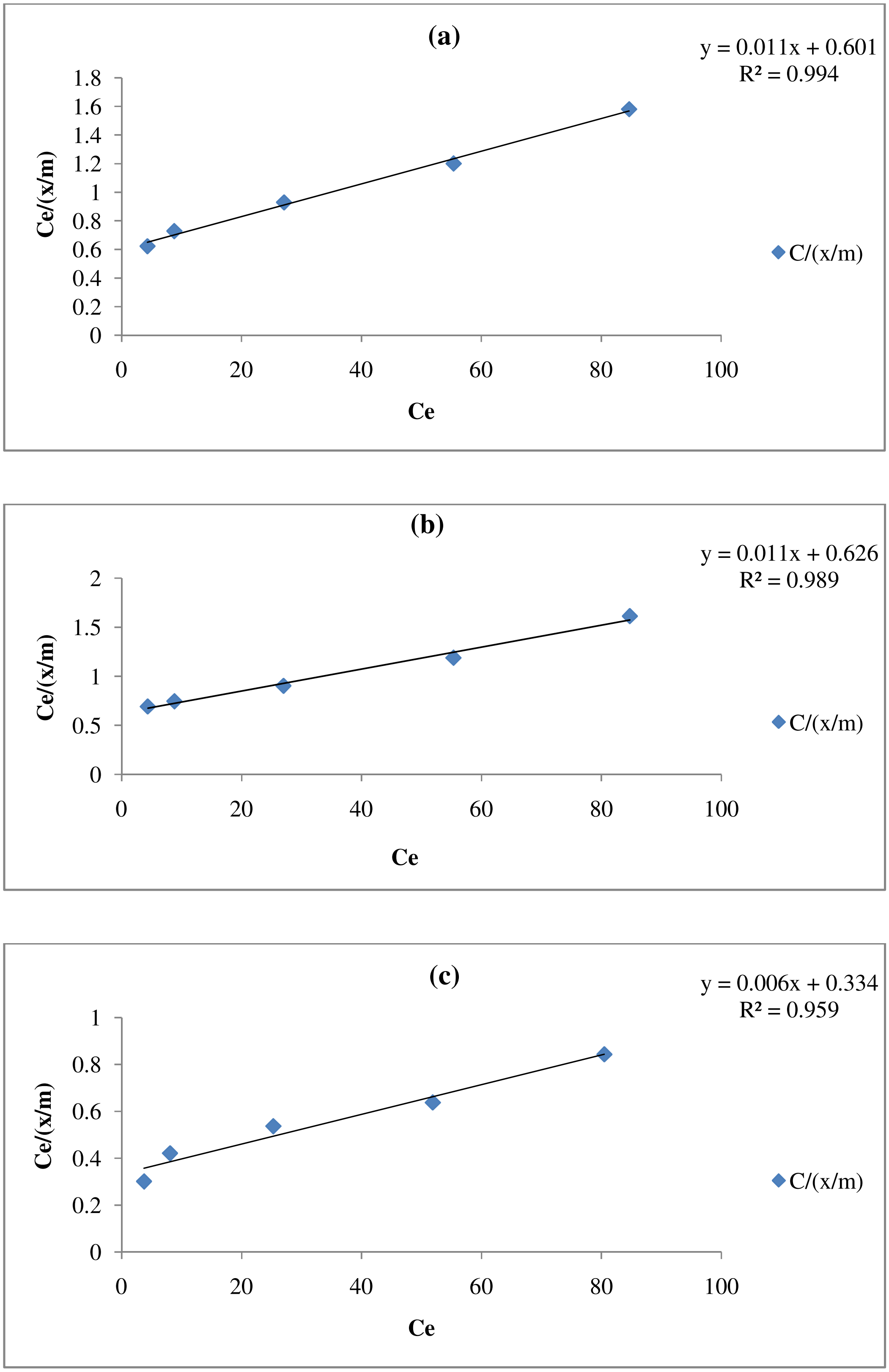


Figure 2. Langmuir adsorption Isotherm for (a) Jalandhar (b) Ludhiana (c) Mandi Gobindgarh soil

Table15. Freundlich equations and Freundlich parameters for various soils

Location	Linear equation	R^2	K_f	N
Jalandhar	y = 0.705x + 0.412	0.992	2.6	0.705
Ludhiana	y = 0.732x + 0.366	0.985	2.3	0.732
Mandi Gobindgarh	y = 0.696x + 0.681	0.994	4.8	0.696

sorption capacity than Ludhiana soil that could be due to its low pH. Luo *et al* (2010) employed both Langmuir and the Freundlich models to sorption data for nine chromium (III) organic complexes and reported that Freundlich model provided good fits for all of the chromium (III) organic complexes. The reason behind good fits to the Freundlich model might be the restrictive assumptions of Langmuir isotherm (i.e. single layer sorption, homogeneous surface and bonding energies and no interaction among the compound and the surface). Chopala *et al* (2013) revealed that Cr sorption by 12 Australian was better explained by the Freundlich isotherm as compared to Langmuir isotherm. Their data showed the higher values of coefficient of correlation which ranged from 0.953 to 0.988 obtained by fitting Freundlich adsoprtion isotherm as compared to Langmuir isotherm in which value of R^2 varied from 0.644 to 0.889. Freundlich sorption coefficients (K_f) from 0.04 to 49.01 L kg^{-1} for Cr (VI).

Chromium sorption by the three soils was also well described by Dubinin Raduhkevitch adsorption isotherm with high value of R^2 (0.926 to 0.973) derived from linear plots between lnQ_e and ε^2 (Table 16, Fig 4a-c). Dubinin Raduhkevitch adsorption isotherm predict the type of sorption whether physi-sorption or chemisorption based on the energy of activation. If the energy of activation is < 8 KJ/mol, the adsorption is physisorption and if the energy of activation is 8-16 KJ/mol, the adsorption is chemisorptions in nature.

Since the energy of activation calculated using $E= 1/\sqrt{(-2B)}$ of all the three experimental soils is less than 8 KJ mol^{-1} which implies that sorption of chromium is physisorption i.e. Cr anions are adsorbed on the soil colloids by vander waal forces. Fonseca *et al* (2009) studied Cr sorption in loamy sand soil was studied at pH 2 and 5 and observed that Cr sorption was well described by Dubinin–Radushkevich model and the value obtained for the mean energy sorption was lower than 8 kJ mol^{-1}, indicating that Cr is retained mainly by physical adsorption by weak Vander Waals forces.

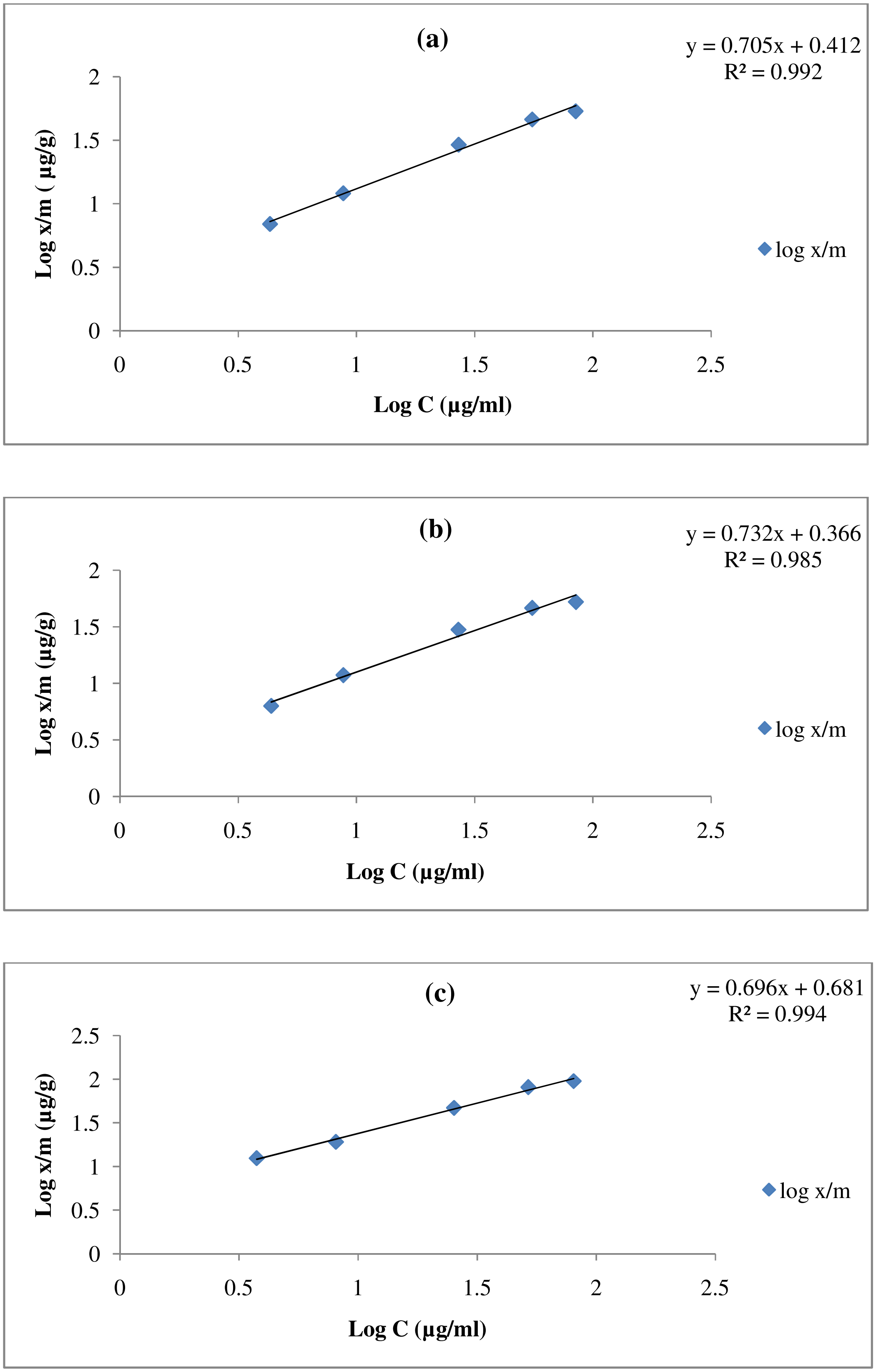


Figure 3. Linearized Freundlich adsorption isotherm for (a) Jalandhar (b) Ludhiana (c) Mandi Gobindgarh soil

Table 16. D-R (Dubinin Raduhkevitch) equations and Dubinin Raduhkevitch parameters for various soils

Sample site	Linear equation	R^2	Q_m (mmol kg^{-1} soil)	E(kJ mol^{-1})
Jalandhar	y = -0.052x - 0.057	0.960	0.94	3.10
Ludhiana	y = -0.055x - 0.038	0.973	0.96	3.02
Mandi Gobindgarh	y = -0.047x + 0.467	0.926	1.59	3.26

4.2.1.2 Chromium Desorption isotherms

The cumulative desorption of sorbed chromium over a period of five desorptions increased with the increase in the number of successive desorptions irrespective of the initial concentration of chromium added to each of these soils, but the amount of chromium desorbed in every successive desorption decreased (Table 17). Also within a soil, cumulative chromium desorbed increased with an increase in initially added chromium concentration from 50 µg g^{-1} to 900 µg g^{-1}. In case of Jalandhar soil, it increased from 1.08 to 39.71 µg Cr g^{-1}, in Ludhiana soil from 1.09 to 41.47 µg Cr g^{-1} and in Mandi Gobindgarh soil from 1.29 to 39.79 µg Cr g^{-1} (Table17).

