Adsorption And Kinetic Study For Removal Of Cr(VI) By Naturally Available Adsorbents

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ABSTRACT

Adsorption technique is one of the most technologies being used for treatment of polluted water, but seeking for the low cost adsorbent is the objective of this study. Hexavalent chromium is a known carcinogen. It is generated by metal plating industries, galvanizing industries, mining operations and tanneries. An attempt for naturally available low cost effective adsorbent was made by utilizing Laterite soil, Black cotton soil and Shahapur sand. Kinetics of adsorption was found to follow first order reaction and the adsorption rate of Cr(VI) are 7.37mg/g, 6.41mg/g and 5.12mg/g by Laterite soil, Black cotton soil and Shahapur sand respectively. Adsorption behavior was found to follow Freundlich, Langmuir and Temkin isotherms. For Column tracer experiment the values of Freundlich coefficient $K^{F,}$ Freundlich Isotherm constant 1/n, Distribution coefficient K^{F}_{d} and Retardation factor R for Laterite soil are 1.210, 0.931, 1.032, 2.070 and for Black cotton soil are 1.10, 0.966, 1.192, 2.560 and for Shahapur sand are 0.890, 1.10, 2.522 respectively. The result of the Column Experiment follows Freundlich Isotherm.

Keywords: Cr(VI), Adsorption, Shahapur sand, Kinerics, Isotherms

I. INTRODUCTION

Water is one of the most essential elements on earth. Every living being needs water for its survival. When we look at the water available on earth, we find that a mere 2.5% of fresh water is what is available to humans. While 68.7% of this accounts for glaciers and ice cap, we are left with 30.1% of groundwater and just 1.2% of surface water. The requirement of the fresh water in various sectors such as domestic, irrigation, industry and others increases significantly all over the world. Thus, water liability, both in terms of quality and quantity, has declined to such an extent to the rapid increase in the population and industrialization.

Heavy metals are most common pollutants found in industrial waste water. Heavy metals enter into the environment due to bioaccumulation. These metals are highly toxic and disturb the ecosystems[2].

Water pollution by Chromium is of considerable concern, as these metals are used in a variety of applications including metal plating industries, galvanizing industries, mining operations and tanneries and are usually present in high concentrations in the liquid wastes which are released directly into the Environment without any pre-treatment.

Cr-containing wastewaters are one of the major pollutants of the environment. It is toxic to the point that it prompts liver harm, Congestion, edema and skin disturbance and results in ulcer. Hexavalent Chromium Cr(VI) is reported to be a powerful carcinogen capable of modifying the deoxyribonucleic acid (DNA) transcription process in both animals and humans that may result in important chromosome aberrations.[3]

II. OBJECTIVES

To evaluate a feasible and economical low cost treatment of Cr(VI), as present in synthetic sample by Black cotton soil, Laterite soil and Fine sand(Shahapur sand) which are naturally available as an adsorbent.

- To study the physical properties of adsorbents like Black cotton soil, Laterite soil and Fine sand (Shahapur sand).
- To study Sorption kinetics
- To study Isothermal patterns
- To study column tracer experiment

III. LITERATURE REVIEW

N. Gandhi, D. Sirisha and KB. ChandraSekhar (2014) have studied the removal of Cr(VI) from aqueous solution by using multanimiti. Batch mode adsorptive removal was carried out at varying pH , adsorbent dosage, agitation time, temperature and initial concentration. It has been reported that multanimitti dose not only has the capacity to remove chromium (VI), it may also decrease acidity, alkalinity, hardness, salinity and conductivity of water. Adsorption with multanimitti is not only cheaper but requires less maintenance and supervision.[2]

Ali S. M, Khalid A. R. and Majid R.M (2014) have studied the removal of Zinc, Chromium and Nickel from industrial waste water using Corn cobs. The aim of this study was to use low cost adsorbents, which consist of corn cobs as plant wastes adsorbents in treatment of Industrial waste water by fixed bed column technique and study the effect of two variables (pH value and contact time). Adsorption tests showed the corn cobs adsorbents had significant heavy metal removal efficiency. [1]

IV. MATERIALS AND METHODOLOGY

4.1 Selection of Suitable Adsorbents

Laterite soil: It is a soil and sedimentary rock type rich in iron and aluminum, and is commonly considered to have formed in hot and wet tropical areas. Nearly all laterites are of rusty-red colouration, because of high iron oxide content as shown in Fig 1. They develop by intensive and long-lasting weathering of the underlying parent rock. Tropical weathering (laterisation) is a prolonged process of chemical weathering which produces a wide variety in the thickness, grade, chemistry and ore mineralogy of the resulting soils. The majority of the land area containing laterites is between the tropics of Cancer and Capricorn.

