Lawrencepur Sand- A Highly Efficient Adsorbent for the Removal of Cr (VI) from Waste Water

[1]NADIA JAMIL*, [2]NAVEED AHSAN AND [3]UMER SHAFIQUE
[1]*College of Earth and Environmental Sciences, University of the Punjab, Lahore-54590, Pakistan.*
[2]*Institute of Geology, University of the Punjab, Lahore-54590, Pakistan.*
[3]*Institute of Chemistry, University of the Punjab, Lahore-54590, Pakistan.*
ndnaveed@gmail.com*

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Summary: For the removal of heavy metal ions adsorption is considered an environmental friendly technique. In this research work lawrencepur sand has been successfully utilized as adsorbent for the removal of Cr(VI) from industrial waste effluents. Effects of pH, shaking speed, contact time and amount of adsorbent were studied. FTIR was used to study basic surface characteristics. Different adsorption models were employed to calculate adsorption capacity. Optimum conditions for Cr(VI) uptake by lawrencepur sand were 3.5g/100ml adsorbent dose, pH 6,shaking speed 200rpm. It has been concluded that lawrencepur sand can be used as low cost adsorbent for removal of Cr(VI) from waste water.

Introduction

At present, heavy metals are the most important pollutants in industrial and municipal wastewaters as well as in source water, and are becoming a severe public health problem [1, 2]. Heavy metal ions are called priority pollutants, because of their mobility in water ecosystems, their toxicity to life and resistance to biodegradation [3, 4]. Chromium compounds are widely used by industries like leather tanning, electroplating and pigments, which result in discharge of large quantities of this element in the aquatic environment. Chromium polluted water can cause serious environmental problems as well as induce toxic and carcinogenic health effects on humans [5]. Chromium mostly occurs in trivalent and hexavalent forms. Hexavalent chromium is relatively more toxic and is powerful carcinogenic that alters the DNA transcription process. For that reason, the removal of chromium from water is an obligation.

Efforts are going on around the world to find cost-effective and efficient processes for treatment of wastewaters polluted with heavy metals. The most important methods that have been used to remove metal ions from wastewaters include, ion exchange, lime coagulation, reverse osmosis, electrolytic extraction, chemical precipitation and membrane filtration, nevertheless, most of the aforementioned techniques have disadvantages like high cost, large input of chemicals and output of waste as well as incomplete removal. Adsorption is an efficient process that is being widely used for removal of metal ions from water and activated carbon is usually employed. Activated carbon is effective in removal of metal ions from wastewaters but it is expensive and requires chelating agents to enhance its performance [6]. For this reason, an extensive search for low-cost and efficient adsorbents is imperative under the situation [7]. A number of low-cost materials such as onions [8], bones [9], fly ash [10], peat [11], rocks [12, 13], minerals [14-16] and sand [17, 18] have been successfully used to adsorb a number of metal ions from aqueous solutions.

Lawrencepur sand has already been used as adsorbent by some researchers, for removal of different metal ions from waste water like Cd(II) and Pb(II) [19, 20]. Present study evaluates the efficiency of Lawrencepur sand to remove Cr(VI) from water which is a potential pollutant.

Lawrencepur sand is the most popular fine aggregate [21-25] used in construction industry of Pakistan [26] for the last hundred years. Trillions of tons of sand deposits occur on terraces around Lawrencepur and Qibla Bandi in Attock district around the Indus River, Fig. 1 (Topographic sheet No.43 C/9). The Lawrencepur sand was derived from denudation of Higher and Lesser Himalayas and Kohistan Island Arc [25] and transported to the Indus River through a number of tributaries [27]. It has excellent engineering properties [22, 25] that conform to prescribed standards for civil engineering projects [28]. However certain constituents are prone to initiate alkali aggregate reaction [25] that may deteriorate the civil structures.

*To whom all correspondence should be addressed.