With the increase in particular level of initially added chromium (50 to 900 µg Cr g^{-1}), the per cent chromium desorbed increased from previously sorbed chromium (Table 17). The percent chromium desorbed increased from 15.7 to 74 % for Jalandhar soil, 17.4 to 79 % for Ludhiana soil and 10.4 to 41.7% for Mandi Gobindgarh soil (Table 17).

Cumulative amount of chromium desorbed as well as per cent chromium desorbed were highest for Ludhiana soil and lowest for Mandi Gobindgarh soil at all the levels of chromium addition. This could be due to relatively higher pH of Ludhiana soil among all three soils. Though the pH of Mandi Gobindgarh soil is similar to the Ludhiana but due to high content of organic carbon sorbed in its trivalent form onto soil after reduction and desorption of trivalent form decreases at higher pH. Also the cation exchange capacity of soil is high which implies trivalent chromium is strongly sorbed onto soil. Due to this reason, desorption of Cr in this soil is relatively lesser. Lesser cumulative Cr desorbed by Jalandhar soil as compared to Ludhiana soil could be due to low pH of the former than later.

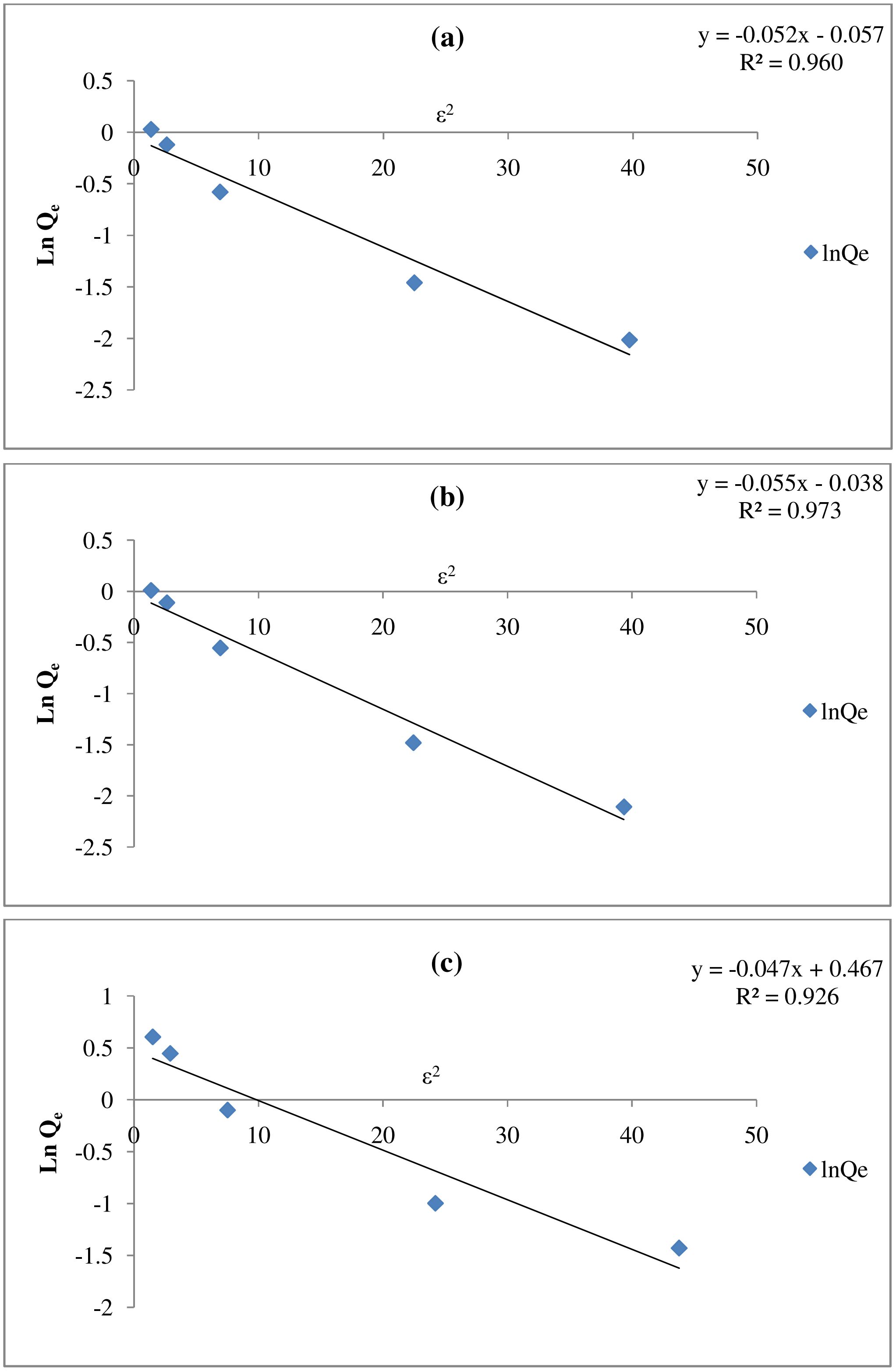


Figure 4. Dubinin–Radushkevich adsorption isotherm for (a) Jalandhar (b) Ludhiana (c) Mandi Gobindgarh soil

Table 17. Desorption of sorbed chromium initially added at different levels (µg g^{-1}) from various soils

Location	Levels of added chromium (µg g^{-1})				
	50	100	300	600	900
Jalandhar	1.08	3.52	11.34	28.17	39.71
	(15.7)	(29.2)	(38.9)	(61.1)	(74.0)
Ludhiana	1.09	3.99	11.93	23.99	41.47
	(17.4)	(33.8)	(39.9)	(64.5)	(79.0)
Mandi Gobindgarh	1.29	1.98	8.92	22.60	39.79
	(10.4)	(10.3)	(18.9)	(27.8)	(41.7)

(Figures in parenthesis denote per cent Cr desorption)

Cumulative chromium desorption graphs at different levels of initially added chromium were plotted for all the soils. The amount of chromium desorbed was higher in first few desorptions and with subsequent desorptions it decreased till it became constant. The cumulative desorption curves become flat with increase in number of desorptions (Fig 5a-c).

Desorption of lead and cadmium in seven alkaline soils of Punjab was studied by modified Langmuir desorption equation (Singh and Sekhon 1977). Desorption data was well fitted to the equation (R^2 varies from 0.967 to 0.992). Desorption parameters i.e. desorption maxima and constant related to chromium mobility ' K_d' were calculated (Table 18). The values of desorption maxima ' D_m' varied from 71.42 to 125 µg $g^{-1}$for the soils under study. The value of K_d ranged from 0.058 to 0.082.

Thus indicating that maximum cummulative desorption and highest Cr mobility occured for Mandi gobindgarh soils mainly due to its high pH values, though the effect of other factor like organic carbon, CEC etc. may had an effect on the amount and pattern of desorption in the three soils under study.

4.2.2 Effect of pH on sorption and desoprtion of chromium

4.2.2.1 Soils

Three surface soils (Near gatta factory, Nahalon, Jalandhar; Opposite to Modern Public School; Malerkotla and Badali I, Mandi Gobindgarh) those differ in physico-chemical properties i.e pH (6.2, 8 and 7.1), cation exchange capacity (5.44, 12.86 and 28.12 cmol (p+) kg^{-1} soil), electric conductivity (0.71, 0.49 and 0.32 dSm^{-1}), organic carbon (0.60, 0.94 and 1.51 %) were selected (Table 19). The pH of the original soil samples were adjusted between 6-8 as described in section 3.3.3. The pH of Jalandhar soil with original pH 6.2 was adjusted to 7 and 8.The pH of Malerkotla soil was adjusted from 8 to 6 and 7 whereas pH of Mandi gobindgarh soil adjusted from 7.1 to 6 and 8 in order to determine the effect of pH on sorption and desorption of chromium.

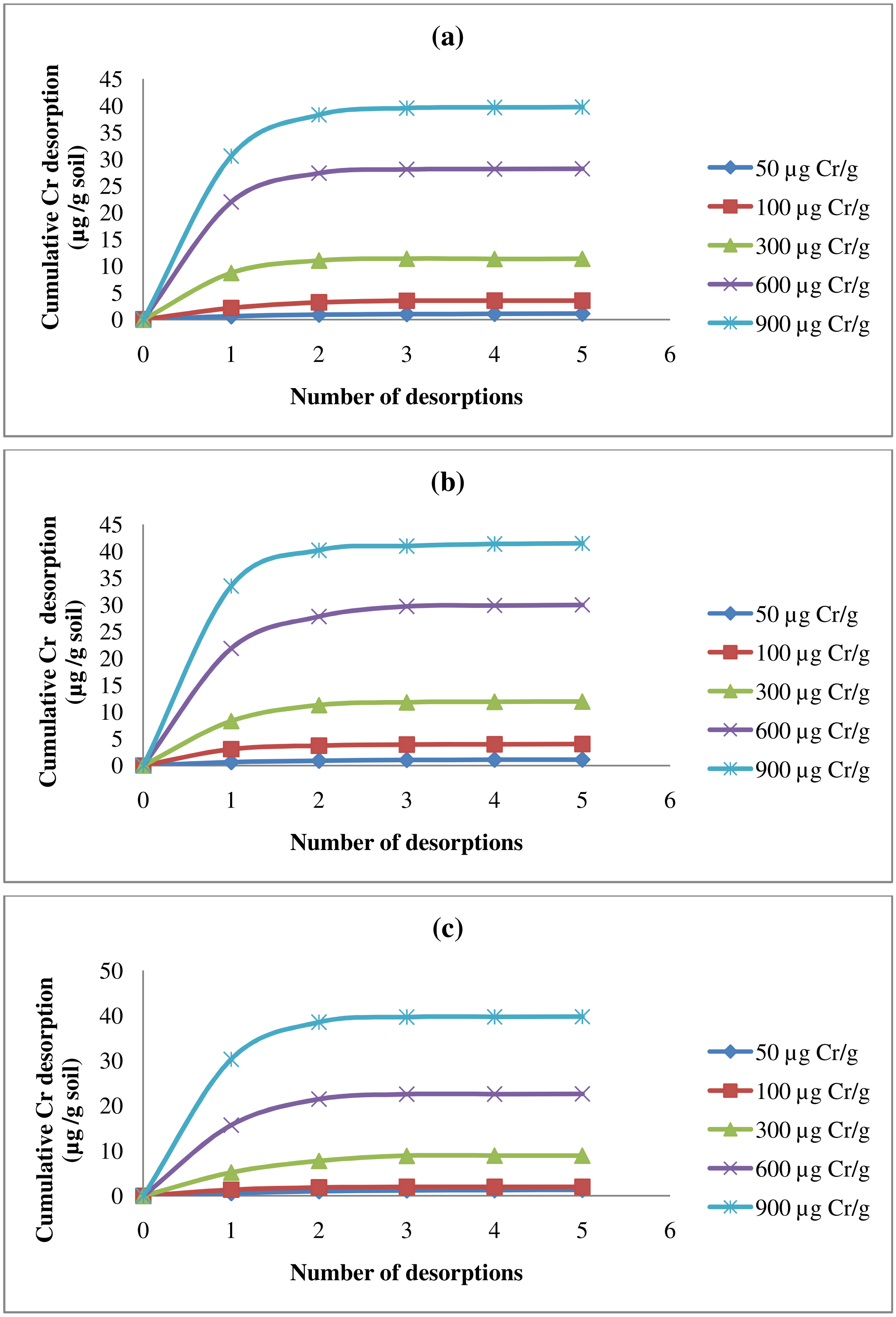


Figure 5. Cumulative chromium desorbed from (a) Jalandhar (b) Ludhiana (c) Mandi Gobindgarh soil after different levels of Cr addition (concentration µg/g)

Table 18. Langmuir desorption equations and Langmuir parameters for various soils

