

Sorption of Heavy Metals in Natural Soils

¹Vinay Kumar

PG Scholar: Environmental Engineering Department
Punjab Engineering College (Deemed to be University)
Chandigarh, India

²S. K. Sharma

Associate Professor: Civil Engineering department
Punjab Engineering College (Deemed to be University)
Chandigarh, India

Abstract— A series of batch experiments are performed in order to access the sorption behavior of Cadmium and Chromium in natural soil samples. The effect of Cation Exchange Capacity, organic matter content, initial concentration of adsorbate, contact time and the amount of adsorbent has been investigated on sorption capacity of soil samples at natural soil pH. The sorption behavior of heavy metals in soil was studied by both Langmuir and Freundlich isotherms using an Ion Chromatograph which has revealed that monolayer adsorption was prevalent in these soils. Also, soil with higher clay and organic matter content was found to have more sorption capacity.

Keywords— Sorption; Heavy metals; Isotherm; Ion chromatograph; Soil Properties

I. INTRODUCTION

Urban and Industrial Pollution are the main contributors in the degradation of our natural environment. Industries causes pollution in many ways one of which is the heavy metals found in the effluents from such pollution hubs. Heavy metal contamination is one of the most important environmental issues which prevail almost in every part of the world. [2] Contamination due to heavy metals is attributed to the waste produced from number of industries like tanning industry, electroplating industry, pulp and paper mills, textile mills and number of such industries. Heavy metals are stable elements and it is very difficult to eliminate or degrade such type of heavy metals. Discharge of wastewater without appropriate treatment leads to residue, and the accumulation of heavy metals in the environment [9]. Interest in heavy metals in soil arises from the fact that soil is the main source of these elements for plants and human nutrition as it is a very good sorbent of such heavy metals and from the possibility of soil pollution due to industrial wastes. Even though the plants need trace amounts of several heavy metals for growing, some heavy metals such as Cadmium, Chromium etc. present a great health and environmental risk; even at low concentrations as these heavy metals have high enrichment factor and slow removal rate [5]. Moreover in certain soils which have less sorption capacity these heavy metals may leach down into the groundwater sources causing pollution and thus affecting our health.

The sorption capacity of soil is attributed to a very important property of soil known as Cation Exchange Capacity (CEC) of the soil [3]. CEC is an important property of almost all soil types however it is more in clayey soils. Also, CEC of the soil increases with increase in organic matter content in the soil [4]. Organic matter present in the soil possesses this property because of the net negative charge due to the

dissociation of organic acids [7]. In this study, the sorption of the most common heavy metals chromium and cadmium by two different natural soils has been investigated. Both these heavy metals are found in the effluent of almost every industry and hence selected for the study. Cr(VI) targets the respiratory tract and is responsible for many lung infections like shortness of breath, coughing, wheezing etc. Cd(II) is one of the few elements present on earth which in all its forms like metal, vapour, salts, inorganic and organic compounds is toxic and has no known function in human or animal life [1].

II. MATERIALS AND METHODS

Soils used for sorption study as sorbent were selected from two different places where the contamination due to industrial effluents was most probable and prevalent. Sample A was collected from Baddi, Himachal Pradesh and Sample B was collected from Ropar, Punjab. The properties of the both the soils are shown in Table 1.

TABLE 1: PROPERTIES OF SOILS

S.No.	Property	Soil A	Soil B
1	Soil Classification (ISSCS)	Clay with Low Plasticity (CL)	Silty Sand (SM)
2	% Sand	6.90	51.65
3	% Silt	61.07	39.04
4	% Clay	32.02	9.30
5	Soil pH	7.83	7.74
6	Specific Gravity	2.67	2.64
7	Permeability (m/s)	2.501×10^{-8}	5.71×10^{-5}
8	CEC (meq/100g)	37.20	18.40
9	Organic Matter Content (%)	11.30	5.90