Black cotton soil: Black soil is also called as Black cotton soil as its colour is black as shown in the Fig 2 Generally, Black cotton soil is found in the central, western and southern states of India, including Karnataka. Black cotton soil is one of major soil deposits of India. They are very tenacious of moisture and exceedingly sticky, when wet. Due to considerable contraction on drying large and deep cracks are formed. These soils contain abundant iron and high quantities of lime, magnesia and alumina. Black soils are poor in nitrogen, phosphorus and organic matter. The soils are generally rich in montmorillonite and bi elliptic group of clay minerals.

Fine sand(Shahapur sand): Generally ,Fine sand(Shahapur sand) is found on the banks of Krishna river. Sand is granular material composed of finely divided rock mineral particles. It is defined by size, being finer than gravel and coarser than silt. Sand can also refer to a textural class of soil or soil type Fine sand(Shahapur sand) is abundantly available in Shahapur Yadgir district of Karnataka. Fine sand(Shahapur sand) is as shown in the Fig 3.

Figure 1. Laterite soil

Figure 2. Black cotton soil

Figure 3. Fine sand(Shahapur sand)

4.2 Preparation of Adsorbent

The adsorbents Laterite soi , Black cotton soil and Fine sand(Shahapur sand) are cleaned. Laterite soil and Black cotton soil broken into very minute particles in order to make it in powdered form. Adsorbents are washed with distilled water for about 2-3 times to make it free from dissolved and floating organic matter and coloured material. Powder is then oven dried at 105±2°C for about 24Hrs. The adsorbents which is passing through 300 micron sieve and retained on 150 micron sieve are used for batch adsorption studies. Table 1 shows Physico-Chemical Characteristics of Adsorbents.

Table 1 Physico-Chemical Characteristics of Adsorbents

Sl. NO	Characteristics	Units	Laterite Soil	Black cotton soil	Shahapur sand
01	Moisture content	%	2.3	6.2	1.3
02	pH values	-------	7.6	7.1	7.2
03	Specific gravity	-------	2.79	2.08	2.63
04	Bulk density	g/cc	1.12	1.36	1.55
05	Colour	-------	Red	Black	Brown and Black
06	Surface area	m^2/g	523	607	468
07	Acid Solubility	%	-----	----	1.22
08	Uniformity coefficient	-------	-----	----	3.16

V. RESULTS AND DISCUSSION

5.1 Sorption Kinetics

The kinetics of Cr(VI) removal was performed at ambient temperature at different time interval of adsorption. The batch sorption kinetic data for the adsorption of the Cr(VI) was tested for the first order reaction as shown in the Fig.4, Fig.5 and Fig.6 for Laterite soil, Black cotton soil and Shahapur sand respectively. Rate constants K are as shown in table 2 for all the adsorbents. The rate equation for the first order reaction is given by levenspiel.

$$\text{Ln } Ca/Co = K*T$$

K = rate constant

5.2 Adsorption isotherm studies

Modeling the equilibrium data is a fundamental for the industrial application of adsorption since it gives information for designing and optimizing operating procedure. The adsorption equilibrium data are conveniently represented by adsorption isotherms, which correspond to the relationship between the mass of the solute adsorbed per unit mass of adsorbent qe and the solute concentration for the solution at equilibrium Ce.

In order to successively represent the equilibrium adsorptive behavior, it is important to have a satisfactory description of the equation state between the two phases composing the adsorption system. Three kinds of isotherms equations were tested to fit the experimental data. The Isotherm constants are presented in table 2.