Sample site	Linear equation	R^2	D_m (µg g^{-1})	K_d (ml µg^{-1})
Jalandhar	y = 0.014x + 0.202	0.970	71.42	0.069
Ludhiana	y = 0.013x + 0.222	0.967	76.92	0.058
Mandi Gobindgarh	y = 0.008x + 0.097	0.992	125	0.082

Table 19. Physico-chemical characteristics of surface soils selected for experiment 3

Sample No.	pH	EC (dS m^{-1})	Organic Carbon (%)	$CaCO_3$ (%)	CEC Cmol (p^+)/Kg)	Clay (%)	DTPA Cr (µg g^{-1})	Total Cr (µg g^{-1})
Soil 8	6.2	0.71	0.60	Absent	5.44	11.5	0.184	17.70
Soil 16	8.0	0.49	0.94	0.55	12.86	13.9	0.172	23.25
Soil 24	7.1	0.32	1.51	Absent	28.12	21.5	0.194	23.90

Soil 8: Near gatta factory Nahalon, Jalandhar

Soil 16: Opposite Modern Public school, Malerkotla

Soil 24: Badali I, Mandi Gobingarh

4.2.2.2 Effect of pH on sorption of added chromium in soils

The adjustment of original pH of the selected soils has a major impact on their abiliy to sorb chromium. In Jalandhar soil at pH 6.2, sorbed chromium varied from 10.39 to 104.9 µg g^{-1} soil (20.8% to 11.7% of added Cr); at pH 7, it varied from 8.32 to 66.57 µg g^{-1}soil (16.6% to 7.4% of added Cr) and at pH 8, it varied from 6.22 to 39.97 µg g^{-1}soil (12.4% to 4.4% of added Cr) depending upon initially added Cr (Table 20). In case of Malerkotla soil, at pH 6, chromium sorbed varied from 6.79 to 37.32 µg g^{-1}soil (13.6% to 4.1% of added Cr); at pH 7, it varied from 1.96 to 20.89 µg g^{-1}soil (3.9% to 2.3% of added Cr) and at pH 8, no sorption occured (Table 21). For Mandi Gobindgarh soil at pH 6, chromium sorbed varied from 8.68 to 79.38 µg g^{-1}soil (17.4% to 8.8%); at pH 7.1, it varied from 5.71 to 60.54 µg g^{-1}soil (11.4% to 6.7% of added Cr) and at pH 8, it varied from 4.99 to 39.50 µg g^{-1}soil (10% to 4.4% of added Cr) (Table 22).

With the increase in initially added concentrations of chromium (50 to 900 µg g^{-1} soil), the amount of chromium sorbed by all the three soils increases at a particular pH. However, the percent chromium sorbed decreased with increase in initial added chromium concentrations as well as with increasing pH (Tables 20, 21 and 22). This may be due to decrease in available sorption sites due to saturation of the surface. Khan *et al* (1995) also reported decrease in percent adsorption of Cr (VI) with increase in pH. Soil pH plays an important role in the adsorption of heavy metal anoins since it affects the solubility, adsorption and speciation of metals (Choppala *et al* 2013). The pH of the soils controls the adsorption capacity due to its influence on the functional groups of the adsorbent and the species distribution of the adsorbate (Matern and Mansfeldt 2016). Barnie *et al* (2018) studied about pH-dependence of Cr (VI) retention by undissolved humic acid (HA). Both of the peat soils Northeast China (EHA) and from Sigma Aldrich (CHA) removed maximum quantities of Cr (VI) (98.98 and 90.20% respectively) in strongly acidic (pH 2.3) media but in slightly acidic pH of 5.86, its removal decreased to 30.66% and 27.04%. Jiang *et al* (2008) also reported that with increase in pH of all three variable charge soils having original pH varied from 4.8 to 5.4 under study, the adsorption capacity of chromate decreased. With the increase of pH by one unit, the decrease in the adsorption was 4.0, 1.8, 2.2 mmol kg^{-1} for the Hyper-Rhodic Ferralsol, the Rhodic Ferralsol and the Haplic Acrisol. The reason is that the increase in pH could have caused the decrease in the positive surface charge and increase in the negative surface charge.

Table20. Sorpion of chromium by Jalandhar soil at different pH levels

	Added Cr (µg g^{-1})				
Soil pH	**50**	**100**	**300**	**600**	**900**
6.2	10.39	18.85	50.19	82.74	104.95
	(20.8)	(18.9)	(16.7)	(13.8)	(11.7)
7.0	8.32	15.83	40.61	60.43	66.57
	(16.6)	(15.8)	(13.5)	(10.1)	(7.4)
8.0	6.22	11.26	25.77	36.09	39.97
	(12.4)	(11.2)	(8.6)	(6.0)	(4.4)

(Figures in parenthesis denote per cent Cr sorbed)

Table 21. Sorption of chromium by Malerkotla soil at different pH levels

	Added Cr (µg g^{-1})				
Soil pH	**50**	**100**	**300**	**600**	**900**
6.0	6.79	12.60	20.77	29.82	37.32
	(13.6)	(12.6)	(6.9)	(5.0)	(4.1)
7.0	1.96	3.59	10.39	15.67	20.89
	(3.9)	(3.6)	(3.5)	(2.6)	(2.3)
8.0	0	0	0	0	0
	0	0	0	0	0

(Figures in parenthesis denote per cent Cr sorbed)

Table 22. Sorption of chromium by Mandi Gobindgarh soil at different pH levels

	Added Cr ($\mu g\ g^{-1}$)				
Soil pH	**50**	**100**	**300**	**600**	**900**
6.0	8.68	16.88	46.96	65.78	79.38
	(17.4)	(16.9)	(15.7)	(11.0)	(8.8)
7.1	5.71	11.23	32.73	48.66	60.54
	(11.4)	(11.2)	(10.9)	(8.1)	(6.7)
8.0	4.99	9.37	19.47	27.01	39.50
	(10.0)	(9.4)	(6.5)	(4.5)	(4.4)

(Figures in parenthesis denote per cent Cr sorbed)

Chromium sorption data of the selected soils at various pH levels was well described by Langmuir adsorption isotherm with high values of R^2 (0.924 to 0.995) as shown in table 23, Fig 6a-c.

Within a soil, the slopes and intercepts of Langmuir plots varied at different pH levels. Generally, the slope was more higher at higher pH than lower pH levels in all the three soils. Also the Langmuir affinity parameter k increases with increase in pH. In Malerkotla soil, at pH 8 no soprtion occured (Table 21). Hence, data points were not available to fit Langmuir isotherm. Matern and Mansfeldt (2016) observed that chromate adsorption was higher in chiwwali subsoil sample from Uttar Pradesh due to its lower pH and high content of pedogenic Fe oxides. Sorption data of three soils from chromium ore residue disposal sites of Uttar pradesh were fitted to both Freundlich and the Langmuir isotherms. The coefficient of determination was relatively higher for the Langmuir Isotherm (R^2= 0.99) as compared to the Freundlich isotherm (R^2=0.96 to 0.99).

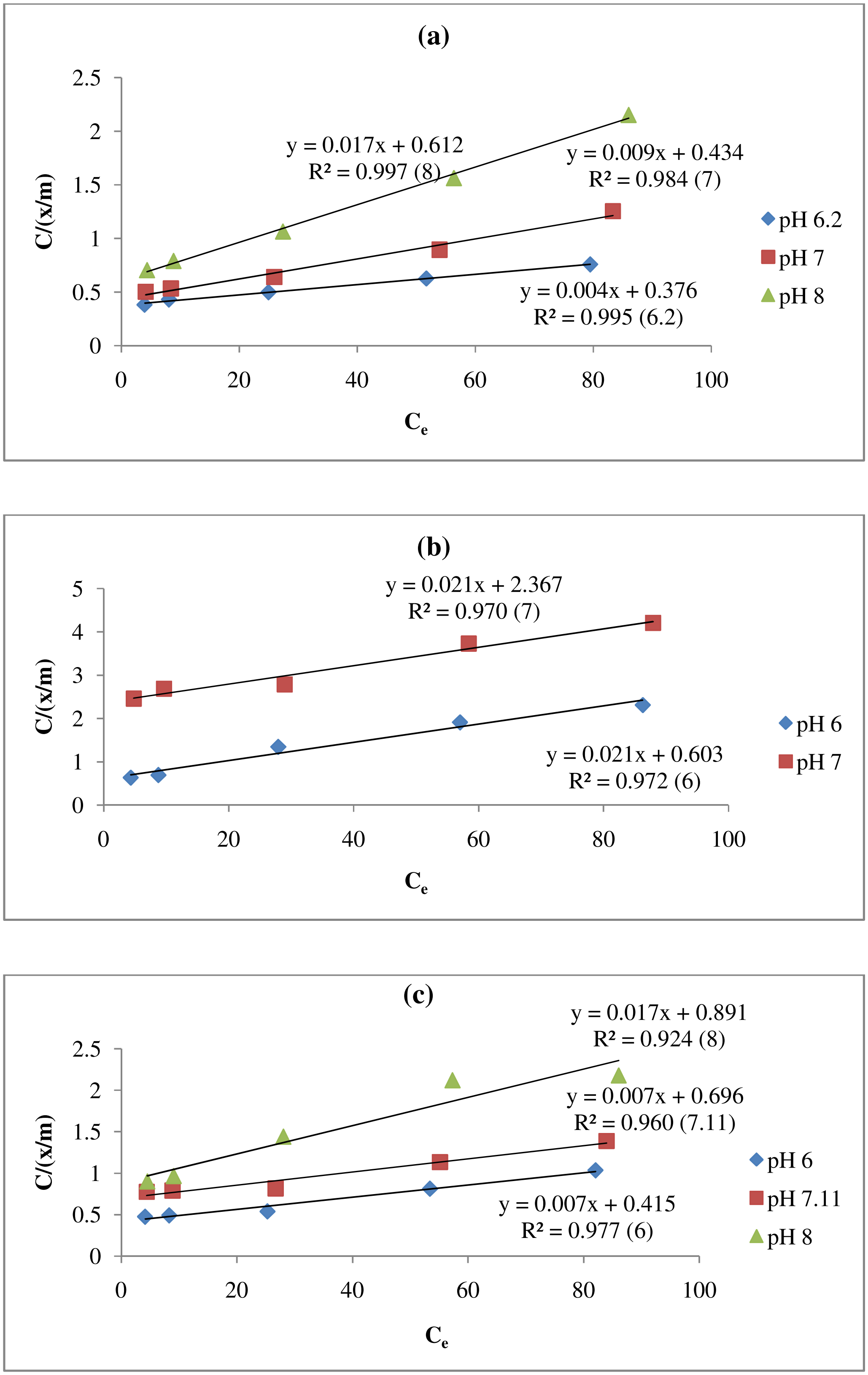


Figure 6. **Langmuir sorption isotherms for (a) Jalandhar (b) Malerkotla (c) Mandi Gobindgarh at different pH levels**

Table 23. Langmuir sorption equations and Langmuir parameters for various soils at different pH levels

Sample site	pH	Linear equation	R^2	K(ml μg^{-1})	b_{max}($\mu g\ g^{-1}$)
Jalandhar	6.2	y = 0.004x + 0.376	0.995	0.011	250.0
	7	y = 0.009x + 0.434	0.984	0.021	111.11
	8	y = 0.017x + 0.612	0.997	0.028	58.82
Malerkotla	6	y = 0.021x + 0.603	0.972	0.035	47.619
	7	y = 0.021x + 2.367	0.970	0.009	47.619
Mandi Gobindgarh	6	y = 0.007x + 0.415	0.977	0.017	142.85
	7.1	y = 0.007x + 0.696	0.960	0.010	142.85
	8	y = 0.017x + 0.891	0.924	0.019	58.82

Chromium sorption data was also fitted to freundlich sorption isotherm and high values of R^2 ranging from 0.977 to 0.995 (Table 24; Fig 7a-c).

