Adsorption of chromium using low cost adsorbent and kinetic modelling
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ABSTRACT

In this study, chromium (VI) ions removal has been investigated by cheap adsorbing agents. Chromium is a hazardous element and it has been a major pollutant in aquatic ecosystem. Removal of chromium from effluent wastes released from industries involves conventional methods. These conventional methods are not economical. Hence to improve the removal of hazardous metal ions and to cut down the cost of the process, a techno-economic process of biosorption has been used. The low cost biosorbents used for the study were bagasse pith, rice husk, neem leaf powder etc.. Biosorption of chromium is highly dependent on chromium concentration, time of retention for adsorption and amount of adsorbent added. Kinetic studies of adsorption showed that the process of biosorption of chromium ions by these low cost catalyst was satisfactorily proved by pseudo second order model. Equilibrium model (Langmuir and freundlich adsorption isotherms) have been analysed.

INTRODUCTION

Environmental pollution owing to toxic heavy metals in water is a main worldwide problem. Heavy metal ions cannot be despoiled; hence they occur in all parts of the environment. Elimination of heavy metal ions from industrial effluents to allowable limit before discharging them into environment is most important for protection and conservation of our resources and ecosystem. Chromium is one of the metal ions which occur in trivalent and hexavalent forms (X. Han, 2007). Cr(VI) is more toxic and highly soluble than Cr(III). Cr (VI) causes cancer in digestive tract and lungs (K. Mohanty, 2006). Therefore, it is essential to remove Cr(VI) from industrial wastewater before disposal. Sources of chromium species are commonly found in many industries such as leather tanning, aluminium productions, dye, electroplating, chromate manufacturing, metal cleaning and processing (M.Y. Arica, 2005; N. Ertugay, 2008; M. Jain, 2009). Conventional methods for eliminating Cr (VI) ions from wastewater include, physical and physico-chemical treatment technologies such as ion exchange, electro dialysis, membrane filtration, reverse osmosis, chemical precipitation and adsorption (S. Tunali, 2005). The main disadvantages of the above mentioned conventional treatment methods are high capital investment as well as frequent expenses and unproductive metal removal, generation of toxic sludge or other waste products that require safe disposal. Continuous search for other effective novel techniques has directed attention to biosorption, a feasible method for removal of metal ions (F. Veglio, 2008). Biosorption has numerous discrete advantages such as high efficiency, complete removal of metal ions even at low concentrations, low retention time and improved selectivity for removal of heavy metals from effluent irrespective of toxicity (Sari, M, 2008). Biosorbeents is used not only removes toxic heavy metals but also for the recovery and reuse of expensive metals such as gold and silver (Volesky, 1994). The scope of this work is the study of a kinetic study of chromium(VI) using low cost adsorbent materials under various conditions. By varying the amount of adsorbent, concentration of chromium solution, contact time and chemically treated adsorbent was studied in the laboratory scale. The chromium concentration in the effluent after adsorption was determined using spectrophotometer. Equilibrium curves and freundlich isotherm curves for the adsorbents were plotted.

Experimental set up: Adsorbent is obtained from from bagasse of sugarcane. It is obtained from the paper industry by depehthing process. 5000 ppm of Cr (VI) were prepared by dissolving 7.0719 gms are AR grade (K2Cr2O7) in 500ml of deionised,double distilled water. From the solution various ppm of known concentrations were prepared (100,200,300,400,500).

In natural water trivalent chromium exist as a as Cr3+,Cr(OH)32-,Cr(OH)2+ and Cr(OH)+. In the hexavalent form chromium exist as a CrO42- and as Cr2O42-. Chromium in hexavalent form is more toxic than trivalent chromium. It is used in alloys, in electroplating and in pigments. Chromate compounds frequently are added to cooling water for corrosion control. The method measures the chromium (VI). The Cr6+ is determined calorimetrically by reaction with Diphenyl carbazide (DPC) In acid solution. The red violet colored complex formed is measured at 540 nm.

Adsorption of chromium: The solution of known concentration and pH is fed in to the shaker. The treated adsorbent is poured in to the conical flask at a specified weight. Continuous stirring is given to the solution for several hours and sample is collected for every 30 minutes. Similarly, carryout the experiments by varying the various parameters involved such as

- Initial chromium concentration (100,200,300,400,500 )ppm
- Amount of adsobents(1,2,3,4,5)gm/ml
- Particle size (30 mesh size)
- Time(30,60,90,120,150)mins

The samples collected were analyzed for the residual chromium in a spectrophotometer at a maximum wavelength of 540 nm.