Langmuir equation: $C_e /q_e = (C_e /q_{max}) + [1/ (q_{max}b)]$

Freundlich equation: $\log q_e = \log K_F + (1/n) \log C_e$

Temkin equation: $q_e = a + b \ln C_e$

Where q_e is the amount adsorbed at equilibrium (mg/g) and C_e is the equilibrium concentration of metal ions in solution (mg/L). The other parameters are different isotherm constants, which can be determined by regression of the experimental data. In the Langmuir equation, q_{max} (mg/g) is the amount of adsorbate per unit weight of adsorbent to form a complete monolayer on a sorbate surface. Freundlich, Langmuir and Temkin isotherms are plotted in Fig.7, Fig.8 and Fig .9 respectively.

5.3 Column Tracer Experiments

To observe the retention and leaching of Chromium (VI) through respective adsorbent column, Perspex plastic columns of 5.5cm diameter were used. The length of the adsorbent filled in the columns is chosen based on texture and compaction.

A series of column tracer experiments have been performed with Chromium (VI) on different adsorbents obtaining retardation coefficients. Results obtained by Column tracer method are interpreted using Freundlich isotherm formulae describing the adsorption isotherms. For all adsorbents of Cr(VI) adsorption, the best fit is obtained for the Freundlich isotherm as shown in the Fig 10, described by the formula:

$$\text{Cads} = \text{KF x} C_{aq}^{1/n}$$

Where,
Cads = balance concentration of the studied compound in the carbon bed;
Caq = balance concentration of the studied compound in the water;
KF and n = coefficients of the Freundlich adsorption isotherm.
Substitute distribution coefficient (determined using the Freundlich isotherm)
K_d^F for a given value of balance concentration of ion adsorbed in the solution equals

$$K_d^F = \frac{\mathrm{KF}C_{aq}^{\frac{1}{n}}}{Caq} = \mathrm{K}^{\mathrm{F}}C_{aq}^{(1/n-1)}$$

For the distribution coefficient determined on the basis of the adsorption isotherm, the retardation has been defined as

$$\mathrm{R}=1+\frac{\rho\,\mathrm{d}}{n}K_d^F$$

The Freundlich constants are presented in table 3.