Table 24. Freundlich sorption equations and Freundlich parameters for various soils at different pH levels

Sample site	pH	Linear equation	R^2	K_f	n
Jalandhar	6.2	y = 0.784x + 0.563	0.995	3.7	0.78
	7	y = 0.713x + 0.523	0.977	3.3	0.71
	8	y = 0.636x + 0.427	0.978	2.7	0.64
Malerkotla	6	y = 0.540x + 0.533	0.984	3.4	0.54
	7	y = 0.823x - 0.251	0.992	1.8	0.82
Mandi Gobindgarh	6	y = 0.749x + 0.524	0.977	3.3	0.75
	7.1	y = 0.813x + 0.269	0.985	1.9	0.81
	8	y = 0.669x + 0.294	0.990	2.0	0.67

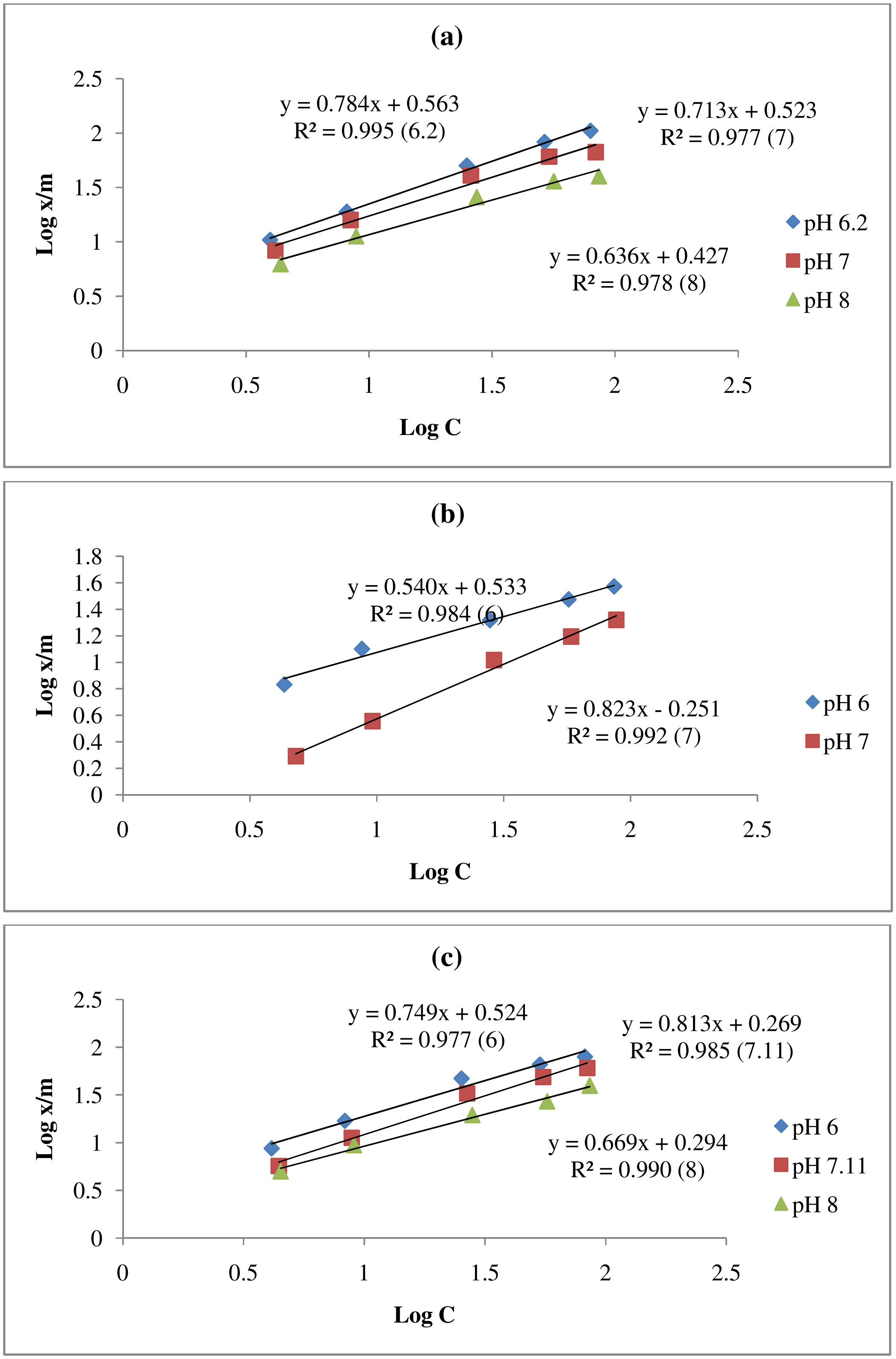


Figure 7. Freundlich adsorption isotherms for (a) Jalandhar (b) Malerkotla (c) Mandi Gobindgarh at different pH levels

The slopes and intercepts of Freundlich plots vary within a soil at different pH. Slopes were more lower at higher pH levels. Freundlich constant K_f (the index of adsorption in its value with the increase in pH, indicating soil at lower pH value had higher affinity for Cr anions. Choppala *et al* (2018) studied the comparative sorption of Cr (III) and Cr (VI) by alteration of the pH of soils from 7.15 to 8.23 and 9.12 by using lime and to 6.24, 5.13 and 4.38 by using sulphur. The sorption of Cr (III) increased with the addition of lime, K_f value increased from 1259.8 L/kg to 4017.9 and 5390.1L/kg. Sorption of Cr (VI) increased with a decrease in soil pH. Addition of elemental sulphur also increased the sorption of Cr (VI) in soils. Freundlich coefficients of soils were 9.84, 16.13 and 21.05 L/ kg in soils that have pH values of 6.2, 5.1 and 4.4. Sorption of Cr (VI) increases with a decrease in soil pH. Earlier, Choppala *et al* (2013) found that sorption of Cr (III) species (K_f = 1259.8) by the soil from South Australia was high compared to Cr (VI) sorption (K_f = 0.079). The difference in the sorption of Cr species was reported to be due to the difference in amount of positive (4.81 cmol/kg) and negative (28.4 cmol/kg) charges in the soil.

The Cr sorption data for all the three experimental soils was also well fitted to Dubinin–Radushkevich adsorption isotherm with the high values of R^2 ranged between 0.954 to 0.981 derived from linear plots between $\ln Q_e$ and ε^2 (Table 25, Fig 8a-c). Dubinin Raduhkevitch adsorption isotherm predict the type of sorption whether physisorption or chemisorptions based on the energy of activation. If the energy of activation is < 8 KJ/mol, the adsorption is physisorption and if the energy of activation is 8-16 KJ/mol, the adsorption is chemisorptions in nature. The energy of activation (E) of all the three experimental soils at all pH values ranging from 6 to 8 is less than 8 KJ mol^{-1} which implies that chromium is sorbed onto soil by physical forces.

Table 25. D-R sorption equations and D-R parameters for various soils at different pH levels

Sample site	pH	Linear equation	R^2	Q_m (mmol kg^{-1} soil)	E($kJmol^{-1}$)
Jalandhar	6.2	y = -0.055x + 0.572	0.956	1.77	3.06
	7	y = -0.053x + 0.231	0.981	1.26	3.08
	8	y = -0.049x – 0.286	0.981	0.75	3.19
Malerkotla	6	y = -0.041x – 0.454	0.962	0.64	3.49
	7	y = -0.065x – 1.055	0.957	0.35	2.77
Mandi Gobindgarh	6	y =-0.055x + 0.379	0.981	1.46	3.02
	7.1	y = -0.062x +0.076	0.974	1.08	2.84
	8	y = -0.051x – 0.468	0.954	0.63	3.13

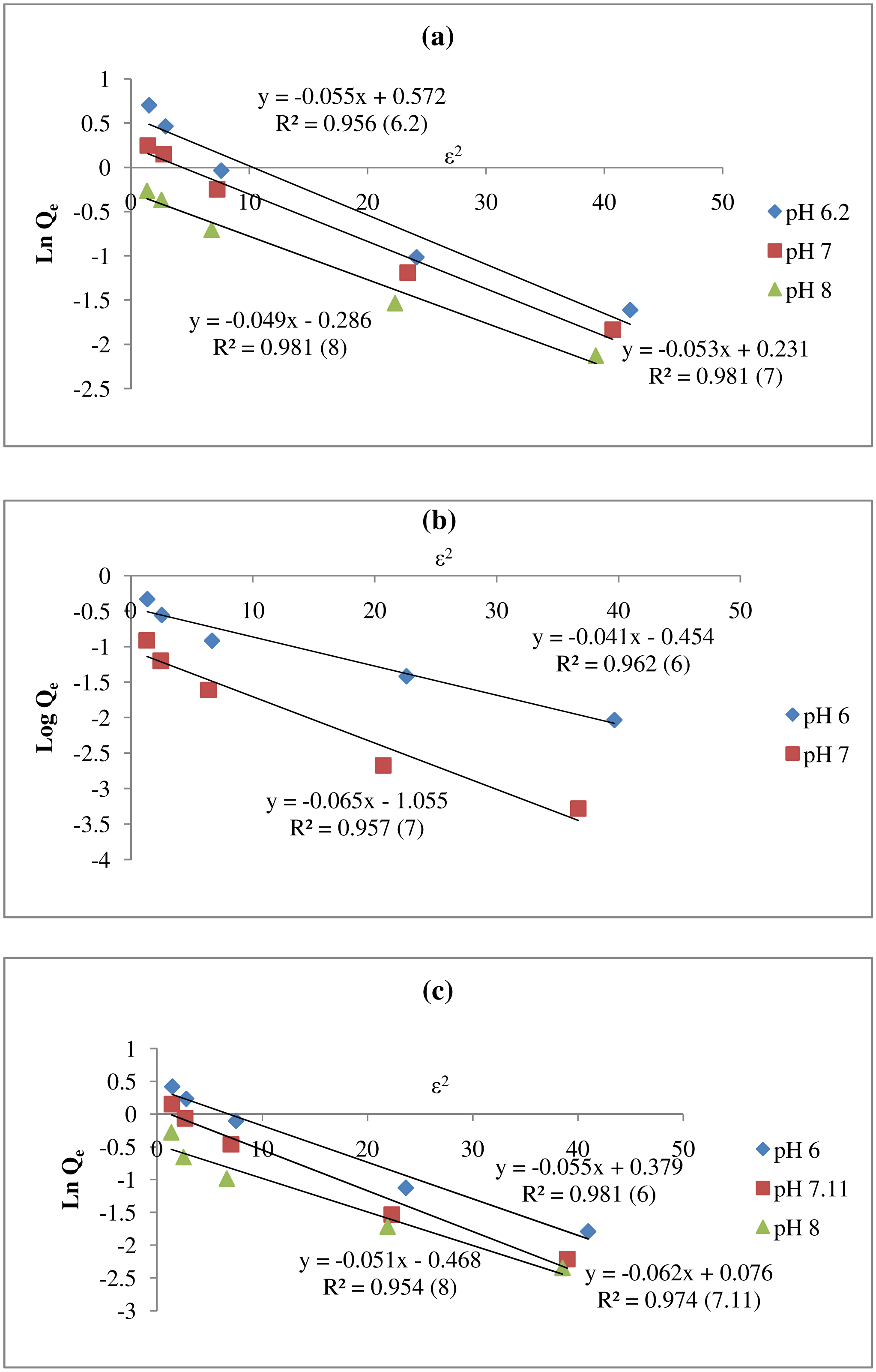


Figure 8. Dubinin–Radushkevich adsorption isotherm for (a) Jalandhar (b) Malerkotla (c) Mandi Gobindgarh soil at different pH levels

Khan *et al* (1995) studied nature of adsorption of Cr (III) and Cr (VI) and at three different temperatures by fitting the sorption data to D-R adsorption equation. They reported that sorption data for Cr (III) did not fit D-R equation, whereas energy of adsorption for chromate sorption was about 10 KJ mol^{-1} at all three temperatures that implied chromate sorption occurs through ion exchange on bentonite.

