Middle-East Journal of Scientific Research 17 (7): 936-940, 2013
ISSN 1990-9233

DOI: 10.5829/idosi.mejsr.2013.17.07.12239

Performance Assessment of Sawdust as Adsorbent for Cr (VI) Removal from Aqueous Solutions: a Kinetic Modeling

Arpit Saran, Hemant Kumar and Prashant Shrivastava

Department of Chemical Engineering,
SOET, ITM University, Gwalior, M.P., India

Abstract: The present work deals with the use of chemically activated Neem (Azadirachta indica) Sawdust and Sheesham (Dalbergia sissoo) Sawdust (SS) as an adsorbent for the retention of Chromium (VI) ions from synthesized aqueous solutions. A Batch wise Experiment was performed in order to investigate the various parameters such as contact time, effect of temperature and initial concentration of the metallic ion. The adsorbent showing highest chromium (VI) removal was found to be Neem Sawdust with highest loading capacity of 24.63 mg/g at 305 K and 100 mg/L of initial chromium concentration. Isothermal models like Langmuir and Freundlich were tested in order to determine the kinetic parameters and it was found that the experimental data fitted convincingly fine with Freundlich Isotherm ($R^2 = 0.991$).

Key words: Chromium · Adsorption · Sawdust · Wastewater

INTRODUCTION

The growth of civilization & industrialization has rooted many harmful changes in environmental problems, [1] consequently the water containing heavy metals have some harmful problems all over the world. Chromium is listed among top pollutants and is ranked 16th harmful pollutant due to its carcinogenic and teratogenic characteristics on the community [2]. In the environment Chromium exists in two stable states, viz. Cr (VI) & Cr (III) [1]. Chromium (VI) discharge into the environment can be due to various large numbers of industrial functions like metal finishing industry, iron & steel industry & inorganic chemical productions [3]. Soils and sediments are polluted with Chromium owing to the dumping of sewage sludge or discarding chromium wastes from industries [4]. Hexavalent Chromium is 100 times more toxic [5] than trivalent chromium and 1000 times more mutagenic as per studies. Non- occupational exposure to the metal occurs via ingestion of chromium containing food & water, whereas occupational exposure occurs via inhalation [6]. Major diseases caused by toxic hexavalent chromium ions are bronchial asthma and lungs cancer. Unlike the organic pollutants, the metals are very harmful because they are not bio-degradable & accumulate in the human body. They are very harmful for human beings, animals & other living organisms [1]. The maximum levels of chromium allowed in wastewater for trivalent chromium and hexavalent chromium are 5 mg/L and 0.05 mg/L respectively [7]. A number of methods are applied to reduce chromium concentration from industrial wastewater. There are various methods that used to remove heavy metal from waste water like chemical precipitation [8], ion exchange [9], reduction [10], electrochemical precipitation [11], solvent extraction [12], membrane separation [13] and evaporation [14]. Above mentioned conventional methods for Cr (VI) elimination are costly or unproductive at small concentrations. On the other hand some agricultural wastes like sawdust, rice husk, coconut shell etc. are preferred because of their low cost, availability at ease and good adsorption capability towards Cr (VI) metal ions removal [15].

MATERIALS AND METHODS

Chemical Reagents: Chemicals used for preparing chromium solution and analyzing chromium metal content in the solution were of analytical grade and purchased from Merck and Rankem, India.

Corresponding Author: Hemant Kumar, Department of Chemical Engineering, SOET, ITM University, Gwalior, M.P., India.

Preparation of Adsorbent: Biowaste adsorbents used for chromium metal ion removal were taken as Neem and Sheesham saw dust, taken from local market. Adsorbents were washed properly with hot distilled water to remove adhering dirt and dried in oven at 80°C. Then adsorbents were chemically activated with sulfuric acid at 150°C and then soaked in Sodium bicarbonate solution overnight to remove extra acid. Activated adsorbent thus obtained for kept in air tight containers for further use.

Determination of Chromium Content: Residual chromium in the aqueous solution was determined with the help of UV Visible Spectrophotometer by colorimetric method at 540nm.