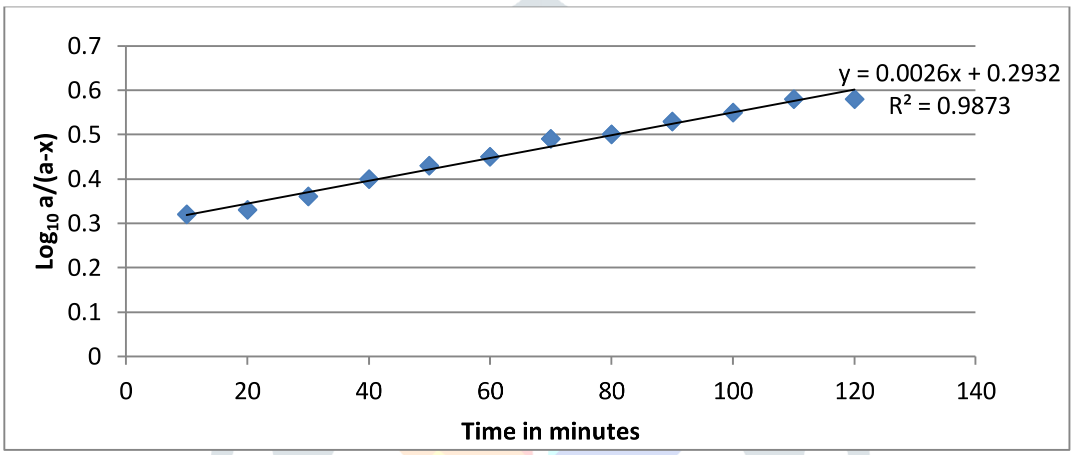

Figure 4 Reaction Rate Constant for Cr(VI) Removal by Laterite soil

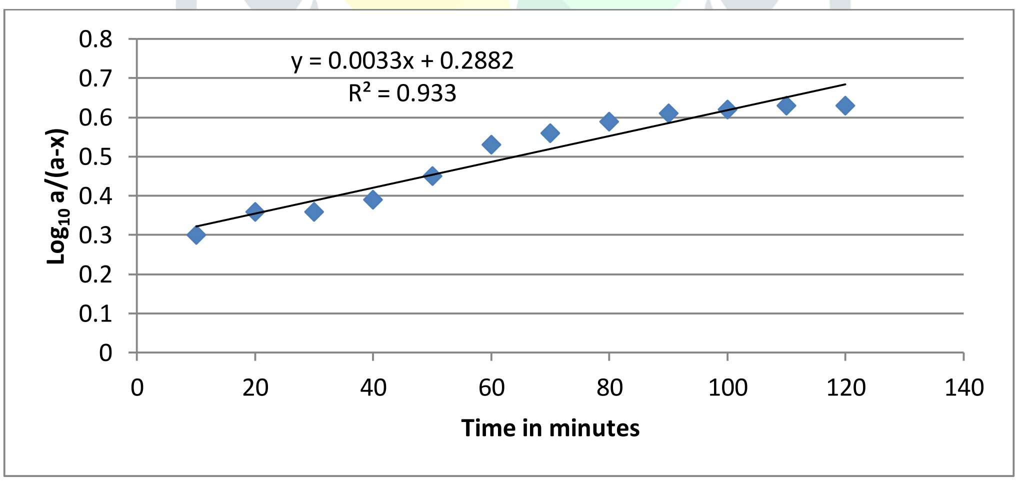

Figure 5 Reaction Rate Constant for Cr(VI) Removal by Black cotton soil

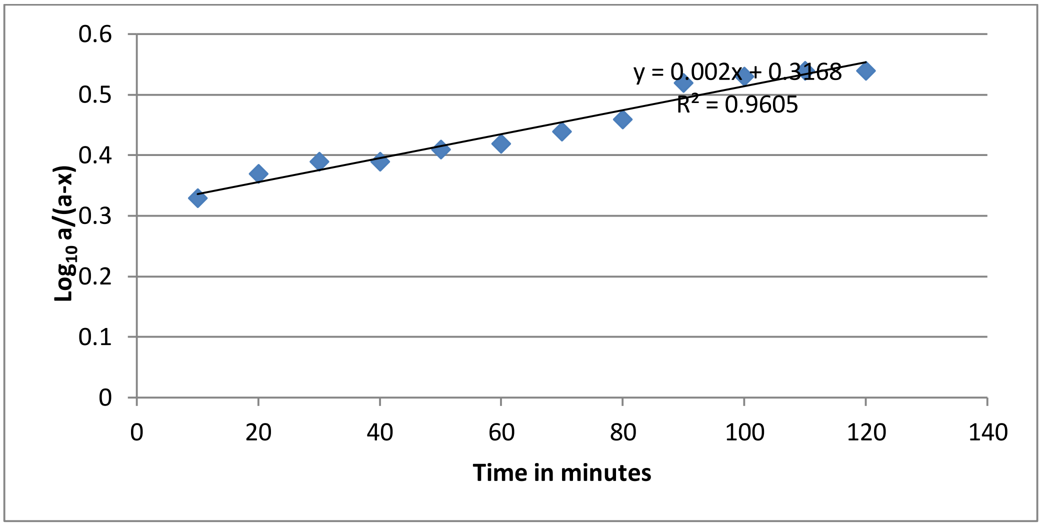

Figure 6 Reaction Rate Constant for Cr(VI) Removal by Shahapur Sand

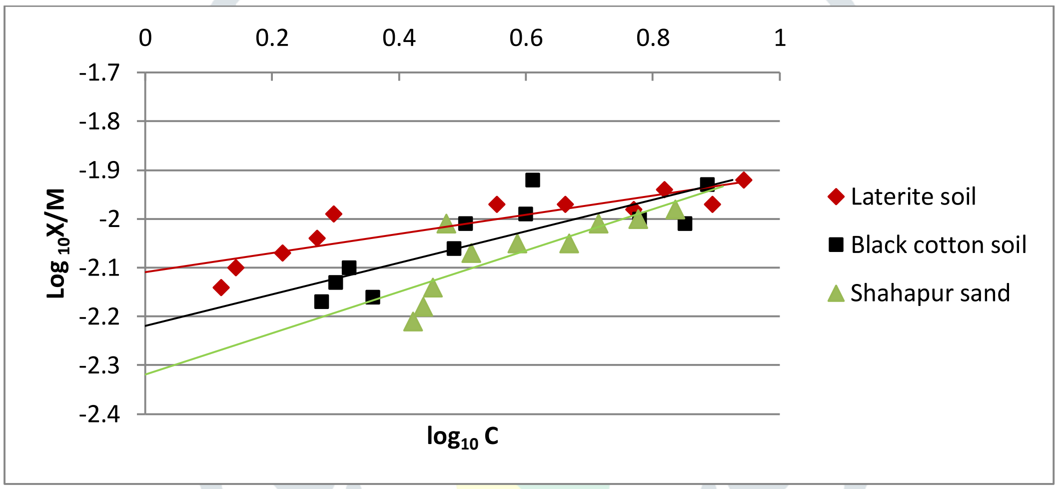