4.2.2.3 Effect of pH on desorption of added chromium in soils

For all three experimental soils, increase in soil pH resulted in increase in the percent chromium desorbed of initially sorbed chromium after five successive desorptions with 0.01 M $Ca(NO_3)_2$. In Jalandhar soil, the cumulative chromium desorbed at pH 6.2, increased from 4.81 to 47.12 µgg^{-1}; at pH 7, it increased from 5.16 to 49.52 µgg^{-1} and at pH 8, it increased from 4.02 to 35.70 µgg^{-1} soil with the increase in initially added concentration of Cr from 50 to 900 µgg^{-1}.From initially added lowest concentration of Cr (50 µgg^{-1}), at pH 6.2, the percent Cr desorption was 46.3%; at pH 7, it increased to 62.0% and at pH 8, it further increased to 64.6%. However from initially added highest Cr concentration (900 µgg^{-1}), at pH 6.2, the percent Cr desorption was 44.9%; at pH 7, it increased to 74.4% and at pH 8, it increased further to 89.3%, respectively (Table 26).

In Malerkotla soil, with increase in soil pH from 6 to 7, a significant increase in desorption was observed, as the cumulative Cr desorbed varied from 0.79 to 1.01, 2.37 to 2.89, 7.38 to 8.55, 13.17 to 14.06 and 18.7 to 19.56 µgg^{-1}soil with initial application of 50 to 900 µg Cr g^{-1} soil. The corresponding percent increase in Cr desorption was 11.6 to 51.7, 18.8 to 80.5, 35.5 to 82.3, 44.2 to 89.8 and 50.1 to 93.6% (Table 27)

In case of Mandi Gobindgarh soil at pH 6, the cumulative Cr desorbed increased from 3.75 to 38.26 µgg^{-1}; at pH 7.1, it increased from 3.35 to 35.36 µgg^{-1}and at pH 8, it increased from 3.11 to 32.34 µgg^{-1} with increase in initially added Cr concentrations ranging from 50 to 900 µg g^{-1}. At lowest concentration of initially added Cr (50 µg g^{-1}), at pH 6, the percent chromium desorbed was 43.2%; at pH 7.1, it increased to 58.7% and at pH 8, it further increased to 62.3%. However, at highest level of initially added chromium (900 µg g^{-1}) at pH 6, the percent chromium desorption was 48.2%, at pH 7.11, it increased to 58.4% and further at pH 8, it increased to 81.9% (Table 28).

Choppala *et al* (2013) found that desorption of Cr (VI) was higher than Cr (III) in experimental soils. Nearly 92.7 and 98.6 % of cumulative Cr (VI) desorbed from ADH (Adelaide Hills) and KPB (Kulpara) soils of South Australia. But only 8.4 and 8.7 % cumulative Cr (III) desorbed from same soils. Due to high alkaline nature of the soils, the desorption of Cr (VI) was high.

Table 26. Desorption of sorbed chromium by Jalandhar soil

Soil pH	Cumulative Cr desorbed (µg g^{-1})				
	50	100	300	600	900
6.2	4.81	12.43	21.05	30.43	47.12
	(46.3)	(65.9)	(41.9)	(36.8)	(44.9)
7	5.16	13.28	23.20	33.29	49.52
	(62.0)	(83.9)	(57.1)	(55.1)	(74.4)
8	4.02	10.55	19.65	27.93	35.7
	(64.6)	(93.8)	(76.3)	(77.4)	(89.3)

(Figures in parenthesis denote per cent Cr desorption)

Table 27. Desorption of sorbed chromium by Malerkotla soil

	Cumulative Cr desorbed (µg g^{-1})				
Soil pH	50	100	300	600	900
6	0.79	2.37	7.38	13.17	18.7
	(11.6)	(18.8)	(35.5)	(44.2)	(50.1)
7	1.01	2.89	8.55	14.06	19.56
	(51.7)	(80.5)	(82.3)	(89.8)	(93.6)

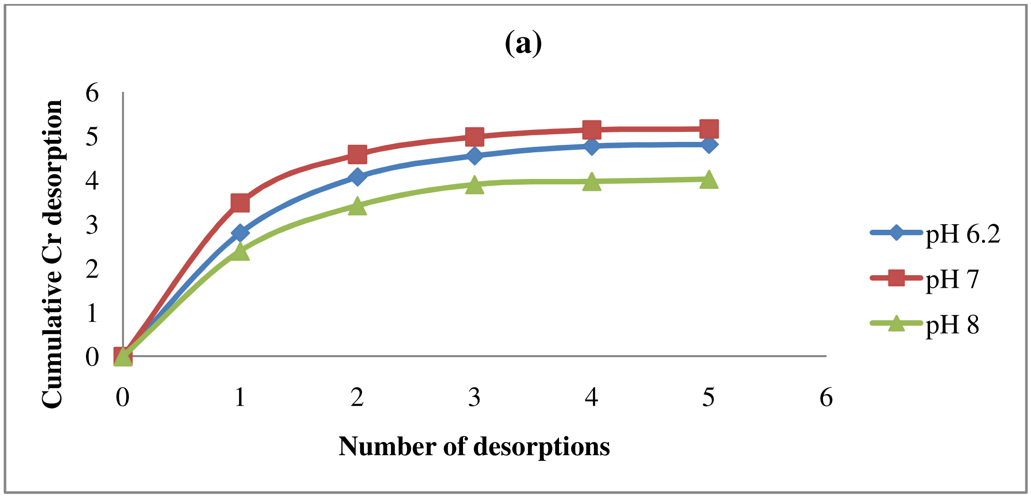
(Figures in parenthesis denote per cent Cr desorption)

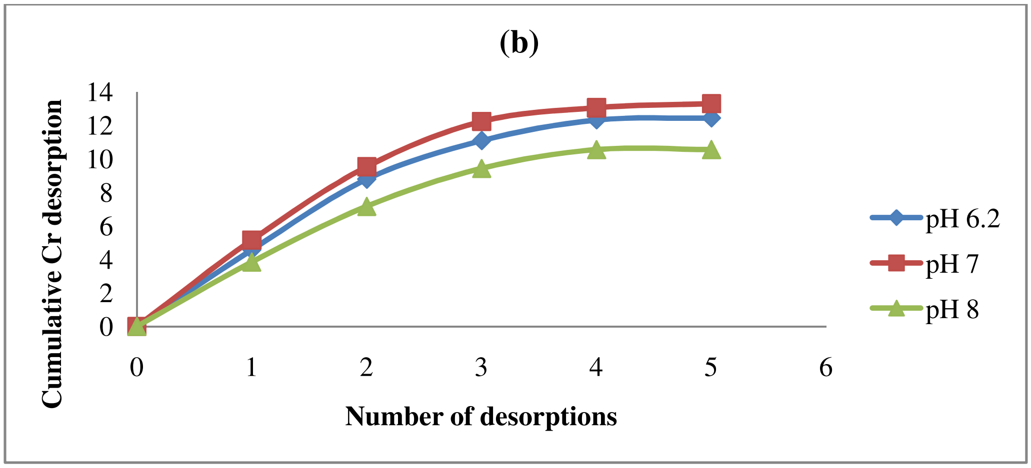
Table 28. Desorption of sorbed chromium by Mandi Gobindgarh soil

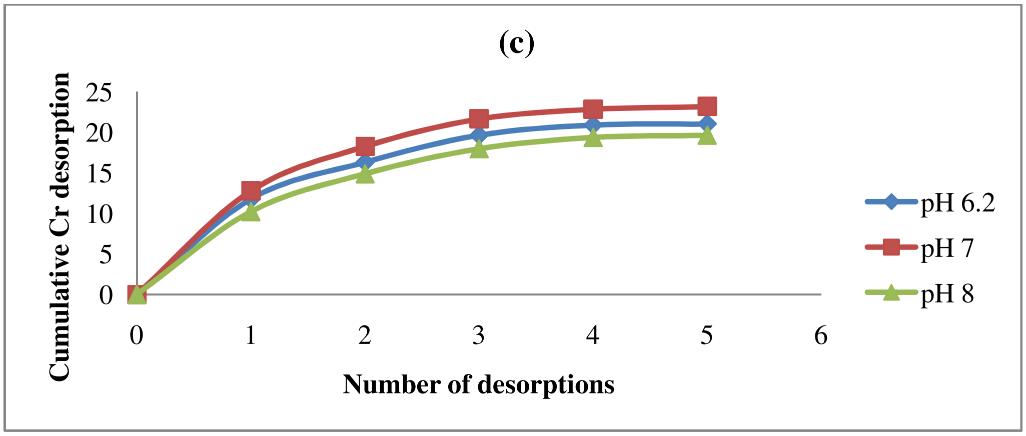
	Cumulative Cr desorbed (µg g^{-1})				
Soil pH	50	100	300	600	900
6	3.75	10.05	17.89	36.81	38.26
	(43.2)	(59.5)	(38.1)	(56.0)	(48.2)
7.11	3.35	7.92	15.61	32.94	35.36
	(58.7)	(70.5)	(47.7)	(67.7)	(58.4)
8	3.11	7.35	13.23	23.99	32.34
	(62.3)	(78.4)	(68.0)	(88.8)	(81.9)

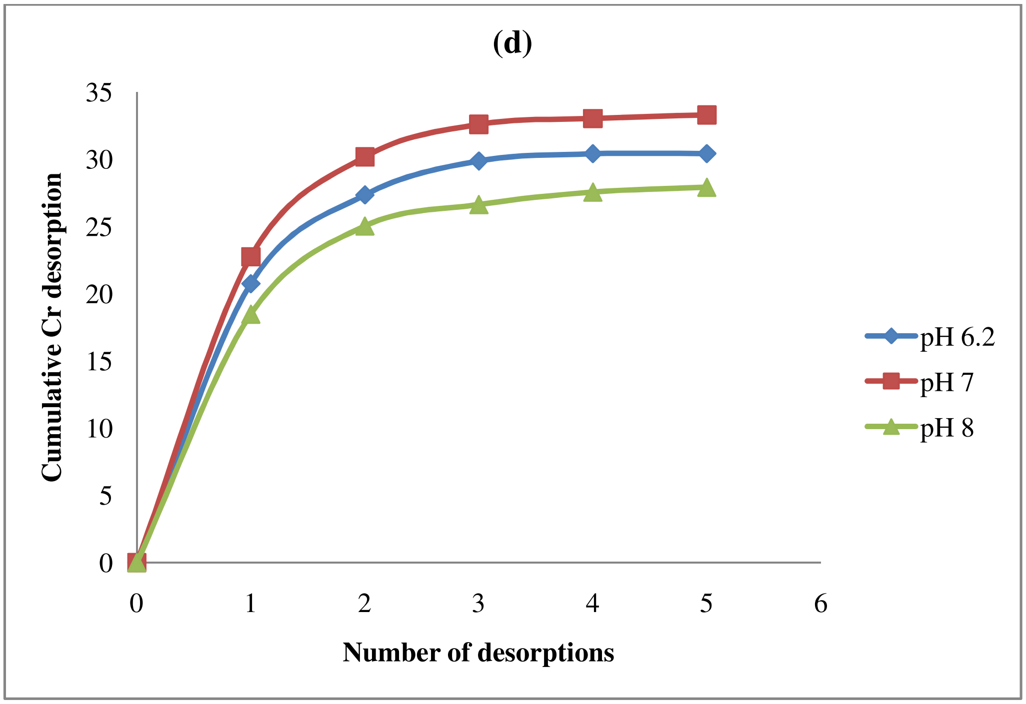
(Figures in parenthesis denote per cent Cr desorption)