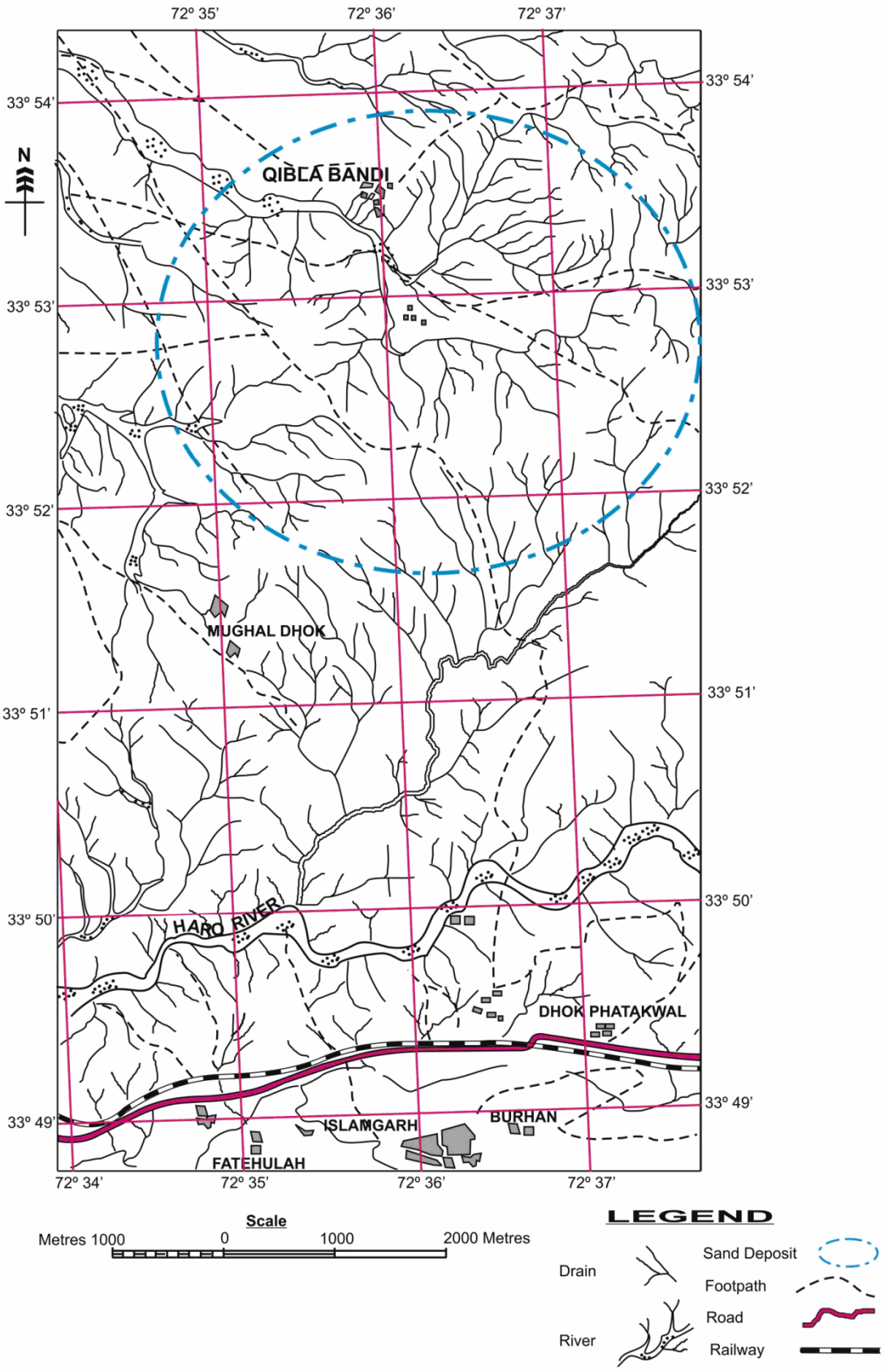

Fig. 1: Lawrencepur sand deposits.