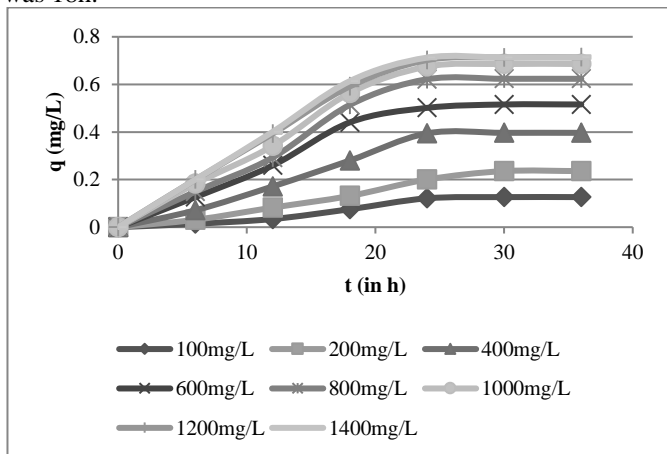
Ion Chromatography technique was used in order to determine the sorption of the heavy metals. Different concentrations of Cr(VI) were prepared using potassium dichromate [8] and of Cd (II) using cadmium chloride. Batch experiments were performed in bottles by mixing 20cm³ of solution of heavy metal with 2g of soil. The mixtures were initially shaken for a period of half an hour using a horizontal shaker and then kept as it is for equilibrium time period. Supernatant obtained after centrifuging was then analysed for heavy metal sorption using Ion Chromatograph. For initial concentration (C_0 in mg/L) and equilibrium concentration (C_{eq} in mg/L), the sorption capacity (q in mg/g) was determined as per equation (1) as [9]

$$q_e = \frac{(C_0 - C_{eq}) \times 20}{2 \times 1000} \quad (1)$$

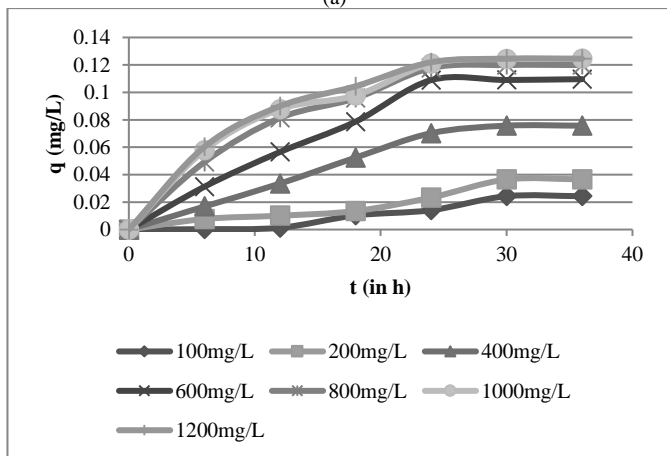
III. RESULTS AND DISCUSSIONS

A. Effect of contact time

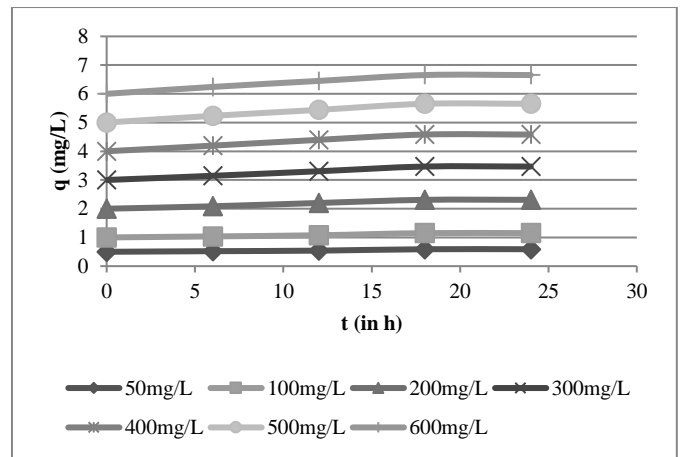
To study the effect of contact time on sorption, different concentrations of both the heavy metals were prepared using standard grade reagents. Sorption capacity of soil was then determined at a particular concentration by varying the contact time. For Cr(VI), the contact time was varied from 0 to 36h at the interval of 6h. Results show that after contact time of 30h, the sorption has reached its saturation value as all the sites were occupied by chromium ion and further no more sorption takes place. For Cd(II), the contact time was varied from 0 to 24h at the interval of 6h. Results revealed that after contact time of 18h, the sorption has reached its saturation value as all the sites were occupied by cadmium ion and further no more sorption has taken place. The sorption capacity vs contact time curves at different concentrations are shown in Fig. 1. For different concentrations of heavy metals the equilibrium time for Soil A and Soil B in case of Cr(VI) is 30h and in case of Cd(II) was 18h.