a. Jalandhar Soil









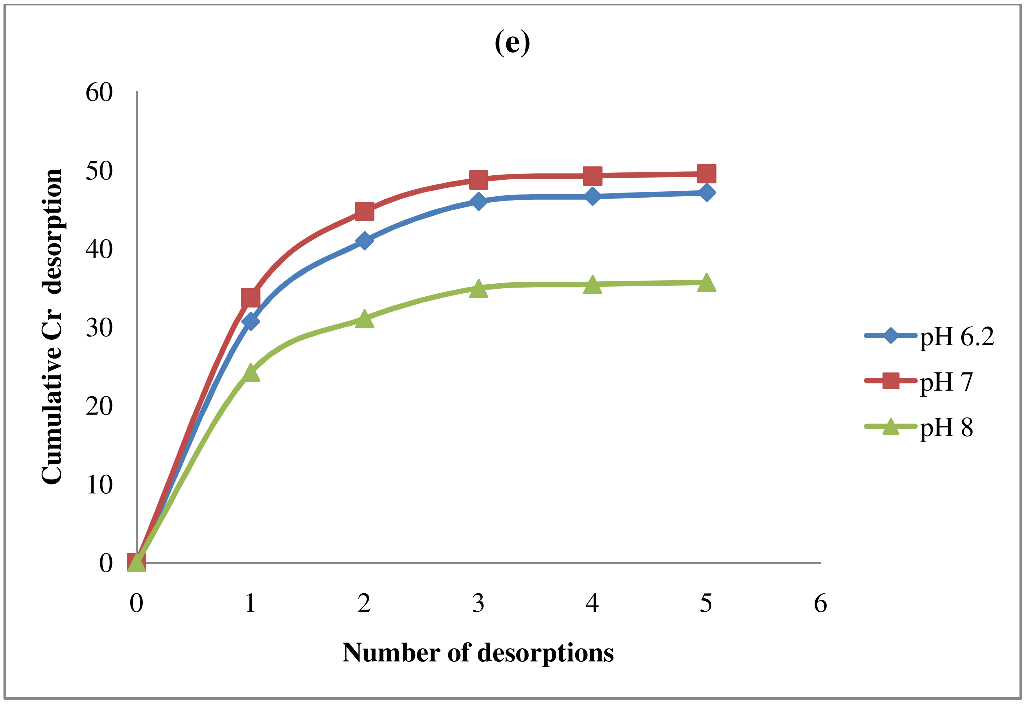
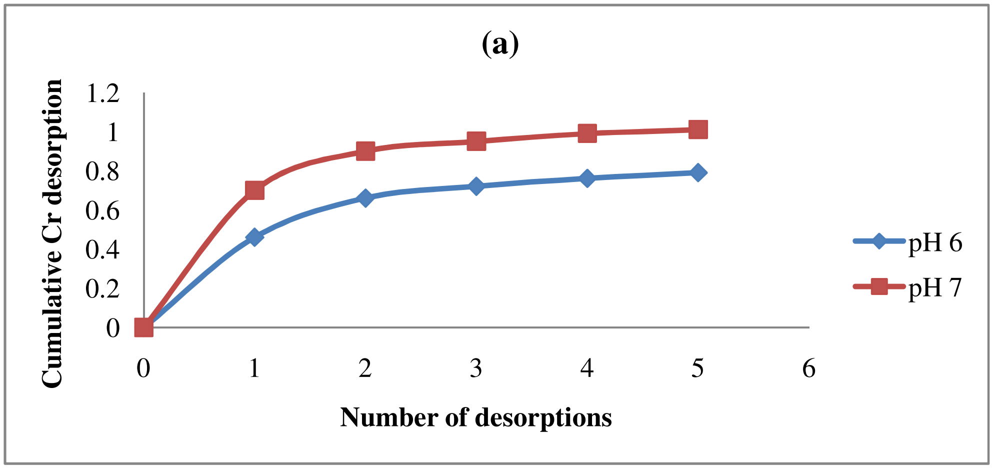
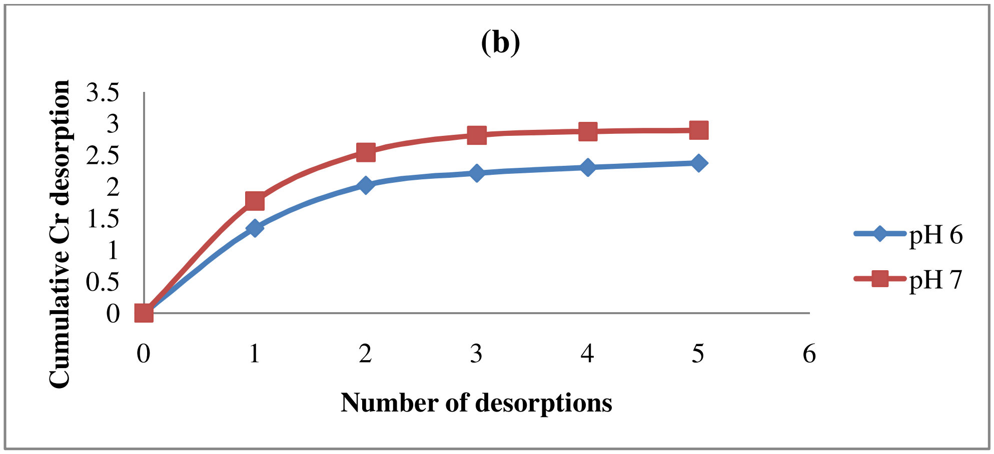
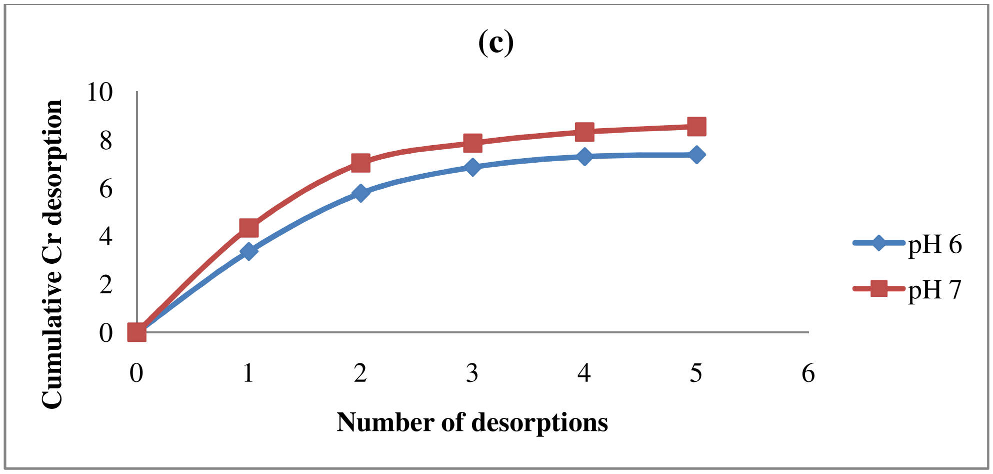


Fig 9(a) Effect of pH on cumulative Cr desorption added at various levels (a) 50 µgg^{-1} (b) 100 µgg^{-1} (c) 300 µgg^{-1} (d) 600 µgg^{-1} (e) 900 µgg^{-1} in Jalandhar soil.