Experimental: Stock solution of chromium (VI) was prepared by adding 2.826 g of $K_2Cr_2O_7$ in 1 liter of deionized water and subsequent solution of desired concentrations were prepared by diluting the stock solution. In the present work adsorption experiment was performed batch wise by taking known amount of chromium concentration (mg/L) in 250 ml conical glass mixed with fixed amount of adsorbent (g/L). Solution mixture was stirrer in shaking incubator at 150 rpm and 38°C. At definite time intervals, 5 ml of sample from solution mixture was taken, filtered and tested for residual concentration of chromium by colorimetric method in UV Visible Spectrophotometer.

Adsorption of Chromium Ion (mg) per unit gram of adsorbent and adsorption efficiency in percent can be calculated as per the following equations [16]:

$$q = \frac{(C_o - C_e)}{M} * V$$

$$E = \frac{(C_o - C_e)}{C_e} * 100$$

where, unit of adsorbent loading, q is mg of chromium adsorbed per gram of adsorbent. C_o and C_e are Initial and Equilibrium chromium concentrations in mg/L. V is the volume of solution in liter. M is mass of adsorbent in gram and E is Sorption Efficiency.

RESULTS AND DISCUSSIONS

Performance Evaluation of Adsorbents for Cr (VI) Removal: To e valuate the comparative performance i.e. Cr (VI) percent removal and loading capacity, two different adsorbents viz., Neem Sawdust and Sheesham Sawdust were used. Experiments were performed by keeping constant values of parameters like initial Cr (VI) metal ions of 50 mg/L, adsorbent dose of 4 g/L and shaking speed of 120 rpm. Results shown in Figure 1 and Figure 2 are percent removal of Chromium Ions and uptake capacity for two adsorbents for 50 mg/L initial chromium ions in the solution. At 311K Chromium percent removal for Neem and Sheesham sawdust are 85 and 19 % respectively. Analysis of results shows high uptake capacity of Neem sawdust (10.71 mg/g) at 311K temperature as compared to Sheesham (3.64 mg/g) when compared at 50 mg/L of initial Cr concentration.

These results indicate that Neem Sawdust has better capability of Chromium removal at 311K compared to Sheesham Sawdust adsorbents.

Effect of Contact Time on Adsorption: Percent removal of Cr (VI) at Equilibrium versus initial chromium (VI) concentration for 380 min contact time is shown in Figure 3. It was observed from figure that the percentage removal of chromium for 30 mg/L and 100 mg/L first increases up to 175 min and then become almost constant as the time proceeds further. The initial faster rate for chromium ions removal was because of the availability of more number of active sites, which were progressively occupied by the chromium ions as time progressed [17].

Effect of Initial Chromium metal ion Concentration: Percent removal of Cr (VI) with respect to Initial concentration of Chromium ions (mg/L) is shown in Figure 4. It is observed from the figure that percent removal of chromium increases as initial chromium concentration increases from 90.41 to 98.53 % as concentration of chromium in the solution increases from 30 mg/L to 100 mg/L respectively. According to Figure 3 Chromium metal uptake q_e at 30 mg/L and 100 mg/L initial Cr (VI) concentration are found to be 7.19 and 24.63 mg/g respectively. This phenomenon can be explained by considering the fact that higher initial adsorbate concentration provides higher driving force to overcome mass transfer resistance of the metal ions from the aqueous to the solid phase.

Biosorption Isotherms: The equilibrium of adsorption of heavy metal chromium ion Cr (VI) on Neem sawdust is modeled using two isothermal adsorption models viz. Langmuir and Freundlich isotherms.

The Freundlich adsorption model is the most extensively used mathematical model in aqueous systems. Equation written below is a nonlinear sorption model.