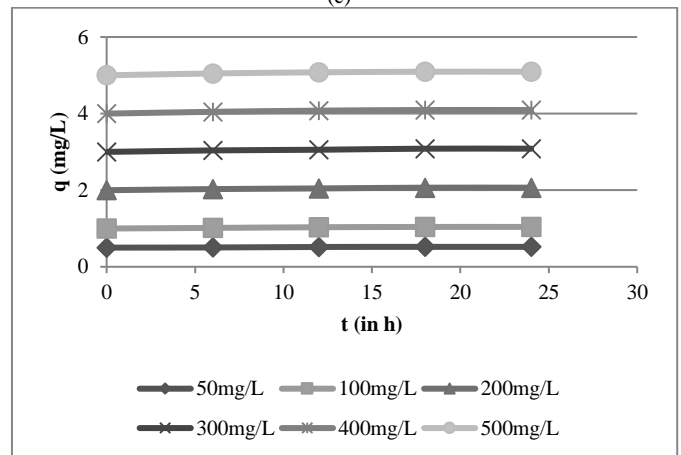
(a)



(b)



(c)

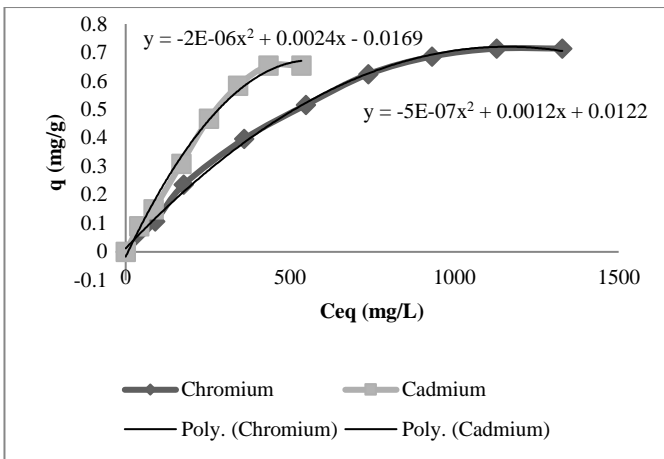


(d)

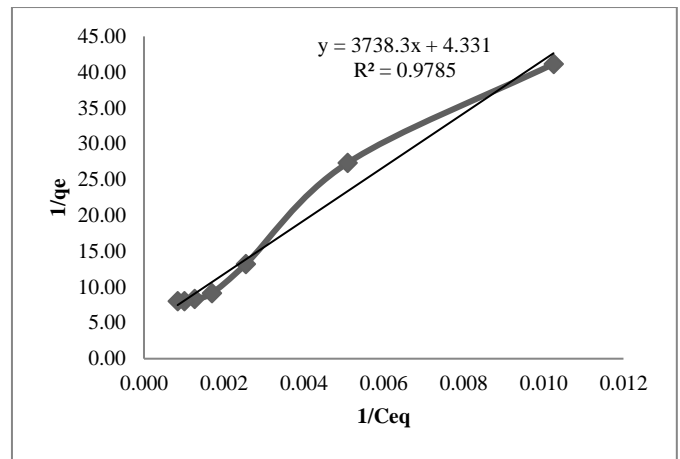
Fig. 1. Variation in sorption Capacity with change in contact time (t) for sorption of (a) Cr(VI) in Soil A (b) Cr (VI) in Soil B (c) Cd(II) in Soil A (d) Cd(II) in Soil B