b. Malerkotla Soil







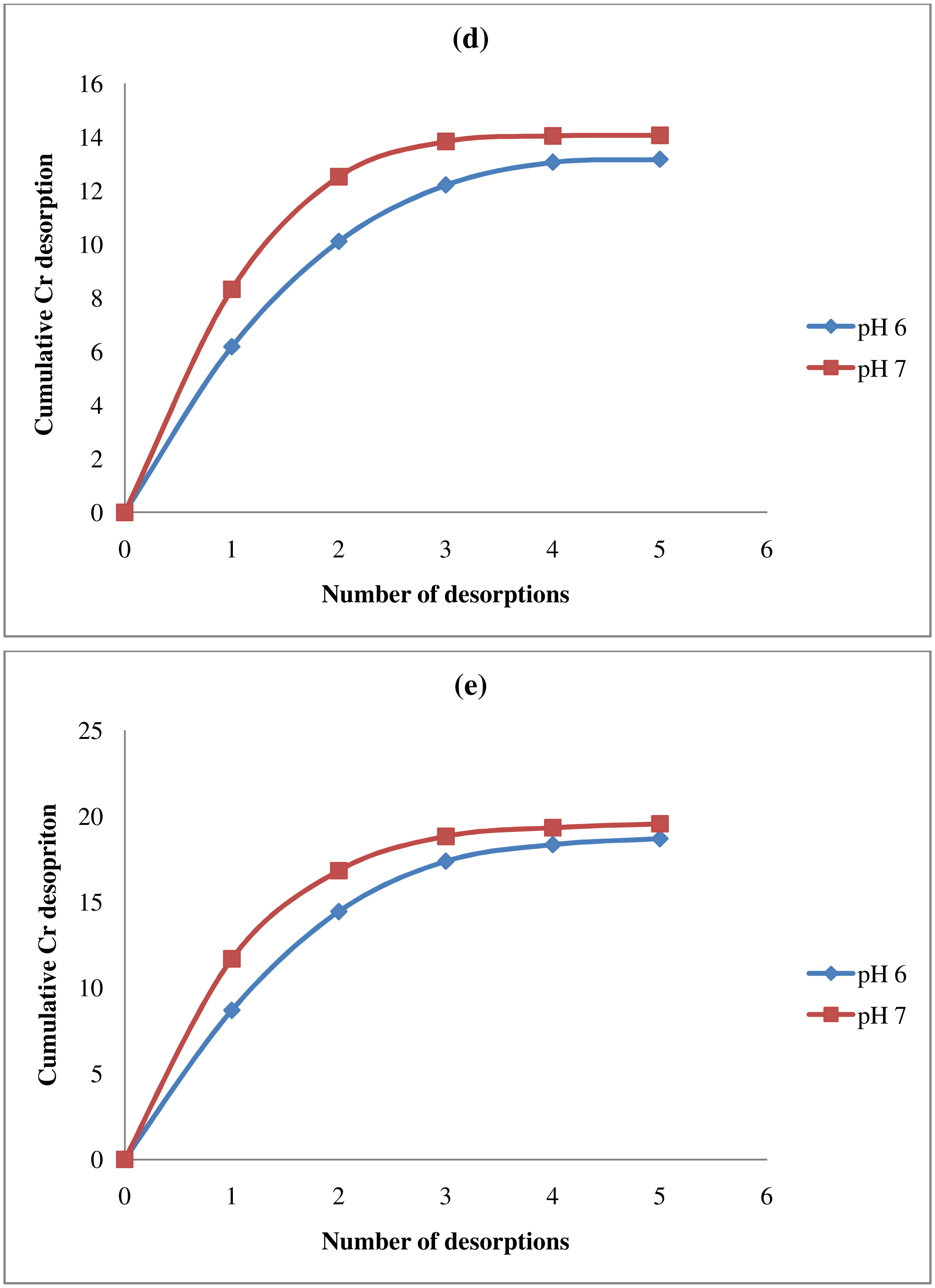
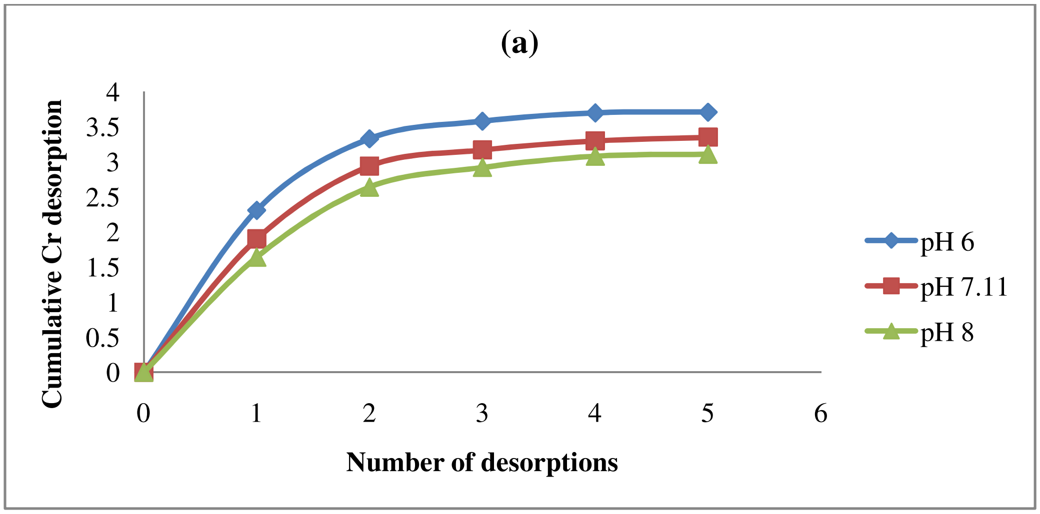
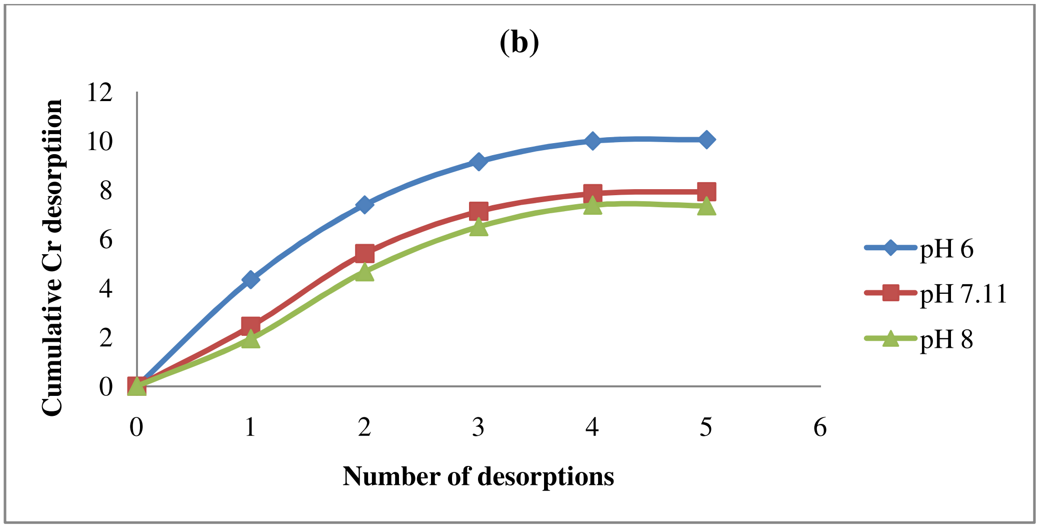
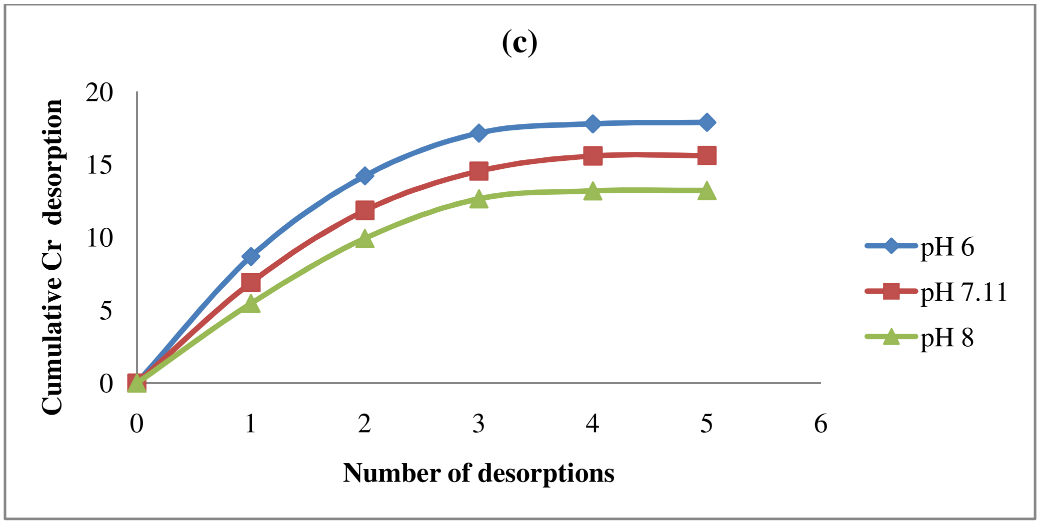


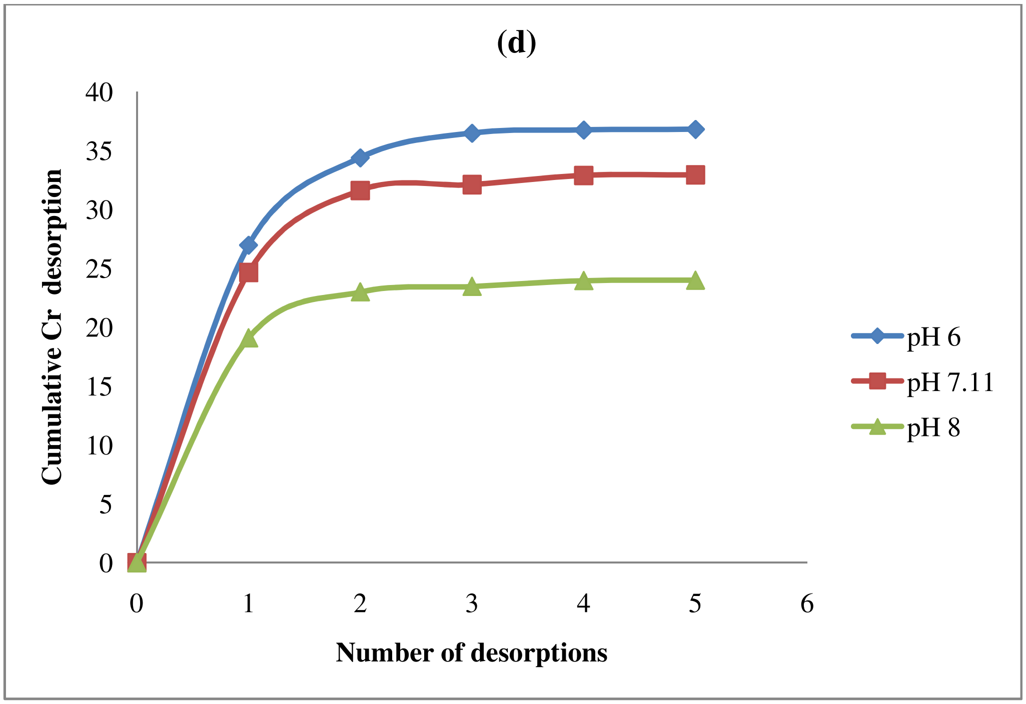
Fig (9b) Effect of pH on cumulative Cr desorption added at various levels (a) 50 µgg^{-1} (b) 100 µgg^{-1} (c) 300 µgg^{-1}(d) 600 µgg^{-1}(e) 900 µgg^{-1}in Malerkotla soil.

c. Mandi Gobindgarh soil









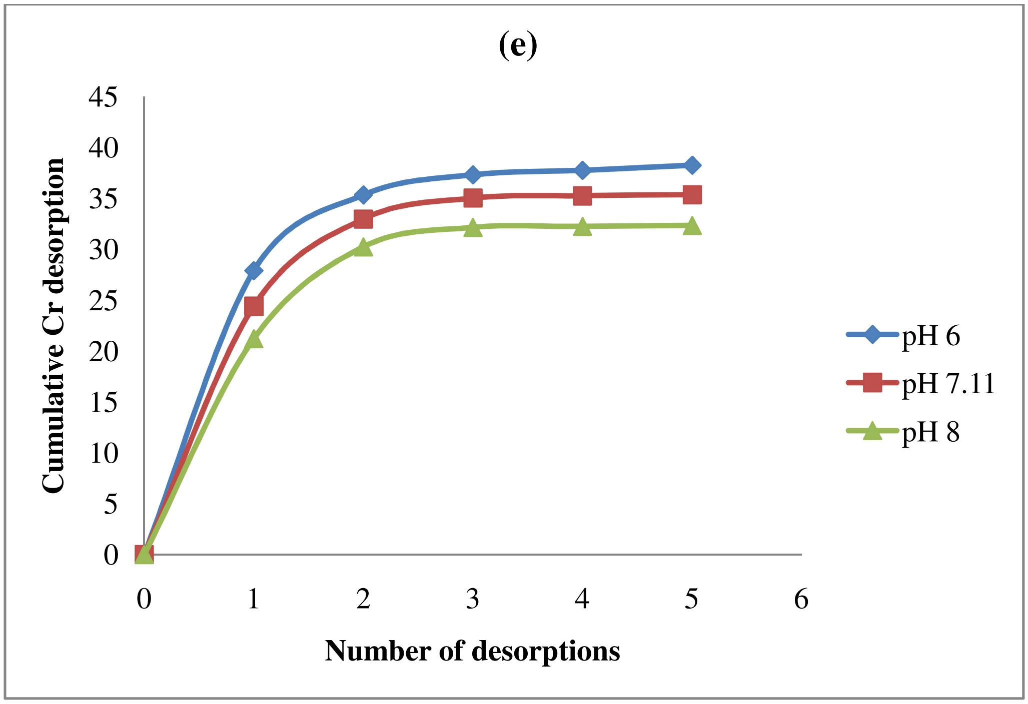


Fig 9(c) **Effect of pH on cumulative Cr desorption added at various levels (a) 50 µgg^{-1} (b) 100 µgg^{-1}(c) 300 µgg^{-1}(d) 600 µgg^{-1} (e) 900 µgg^{-1} in Mandi Gobindgarh soil.**

CHAPTER V

SUMMARY

5.1 Sorption and desorption of chromium in relation to soil properties

Twenty eight surface (0-15 cm) and sub-surface (15-30 cm) soil samples expected to differ in physico-chemical properties, were collected from four different locations *viz* Ludhiana, Jalandhar, Malerkotla and Mandi Gobindgarh. The samples were air dried, ground to pass through a 2 mm sieve and were analysed for different physico-chemical characteristics using standard recommended procedures. Chromium (Cr) was sorbed on soils by equilibrating 3 gm of each of the soil sample with 30 ml of 0.01M $Ca(NO_3)_2$ containing 40 µg ml^{-1} (equivalent to 400 µg g^{-1}) for 24 hrs and then shaking the samples for 2 hrs. After decanting the equilibrating solution, desorption study was conducted by re-suspended the same soil samples in fresh chromium free 0.01M $Ca(NO_3)_2$ solution and equilibrated for 24 hrs and then shaking was done for two hrs. Five consecutive desorptions were performed in the same way.