Results and Discussion

Petrographic Study of Sand

Physical properties [29] of the sand used in present study like bulk density, specific gravity and water absorption are 90Ib/cft, 2.87 and 0.51%, respectively. Gradation of sand varies from place to place. Chemical analysis [29, 30] indicates that sand is free from organic impurities and chloride content. Petrographic modal analysis of Lawrencepur sand shows that the sand is composed of rock fragments and mineral grains that are quartz (47.1%), amphibole (7.7%), quartzite/polygrain quartz (7.2%), quartz mica schist (6.4%), biotite (6.1%), granite (5.8%), carbonate (5.5%), feldspar (4.5%), slate/argillite (2.4%), magnetite (1.9%), epidote (1.8%), muscovite (0.9%), acid to intermediate volcanic (0.7%), greywacke (0.6%), chert (0.5%), garnet (0.3%), lithic arenite (0.2%), zircon (0.2%) and tourmaline (0.2%).

Effect of Shaking Speed

Effect of shaking speed on percentage adsorption of Cr(VI) on Lawrencepur sand is presented in Fig. 2. Initially by increasing the shaking speed percentage adsorption increases. This effect can be explained on the basis of fact that at low shaking speed particles of adsorbent and metal ion Cr(VI) move slowly. Subsequently, exposure of metal ions towards available active sites on adsorbent decrease. By increasing the shaking speed metal ions and particles of sand move rapidly around each other that increases the relative concentration of metal ions resulting in more adsorption. Best results were obtained at 200rpm however, after crossing this limit kinetic energy of metal ions as well as sand particles increase so much that they start colliding with each other due to which some loosely bounded metals ions become detached. This results in decreased adsorption of ions. Different workers also reported the same observations for Cr(VI) on different adsorbents [31, 32].

Effect of Adsorbent Dosage

Effect of adsorbent dose on the percentage adsorption of Cr(VI) on Lawrencepur sand is given in Fig. 3. It can be seen that by increasing the dose of adsorbent percentage adsorption also increases, which can be related with increased number of available active sites [33]. Best adsorption occurs at 3.5g/100ml, further increase in adsorption dose results in decrease in percentage adsorption. The same observation was reported and explained by different workers.

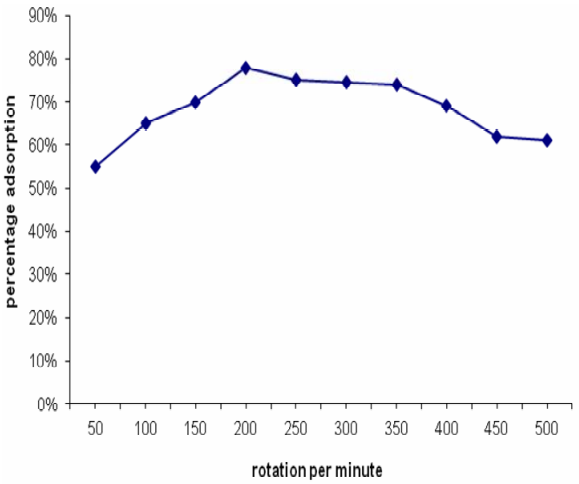

Fig. 2: Effect of shaking speed on percentage adsorption of Cr(VI) on Lawrencepur sand.

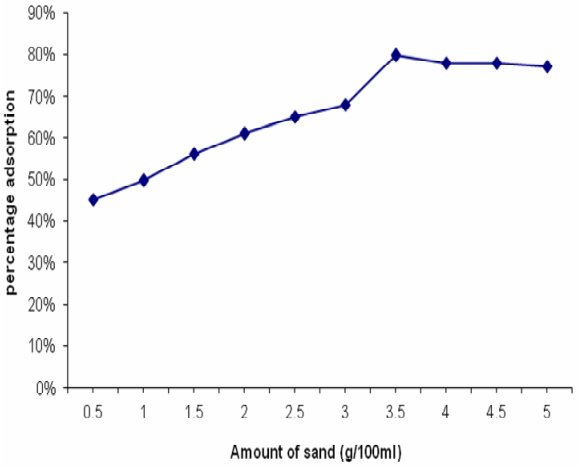

Fig 3: Effect of amount of adsorbent on percentage adsorption of Cr(VI) on Lawrencepur sand.