Equilibrium studies

Adsorption Isotherms: An isotherm is favorable when its fixation capacity grows rapidly with concentration in equilibrium in the liquid phase. Knowledge of adsorption isotherm is most important; in addition to informing us the adsorption capacity. It enables us to evaluate to what extent an adsorption system can be improved, as well as helping us to foresee the type of conditions in which we have to work in order to broaden our study to adsorption in and open reactor and estimate the necessary operation conditions for the system to be as effective as possible. The commonly applied isotherms for the adsorption process are freundlich isotherm and the langmuir isotherm.
Langmuir adsorption isotherm: The Langmuir equation was developed by Irving Langmuir in 1918 to describe the adsorption of gas molecules on a planar surface. Since then, it has been widely applied in many fields to describe sorption on solid surfaces. The Langmuir model assumes that uptake occurs on a homogenous surface by monolayer sorption without interaction between sorbed molecules. The Langmuir equation, which has been successfully applied to adsorption, is given by

\[
q_e = \frac{K_L S_m C_e}{1 + K_L C_e}
\]

Where, \( S_m \rightarrow \) Maximum amount of adsorption corresponding to complete monolayer coverage on the surface (mg.g\(^{-1}\))

\( K_L \rightarrow \) Langmuir constant (L.mg\(^{-1}\))

Equation can be rearranged to linear form

\[
\frac{C_e}{q_e} = \frac{1}{K_L S_m} + \frac{C_e}{S_m}
\]

A linearised plot of \( C_e/q_e \) Vs \( C_e \) is obtained. This suggests the applicability of the Langmuir model for the investigated system; the results will depend on the type of coverage of chromium. \( K_L \) and \( S_m \) are computed from the slopes and intercepts. From the calculated values a rough parameter of \( R \) can be found. \( R \) was calculated from the relation

\[
R_L = \frac{1}{(1 + K_L C_e)}
\]

The value of \( R \) will decide on the favorability of the adsorption process.

If \( R > 1 \) adsorption is favorable.

R=1 adsorption is linear

0 < R < 1 adsorption is unfavorable.

R=0 adsorption is irreversible.

Freundlich isotherm: The Freundlich model proposes a monolayer sorption with the heterogenous energetic distribution of active sites and with interactions between sorbed molecules, as described by the equation

\[
q_e = K_F C_e^{1/n}
\]

where,

\( K_F \rightarrow \) roughly as indicator of the adsorption capacity (mg\(^{1-1/n}\).g\(^{-1}\).L\(^{1/n}\))

\( 1/n \rightarrow \) adsorption intensity (dimensionless)

In general as the \( K_F \) value increases the adsorption capacity of the adsorbent increases. The magnitude of the exponent \( 1/n \) gives an indication of the favorability of adsorption. Values \( n > 1 \) represent favourable adsorption conditions. Equation can be rearranged to linear form

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

Linear plots of log \( q_e \) vs. log \( C_e \) shows the Freundlich isotherm. Values of \( K_F \) and \( n \) were calculated from the intercepts and slopes of the plots. From the values of \( n \) the favorability of adsorption can be determined.

If \( n > 1 \) adsorption is favorable

\( n < 1 \) adsorption is unfavorable.

KINETIC STUDIES

The adsorption reaction of chromium ions with bagasse pith is a chemisorption reaction which follows pseudo second order kinetics. The plot of \( q/t \) vs \( t \) is a linear curve

\[
Q_t = k_2 q_e^2t/1+k_2 q_e t
\]

Optimisation:

For this adsorption study parameters such as amount of particle, Time, concentration are varied and from the bench scale experiments, the optimized values for these parameters have been found to be

- Optimum amount – 500mg/100ml
- Optimum concentration - 500ppm
- Optimum time - 150min

CONCLUSION

From the present study, it can be seen that the removal of chromium from aqueous solutions by using the low cost absorbent bagasse pith, the % removed was found to depend on dose of adsorbent, contact time, concentration of the adsorbate. The adsorption of chromium by bagasse pith is minimum, with an average efficiency of 90%. An empirical reactionship has been obtained, which can predict the % removal of chromium(VI) at any time for a given sorbent dose and given concentration.
REFERENCES