The experimental soils differ widely in their ability to sorb chromium. With initial addition of 400 µg Cr g^{-1}, sorption of chromium by the soils ranged from 0 to 97 µg g^{-1} for surface samples (0-15 cm) and 0 to 84 µg g^{-1}for sub-surface samples (15-30 cm). Highly Significant and negative correlation was observed between chromium sorbed and pH both in surface as well as sub-surface soils ($r = -0.764$ for surface samples and $r = -0.757$ for sub-surface samples). Hence, pH is the most important factor in Punjab soils on which the Cr sorption largely depends. No Cr sorption occurs in Malerkotla soils, both in surface as well as sub-surface samples, probably due to their high pH range from 7.64 to 8.39 in surface samples and 7.55 to 8.47 in sub-surface samples. Soil pH explained 58 % of the variability in Cr sorption in surface samples and 57% variability in case of sub-surface samples as explained by simple regression equations. In surface samples, pH along with EC and total Cr explained 68% variability in Cr sorption. In case of sub-surface samples, pH along with organic carbon could explain 61 % of the variability in Cr sorption by these soils.

The cumulative chromium desorbed after five consecutive desorptions from initially added 400 µg g^{-1}soil ranged from 7.22 µg Cr g^{-1} to 37.68 µg Cr g^{-1}in surface samples and 9.89 µg Cr g^{-1} to 40.46 µg Cr g^{-1} in sub-surface samples. It was observed that in most of the Ludhiana soils, more than 70 % of the sorbed chromium desorbed back from the soil solid phase into soil solution. In Malerkotla soils, varied from 23.56 µg Cr g^{-1} to 37.68 µg Cr g^{-1} in surface samples and from 22.94 µg Cr g^{-1} to 40.46 µg Cr g^{-1} in sub-surface soils. The reason for high desorption is relatively higher pH of these soils. The pH of the Jalandhar soils is less so the percent desorption is lowest in Jalandhar soils among all the samples. The amount of cumulative Cr desorbed increased with the increase in number of successive desorptions, but reached about a plateau due to decrease in amount of chromium extracted in every next desorption. Cumulative chromium desorbed from 28 experimental soils was found to be significantly and positively correlated with pH (r = 0.635 for surface samples and r = 0.438 for sub-surface samples). For better explanation of chromium desorption dependence on soil variables (pH, EC, CEC, $CaCO_3$ and clay content), the multiple regression model was worked separately on polluted and non polluted soil samples. In surface polluted soils, pH explained 51 % variability in chromium desorption.The pH and EC together improved the variability in chromium desorption to 68% in case of polluted sub-surface soil samples. In case of non-polluted surface samples, CEC, $CaCO_3$,DTPA extractable chromium and total chromium together improved the variability in chromium desorption to 91% whereas in sub-surface samples, OC along with CEC and DTPA extractable chromium improved the variability in chromium desorption to 66%. Hence, pH is the major factor that influences sorption and desorption of chromium in soils.

5.2 To characterize the Cr behaviour in soil and influence of pH as described by sorption/desorption isotherms

5.2.1 Chromium behaviour in soil as described by sorption- desorption isotherms

Sorption and desorption of chromium was carried out in similar way as earlier, except in this study, five different concentrations of added chromium (50, 100, 300, 600, 900 µg g^{-1} soil) were used. It was observed that with an increase in amount of initially added chromium, sorption by the three selected soils (one each from Jalandhar, Ludhiana and Mandi Gobindgarh) increased but the percent sorption decreased. In the selected soils, chromium sorption increased from 6.92 to 53.52 µg g^{-1} for Jalandhar soil, 6.31 to 52.51 µg g^{-1} for Ludhiana soil and 12.44 to 95.35 µg g^{-1} for Mandi Gobindgarh soil. The percent sorption decreased from 13.8 to 5.9, 12.6 to 5.8 and 24.9 to 10.6 for Jalandhar, Ludhiana and Mandi Gobindgarh soil, respectively with increasing levels of chromium addition from 50 to 900 µg g^{-1}. Among polluted soils i.e. Jalandhar and Mandi Gobindgarh soil, the later had higher Cr sorption capacity though the pH of the former was lesser indicating that sorption of chromium also depends on physico-chemical factors other than pH. The Cr sorption data was explained using three adsorption isotherms i.e. Langmuir, Freundlich and Dubinin Raduhkevitch adsorption isotherms. It was observed that the Cr sorption data was well described by Langmuir adsorption isotherm with high values of R^2 (0.959 to 0.994) derived from data pairs of C/(x/m) and C_e of three soils. The value of adsorption maxima was highest for Mandi Gobindgarh soil indicated its high sorption capacity. Chromium sorption data was also well explained by Freundlich adsorption isotherm as indicated by high R^2 values (0.985 to 0.994). The value of Freundlich constants, relative affinity between adsorbate and adsorbent ‘ K_f’ and rate of adsorption ‘ n’ ranged from 2.3 to 4.8 and 0.696 to 0.732. The relative affinity between chromium ions and soil colloids was highest in Mandi Gobindgarh soil. Sorption data was well described by Dubinin Raduhkevitch adsorption isotherm with high R^2 values (0.926 to 0.973) derived from linear plots between $\ln Q_e$ and ε^2. The values of energy of activation ' E' varied from 3.01 to 3.26 KJ mol^{-1} which implies that sorption of chromium is physisorption in three experimental soils since the activation energy is less than 8 KJ mol^{-1}.

Desorption of sorbed chromium over a period of five desorptions increased with the increase in number of subsequent desorptions. However, per cent chromium desorbed from previously sorbed chromium increased with initial addition of particular concentration of chromium. The cumulative chromium desorption increased with an increase in initially added chromium concentration from 50 μg g^{-1} to 900 μg g^{-1} within a soil. In the experimental soils (Jalandhar, Ludhiana and Mandi Gobindgarh), cumulative chromium desorbed increased from 1.08 to 39.71 μg Cr g^{-1} , 1.09 to 41.47 μg Cr g^{-1} and 1.29 to 39.79 μg Cr g^{-1}. The percent chromium desorbed increased from 15.7 to 74%, 17.4 to 79% and 10.4 to 41.7% for Jalandhar, Ludhiana and Mandi Gobindgarh soils, respectively. Among the three soils, the amount of Cr desorbed was highest in Ludhiana soil followed by Jalandhar and Mandi Gobindgarh soils.

Desorption data was well fitted to modified Langmuir desorption isotherm (R^2 = 0.967 to 0.992). The values of desorption maxima ' D_m' varied from 71.42 to 125 μg g^{-1} and value of K_d ranged from 0.058 to 0.082 μg^{-1} for the soils under study.

5.2.2 Effect of pH on sorption and desorption of chromium

The effect of pH on sorption-desorption of chromium in soils was studied by adjusting pH of three soil samples (one each from Malerkotla, Jalandhar and Mandi Gobindgarh) in a range of 6-8 by adding different concentrations of HCl and NaOH and incubating these soil samples at 25°C maintaining field capacity moisture level until pH of the soil samples become constant. In all the three selected soils, with the increase in pH from 6 to 8, there was a decrease on sorption of chromium. In Jalandhar soil at pH 6.2, sorbed chromium varied from 10.39 to 104.95 μg g^{-1} soil (20.8% to 11.7% of added chromium); at pH 7, 8.32 to 66.57 μg g^{-1}soil (16.6% to 7.4% of added chromium) and at pH 8, 6.22 to 39.97 μg g^{-1}soil (12.4% to 4.4% of added chromium) depended upon initially added chromium. In case of Malerkotla soil, chromium sorbed at pH 6 varied from 6.79 to 37.31 μg g^{-1}soil (13.6% to 4.1% of added chromium); at pH 7, 1.96 to 20.89 μg g^{-1}soil (3.9% to 2.3% of added chromium); at pH 7.99, no sorption occcurs. For Mandi Gobindgarh soil, chromium sorbed at pH 6 varied from 8.68 to 79.38 μg g^{-1}soil (17.4% to 8.8% of added chromium), at pH 7.11, 5.71 to 60.54 μg g^{-1}soil (11.4% to 6.7% of added chromium) and 4.99 to 39.5 μg g^{-1}soil (10% to 4.4% of added chromium).

The amount of chromium sorbed ranged from 10.39 to 104.9 μg Cr g^{-1} soil to 6.22 to 39.97 μg g^{-1}soil (ie 20.8 to 11.7% to 12.4 to 4.4%) for Jalandhar soil; 6.79 to 37.31 to 0 μg g^{-1}soil (13.6 to 4.1% to 0%) for Malerkotla soil and 8.68 to 79.38 μg g^{-1}soil to 4.99 to 39.50 μg

g^{-1}soil (17.4 to 8.8% to 10 to 4.4%) for Mandi Gobindgarh soil with increase in pH from 6 to 8 range with initial application of Cr from 50 to 900 µg g^{-1}soil.

At all pH levels for all the soils, the chromium sorption data well fitted to Langmuir sorption isotherm (R^2 = 0.924 to 0.995). The slope of Langmuir plots was more at higher pH than lower pH levels in all the three soils which implies that higher sorption capacity of soils at lower pH. The sorption data well fitted to Freundlich adsorption isotherm with high values of R^2 ranging from 0.977 to 0.995. Freundlich constant K_f (the index of adsorption affinity of the adsorbent for the adsorbate) decreased in its value with increase in pH indicating soil at lower pH value had higher affinity for Cr anions. The sorption data of all the three soils well fitted to Dubinin–Radushkevich adsorption isotherm with high value of R^2 ranged from 0.954 to 0.981 derived from linear plots between $\ln Q_e$ and ε^2. The energy of activation (E) of all the three experimental soils at all pH values ranging from 6 to 8 is less than 8 KJ mol^{-1} which implies that chromium is sorbed onto soil by physical forces i.e. through vanderwaal forces.

In all the three experimental soils, increase in soil pH resulted in a substantial increase in per cent chromium desorbed at any of added chromium level from 50 to 900 µg g^{-1}. The percent Cr desorbed increased from 46.3 to 64.6%, 65.9 to 93.8%, 41.9 to 76.3%, 36.8 to 77.4% and 44.9 to 89.3% with increase in pH from 6.2 to 8 at various initially added Cr concentrations (50 to 900 µg g^{-1}) in Jalandhar soil. In Malerkotla soil, with increase in soil pH from 6 to 7, a significant increase in desorption was observed, as the cumulative Cr desorbed from 0.79 to 1.01, 2.37 to 2.89, 7.38 to 8.55, 13.17 to 14.06 and 18.70 to 19.56 µgg^{-1}soil with initial application of 50 to 900 µg Cr g^{-1} soil. The corresponding per cent increase in Cr desorption was 11.6 to 51.7%, 18.8 to 80.5%, 35.5 to 82.3%, 44.2 to 89.8% and 50.1 to 93.6%. The per cent Cr desorbed increased from 43.2 to 62.3%, 59.5 to 78.4%, 38.1 to 68%, 56 to 88.8% and 48.2 to 81.9% with increase in pH from 6 to 8 at various initially added Cr concentrations (50 to 900 µg g^{-1}) in Mandi Gobindgarh soil.

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VITA

Name : **Satnam Kaur**

Father's Name : S. Jasvir Singh

Mother's Name : Sd. Satvir Kaur

Nationality : Indian

Date of Birth : 11 May 1993

Permanent Address : V.P.O. Sarawan Teh. Jaitu
District Faridkot, Punjab

EDUCATIONAL QUALIFICATION

Bachelor's Degree : B.Sc. (Hons) Agriculture

University : Punjab Agricultural University, Ludhiana

Year of award : 2016

OCPA : 8.23/10.00

Master's Degree : M.Sc. (Soil Science)

University : Punjab Agricultural University, Ludhiana

Year of Award : 2019

OCPA : 8.44/10.00

Title of Master's Thesis : Sorption and desorption behaviour of chromium (VI) in soils