Figure 7 Freundlich Isotherm Data for Cr(VI) Removal by Laterite soil, Black cotton soil and Shahapur sand

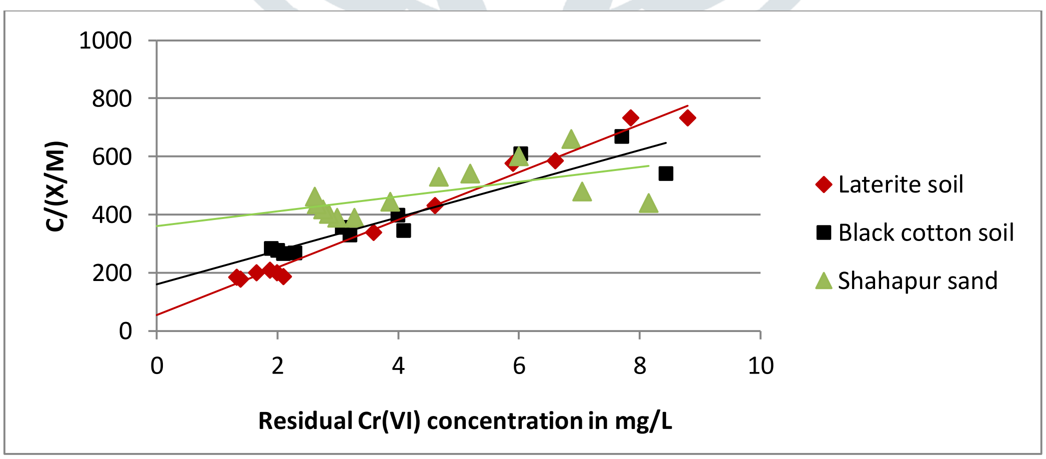

Figure 8 Plots of Langmuir's Isotherm for Cr(VI) Removal by Laterite soil, Black cotton soil and Shahapur sand

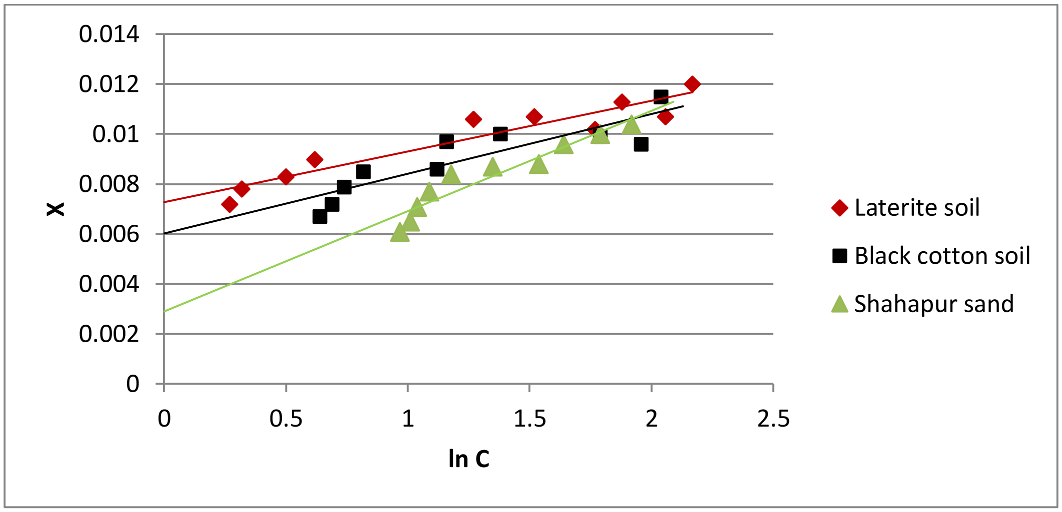

Figure 9 Plots of Temkin Isotherm for Cr(VI) Removal by Laterite soil, Black cotton soil and Shahapur sand