This may be presumed that at high adsorbent dosage the interaction between adsorbent – adsorbent particles increases than adsorbent- adsorbate particles [34] or adsorbent particles aggregate with each other due to which available number of active sites can reduce, resulting in decreased percentage adsorption [35].

Effect of pH

The effect of pH on adsorption of chromium (VI) was studied at room temperature by varying the pH of metal solution–sand suspension from 2 to 9 (Fig. 4). The pH range 2-9 was selected because below pH 2, there was very little or no adsorption, whereas at pH above 9, chromium precipitates out as

hydroxide. The percent adsorption increased in the pH range of 2–8, showing the maximum adsorption at pH 6 (about 80%). The optimum pH value depends upon type of functional groups available on adsorbent and ionic state of the metal ion present in solution [36]. Hexavalent chromium exists primarily as H_2CrO_4, $HCrO_4^-$ and CrO_4^{2-}. H_2CrO_4 dominates at pH < 1.0 (because of being neutral, this specie is not capable of being adsorbed), $HCrO_4^-$ between 1.0 and 6.0, and CrO_4^{2-} above 6.0. In general, sands have a silicon atom at the center of three dimensional tetrahedron structure surrounded by oxygen atoms at the corners. Hydroxyl groups (-OH) are attached at the edges of tetrahedral silicate structural units (as shown in Fig. 5 A by IR peaks at or around 3600 cm^{-1}). At pH < 7, -OH groups become $–OH_2^+$ because of protonation and thus, adsorbent possesses a net positive charge on the surface. The conditions become ideal for adsorption of negatively charged metal species (CrO_4^{2-}) onto the positive surface of sand. Disappearance of –OH peaks in IR spectra of metal bearing sand is an evidence of the stated fact (Fig.5B). Further decrease in pH will result in converting CrO_4^{2-} to $HCrO_4^-$ that would cause a decrease in percent adsorption because of reduction in negative charge. At pH 7 and above, the decline in percent adsorption can be attributed to the fact that protonation or positive charge on the surface would reduce that would cause less adsorption.

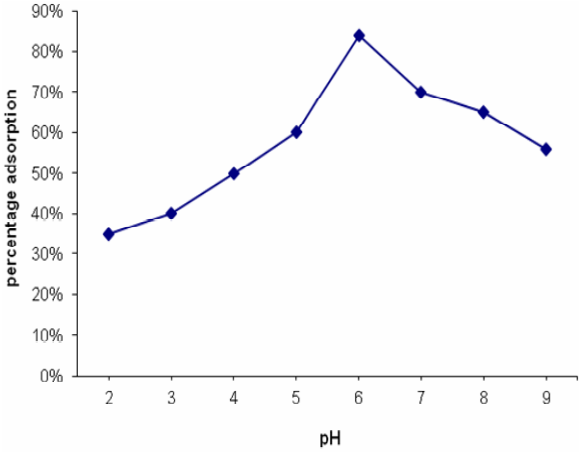

Fig. 4: Effect of pH on percentage adsorption of Cr(VI) on Lawrencepur sand.

Effect of Time

Contact time between two phases (adsorbent and solution containing Cr (VI) ions) influence the adsorption process. Fig. 6 explains that the adsorption of Cr (VI) initially increased rapidly by increasing contact time between two phases. Maximum adsorption occurred at 60minutes after that there is a slight decline before achieving equilibrium.