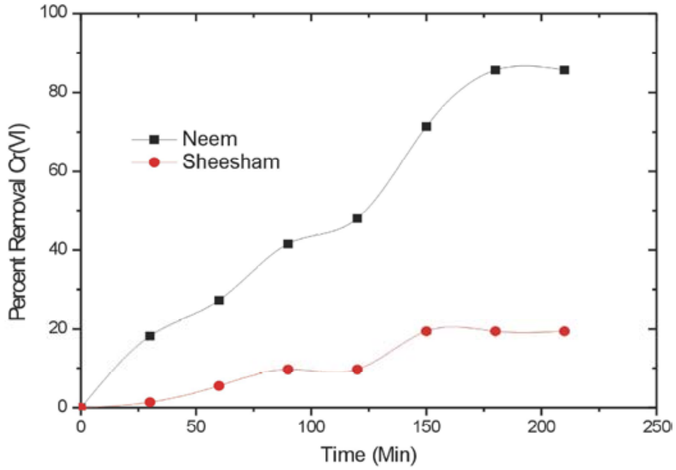

Fig. 1: Percent Removal of Chromium Ions on Neem and Sheesham Sawdust at 50 mg/L of Initial Chromium Concentration

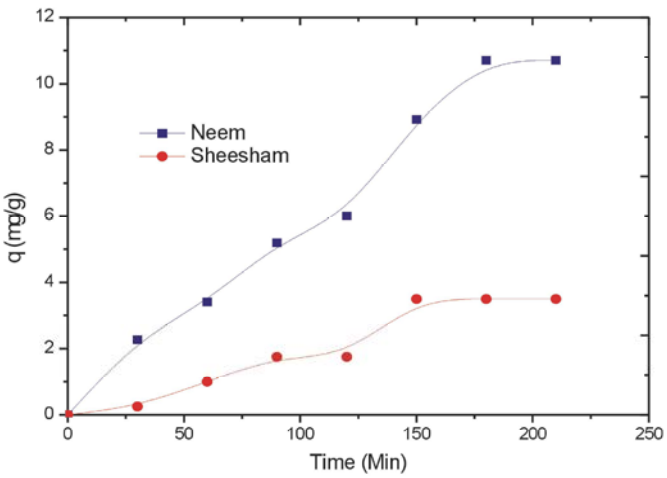

Fig. 2: Comparison of uptake capacity q (mg/g) between Neem and Sheesham Sawdust

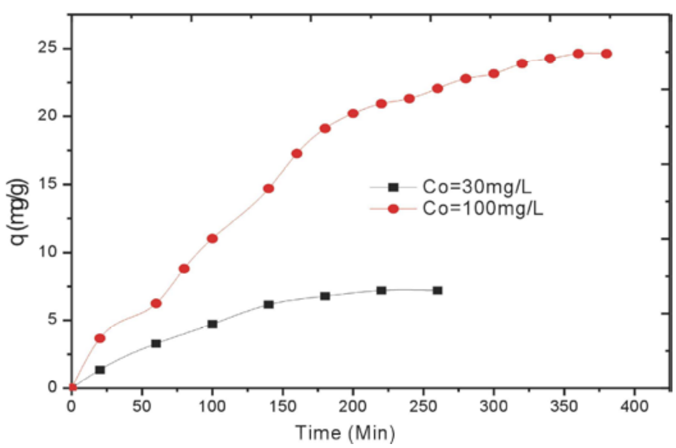

Fig. 3: Effect of contact time on chromium (VI) metal ion removal

$$q_e = K_f C_e^{1/n}$$

where, K_f is Adsorption capacity (mg/g), n is Adsorption intensity. C_e is Equilibrium chromium concentration and q_e = chromium uptake on dry adsorbent (mg/g).

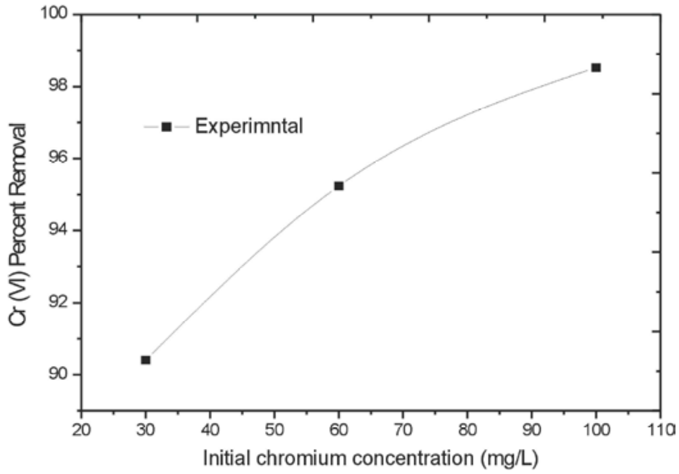

Fig. 4: Effect of Initial Chromium metal ion Concentration

Table 1: Linear regression data for Langmuir and Freundlich isotherms for chromium (VI) Biosorption