B. Adsorption isotherm

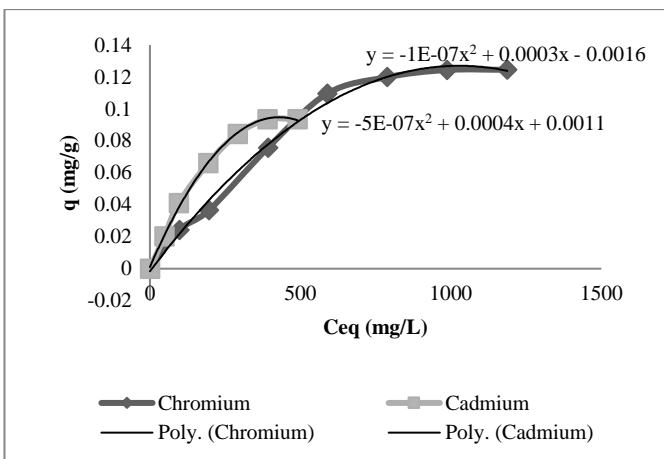
For plotting Langmuir and Freundlich isotherms, initial concentration of heavy metals was increased and sorption capacity was determined. Initial Concentration of chromium was increased as 100, 200, 400, 600, 800, 1000, 1200, 1400 mg/L in both the soils whereas initial concentration of cadmium was increased as 50, 100, 200, 300, 400, 500, 600 mg/L according to the range in which they were showing sorption. Fig. 2 shows the concentration in each case after which the sorption capacity has become constant. Also, initially the sorption capacity has increased with increase in concentration and later it has become constant. [10]



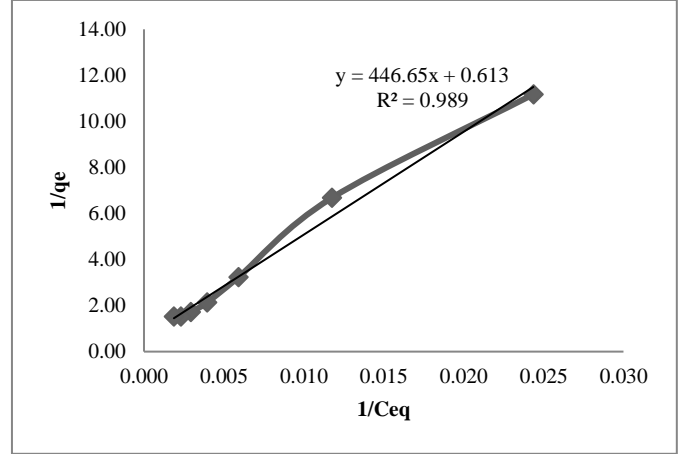
(a)



(b)



(b)



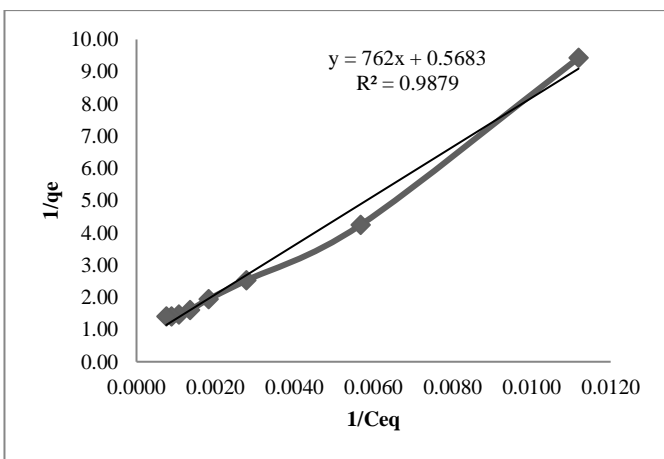
(c)

Fig.2. Sorption Capacity v/s Equilibrium Concentration curve showing saturation concentration for (a) Soil A (b) Soil B.

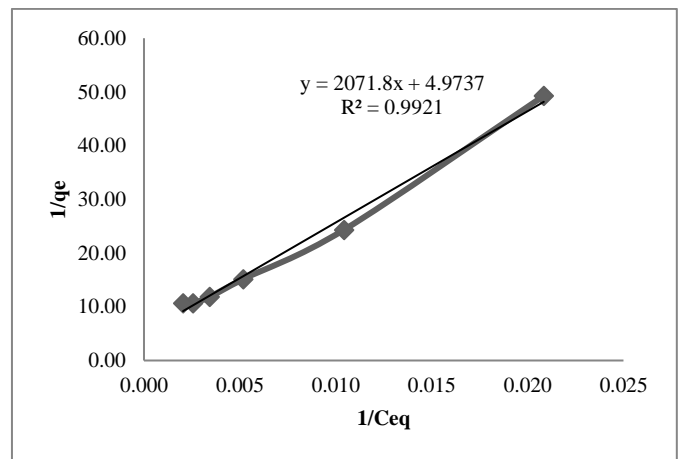
Langmuir Isotherm as shown in Fig. 3 has been plotted using the equation (2) which is given by

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K} \frac{1}{C_{eq}} \quad (2)$$

where q_m and K are the Langmuir constants, which represents maximum sorption capacity and the energy constant related to heat of sorption respectively.