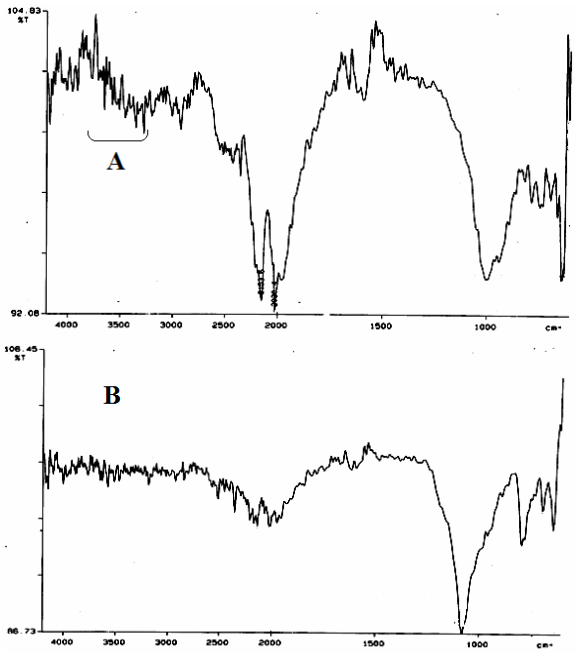

Fig. 5: FT-IR spectra of unused (A) and metal loaded (B) Lawrencepur sand.

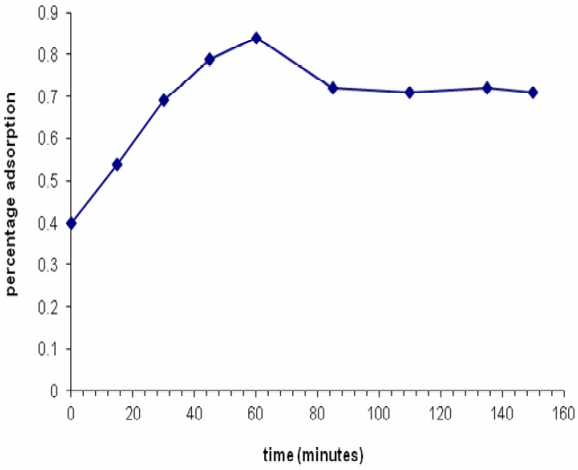

Fig. 6: Effect of time on percentage adsorption of Cr(VI) on Lawrencepur sand.

The same pattern for different metals and adsorbent systems has also been observed by different researchers [37, 38]. This may be due to the fact that in start maximum number of active sites is available and Cr (VI) ions become easily attached to these sites. At optimum time value all available active sites become occupied and after that an equilibrium was attained at which a continuous adsorption desorption process starts due to which no

further increase or decrease in percentage adsorption occurs.

Adsorption Isotherm

Two different isotherms were studied with concentration varied from 5 to 50mg/L. Langmuir and Fruendlich parameters were calculated for adsorption of Cr(VI) at shaking speed 200rpm,pH 7,and contact time 60minutes. Fig 7 and 8 show plots of Langmuir and Fruendlich isotherm respectively. Values of parameters of Langmuir and Fruendlich were calculated from the slopes and intercept of these plots given in Table-1.

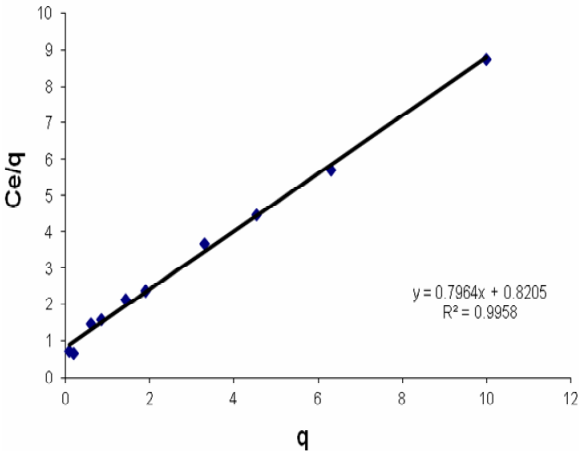

Fig. 7: Langmuir adsorption isotherm for Cr(VI) on Lawrencepur sand.