Table 2 Parameters of Freundlich, Langmuir and Temkin Isotherm models

	Freundlich Isotherm		Langmuir Isotherm			Temkin Isotherm		
	1/n	K	A	b	R	a	B	Rate constant 'K'
Laterite Soil	0.179	0.0081	0.012	0.098	0.098	0.007	0.001	0.023
Black cotton soil	0.390	0.0057	0.015	0.046	0.098	0.005	0.003	0.025
Shahapur sand	0.738	0.0036	0.044	0.059	0.095	0.001	0.007	0.027

From the table 2 it is clear that follows Freundlich isotherm and proves to be a favourable adsorption as 1/n values are less than unity. It obeys Langmuir isotherm as separation factor 'R' is lesser than 1 and greater than 0 (0<R<1). It also follows Temkin isotherms as the values of constants a and b are less than 1.

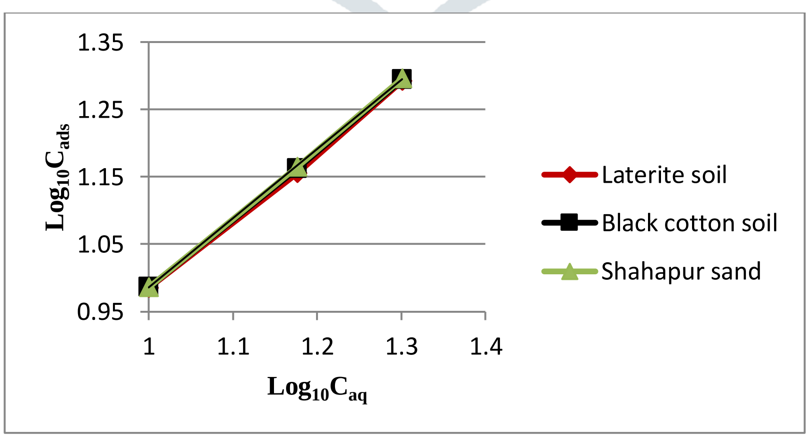

Figure 10 Freundlich Isotherm of adsorption of Cr(VI) on Laterite soil, Black cotton soil and Shahapur sand

Table 3 Data showing the values of Freundlich Coefficients

Adsorbent	K^F(Coefficient of Freundlich Isotherm)	1/n (Coefficient of Freundlich Isotherm)	K^F_d (Distribution coefficient)	R(Retardation coefficient)
Laterite soil	1.210	0.931	1.032	2.070
Black cotton soil	1.10	0.966	1.192	2.560
Shahapur sand	1.420	0.890	1.10	2.522

From the table 3 it is clear that follows Freundlich isotherm and proves to be a favourable adsorption as 1/n values are less than unity.

VI. CONCLUSION

- From the kinetic study rate of reaction follows first order and the adsorption rate of Cr(VI) are 7.37mg/g, 6.41mg/g and 5.12mg/g by Laterite soil, Black cotton soil and Shahapur sand respectively.
- From the Isotherm constants it is concluded that adsorption process obeys Freundlich, Langmuir and Temkin isotherms.
- For Column tracer experiment the values of Freundlich coefficient $K^{F,}$ Freundlich Isotherm constant 1/n, Distribution coefficient K^F_d and Retardation factor R for Laterite soil are 1.210, 0.931, 1.032, 2.070 and for Black cotton soil are 1.10, 0.966, 1.192, 2.560 and for Shahapur sand are 0.890, 1.10, 2.522 respectively.
- The result of the Column Experiment follows Freundlich Isotherm as 1/n<1.

VII. ACKNOWLEDGMENT

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