(a)



(d)

Figure 3: Langmuir Isotherms for sorption of (a) Cr(VI) in Soil A (b) Cd(II) in soil A (c) Cr(VI) in Soil B (d) Cd(II) in Soil B.

Freundlich Isotherm has been plotted using the equation (3) as

$$\log q_e = \log K_f + \frac{1}{n} \log C_{eq} \quad (3)$$

where K_f and n are Freundlich constants, which represents maximum sorption capacity and the sorption intensity [6]. In both the soils, monolayer sorption was found to be predominant as Langmuir isotherms have shown better results as compared to Freundlich isotherms. Hence, from

Langmuir Isotherm the value of maximum sorption capacity and correlation coefficient (R^2) were calculated which is shown as in Table 2.

TABLE 2: MAXIMUM SORPTION CAPACITY USING LANGMUIR ISOTHERM

Soil Type	Heavy Metal	Langmuir Isotherm	
		q_m (mg/g)	R^2
A	Cr (VI)	1.760	0.987
	Cd (II)	1.631	0.989
B	Cr (VI)	0.231	0.978
	Cd (II)	0.201	0.992

The maximum sorption capacity as obtained from the plot was found more in case of chromium than cadmium. This is attributed to more ionic charge of chromium as compared to cadmium. Also, the soil has shown faster sorption to cadmium compared to chromium because of more ionic radius of cadmium as compared to chromium.

IV. CONCLUSION

The results have revealed that it is possible to develop a correlation based on the type of soil and its characteristic parameters. The above study has confirmed that soil is a very good material for sorption of heavy metals and more particularly the soil with higher CEC and organic matter content. Following conclusions are drawn from the above study:

- The maximum sorption capacity given by Langmuir constant q_m was 1.760 for Cr(VI) sorption in soil A which was about eight times higher than for soil B which is 0.231. Similarly q_m is 1.631 for Cd(II) in soil A which was very much high as compared to the value of constant q_m i.e. 0.201 for soil B. Also CEC of Soil A was 37.2 meq/100g which was almost twice the CEC of Soil B which was 18.4 meq/100g. Thus soil A gives better sorption capacity as compared to soil B and higher value of CEC in soil A than soil B also justifies this fact.
- The maximum sorption capacity in both soils was found to be more than what is permissible as shown in Annexure A and hence alarming.
- Initially the sorption capacity has increased with increase in concentration and later it has become constant. Thus, in the process of sorption of both the heavy metals, a large amount of heavy metal was adsorbed in initial period and later sorption has become constant because of the occupation of all the active sites by these heavy metals.
- The value of regression coefficient in Langmuir isotherm for soil A was higher than that in Freundlich isotherm. Hence, in both the soils monolayer sorption was found to be predominant as

Langmuir isotherms has shown better result as compared to Freundlich isotherm.

- The maximum sorption capacity for Cr(VI) in soil A was 1.760 and in soil B was 1.631. Similarly, the maximum sorption capacity for Cd(II) in soil A was 0.231 and in soil B was 0.201. Thus for both the soils maximum sorption capacity obtained from the plot was found more in case of chromium than cadmium. This is attributed to more ionic charge of chromium as compared to cadmium.
- For both the soils, the maximum sorption for cadmium was achieved just in 24h whereas for chromium it took 36h. Thus the soil show faster sorption to cadmium compared to chromium because of the more ionic radius of cadmium as compared to chromium.

These heavy metals after getting adsorbed into the soil stay in plant roots for a very long period of time and thus are readily available for plant uptake. Both these heavy metals even at very low concentrations if enters into the food chain, can badly affect the living organisms. Moreover if they migrate down then they can affect groundwater as well.

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