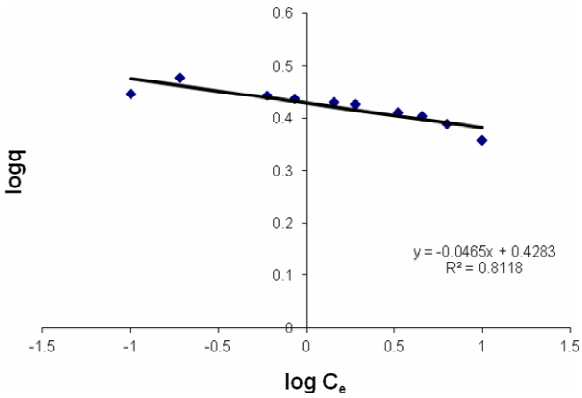

Fig. 8: Fruendlich adsorption isotherm for Cr(VI) on Lawrencepur sand.

Table-1: Langmuir and Fruendlich parameters for adsorption of Cr(VI) on Lawrencepur sand.

Langmuir Parameters				
Slope	**intercept**	**R^2**	**Q(mg/g)**	**b**
0.796	**0.820**	**0.995**	**1.25**	**1.030**
Fruendlich Parameters				
Slope	**intercept**	**R^2**	**K(mg/g)**	**n**
0.0465	**0.428**	**0.811**	**2.681**	**2.15**

Adsorption Thermodynamics

For thermodynamics studies the adsorption of Cr(VI) on Lawrencepur sand was monitored over a range of temperature from 293-323K atoptimal conditions. The changes in enthalpy (ΔH) and entropy (ΔS) were calculated from slopes and intercepts of the plots of ln Q against 1/T in Kelvin (Fig. 9). Another important thermodynamic parameter is ΔG and its values were calculated by using equation 4. Results are given in Table-2 .The positive values of ΔH shows that in both cases process of adsorption is of endothermic nature while negative values of ΔG indicates the spontaneous nature of the adsorption processes.

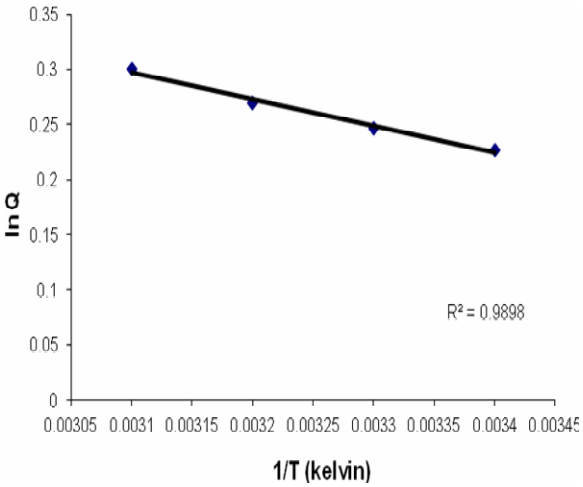

Fig. 9: Plot of Langmuir isotherm constant (lnQ) vs temperature (1/T).

Table-2: Thermodynamic constants for the adsorption of Cr(VI) on Lawrencepur sand at various temperatures.

Temperature(K)	**ΔG(kJmol^{-1})**	**ΔH(kJmol^{-1})**	**ΔS(kJmol^{-1}K^{-1})**
293	**- 23.183**		
303	**- 24.042**	**2.016**	**0.086**
313	**- 24.902**		
323	**- 25.76**		

Experimental

Sampling and Preparation of Adsorbent

Representative samples of Lawrencepur Sand (1000 gm) were collected [39] from an open pit located at QiblaBandi and reduced to test size in accordance with ASTM C 702. Samples were dried to constant weight in an oven at 110 ± 5°C and reduced to test sample size [40] and sieved in mechanical sieve shaker for gradation. Pass of ASTM sieves No. 30 and retain of sieve No. 50 was taken for present studies. Physical properties of sand were

calculated in accordance to British Standards (BS) and American Society for Testing and Materials (ASTM). For petrographic model analysis of sand a binocular petrographic microscope was used.

Reagents and Standards

Analytical grade chemicals, purchased from Merck and Sigma-Aldrich were used without further refinement. Stock solution (1000ppm) of Cr(VI) was prepared by from $K_2Cr_2O_7$. Doubly distilled deionized water was used for dissolving and further dilutions.The glassware used was of Quick-fit grade (England).

Characterization of Adsorbent

The surface chemical characterization sand (adsorbent) was performed by Fourier Transform Infrared Spectroscopy (FTIR) in Perkin Elmer, Spectrum R XI.

Analyte Analysis

The atomic absorption spectrophotometer (Perkin Elmer Analyst 800) was used toanalyze Cr(VI). The pH measurements were made by using Hanna pH 211 with glass electrode. To control shaking speed mechanical shaker (SHO-2D WiseMix, Daihan Scientific) was used.

Batch Sorption Studies

To study the effect of different parameters like shaking speed, adsorbent dose, pH, time and concentration of Cr (VI) ions in solution, a set of experiments was carried out. For this purpose only one parameter which is under study has been varied while all other kept constant. After adsorption under specific conditions, contents of the flasks were filtered and filtrates were subjected to analysis of Cr(VI).

The effect of the shaking speed on adsorption of Cr(VI) on Lawrencepur sand was studied by varying the speed from 50rpm to 500rpm. Other operational parameters were 30ppm concentration of metal ions, pH 7, adsorbent dose 2g/100ml and 30min time of contact between two phases. Adsorbent dose was also studied to find out its effect on adsorption process. For this purpose adsorbent dose was varied from 0.5g/100ml to 5g/100ml with 200rpm shaking speed, 30ppm concentration of metal ions, pH 7, and 30min contact time. The effect of pH was studied by varying pH from 2 to 9 at optimum shaking speed and adsorbent dose i.e. 200rpm and 3.5g/100ml, respectively. Concentration of analyte was 30ppm and time of contact was 30 minutes.

Effect of time was studied at last when all the other conditions become optimized, for this contact time of two phases varied from 0 minutes to 150 minutes at all other optimum conditions.

Adsorption Isotherms

Solutions of concentration from 5-50ppm of Cr(VI) were tested to find out up-taking capacity of Lawrencepur sand at optimum conditions determined by early experiments.Two major adsorption isotherms Langmuir, (Equation 1) and Freundlich, (Equation 2) were plotted by using straight line equations of these models and corresponding parameters were calculated from the slopes and intercepts of respective graphs.

$$\frac{Ce}{q} = \frac{1}{Q.b} + \frac{Ce}{Q} \qquad (1)$$

$$\log q = \frac{1}{n}\log Ce + \log K \qquad (2)$$

where
q (mg/g of adsorbent) is the amount of Cr (VI) adsorbed
Ce (mg/L) is concentration at equilibrium.
Q (mg/g) andb are Langmuir isotherm constants
K (mg/g, sorption capacity) and n (energy distribution of sorption sites) are Freundlich isotherm parameters

Thermodynamic calculations, were made by using equation 3

$$\ln Q = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (3)$$

Values of ΔS and ΔH were calculated from Slope and intercept of plot between ln Q and 1/T [41]. R is gas constant and T is operating temperature. By using the values of ΔS and ΔH the value of Gibb's free energy can be calculated by using equation 4.

$$\Delta G = \Delta H - T\Delta S \qquad (4)$$

Conclusion

In this study we can easily conclude that Lawrencepur sand is an efficient and low cost adsorbent for the removal of Cr(VI). Adsorption was favored at pH 7with optimum shaking speed 200rpm, adsorbent dose 3.5g/100ml for 30ppm Cr(VI) solution.Different adsorption models were used to

explain the adsorption phenomenon. The negative values of Gibbs free energy and positive values of enthalpy changes show the feasibility and endothermic natureof adsorption process. So Lawrencepur sand can be use to remove Cr(VI) from waste water and industrial effluents and it is a good alternative of costly and hazardous synthetic materials [42-44]

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