	Freundlich			Langmuir		
Parameters	K_f (L/mg)	1/n	R^2	q_{max} (mg/g)	b (L/mg)	R^2
Values	0.355756	0.4316	0.991	114.03599	0.0026716	0.961

Freundlich model offers a monolayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules.

The logarithmic form is:

$$\ln q_e = \ln K_f + \frac{1}{n} C_e$$

The Langmuir model predicts the maximum chromium uptake q_{max} and represents one of the first theoretical treatments of nonlinear sorption and suggests that chromium uptake occurs on a homogeneous surface by monolayer sorption, where no interaction between adsorbed molecules takes place. In addition, the model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbate. The Langmuir isotherm is written according to following equation:

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e}$$

where q_{max} (mg/g) and b are Langmuir constants related to adsorption capacity and the energy of Biosorption, respectively.

The adsorption data obtained for chromium metal ions adsorption onto the Neem sawdust used as Biosorbents in the present analysis were modeled. Values of the Freundlich constants (K_f, 1/n) and Langmuir constants (q_{max} b) are listed in Table 1. In the present work Neem sawdust was found to have the maximum metal uptake capacity of 24.63 mg/g at 100 mg/L of initial chromium concentration when compared to Sheesham sawdust. Model prediction shows that the R^2 value is more in Freundlich isotherm compared to Langmuir isotherm. In the Langmuir model, the linear plot of $1/q_e$ vs. $1/c_e$ give a straight line for Neem sawdust ($R^2 = 0.961$) with slope $1/q_m b$ and intercept $1/q_m$. For Freundlich model, the linear plot of log q_e vs log c_e give a straight line ($R^2 = 0.991$) with slope (1/n) and intercept log K_f. The present study of model fitting concludes that Freundlich isotherm model fits best to the sorption data of chromium (VI).

CONCLUSION

The aim of this work was to find out the adsorption characteristics of bio-waste materials for the removal of Cr (VI) ions. Effect of contact time on loading capability shows that most of the adsorption takes place in first 175 minutes, chromium uptake capacity increased with increase in initial chromium concentration in the aqueous mixture [18-21]. The Freundlich and Langmuir Biosorption models were used for the mathematical description of the Biosorption equilibrium of Cr (VI) ions to Biosorbents. The Biosorption equilibrium data fitted well to the Freundlich isotherm ($R^2 = 0.991$). The sorption capacities obtained as 7.19, 14.28 and 24.63 mg/L at 30, 60 and

100 mg/L of initial Cr (VI) concentration respectively. Neem sawdust (NS) presented the low cost and higher adsorption capacities for the Chromium ions as compared to Sheesham sawdust.

REFERENCES

1. Barrera-Díaz, C.E., V. Lugo-Lugo and B. Bilyeau, 2012. A Review of chemical, electro chemical and biological methods for aqueous Cr (VI) reduction. Journal of Hazardeous Material, 223-224: 1-12.
2. Geleel, M.A., S.T. Atwa and A.K. Sakr, 2013. Removal of Cr (III) from aqueous waste using Spent Activated Clay, Journal of American Society, 9(2): 256-262.
3. Madhavi, V., A.V.B. Reddy, K.G. Reddy, G. Madhavi and T.N.V.K.V. Prasad, 2013.An Overview on Research Trends in Remediation of Chromium, Research Journal of Recent Sciences, 2(1): 71-83.
4. McGrath, S.P. and S. Smith, 1990. Heavy metals in soil. John Wiley and Sons, New York, pp: 125-147.
5. Beszedits, S., 1988. Chromium removal from industrial wastewaters, John Wiley, New York, pp: 232-263.
6. Pedersen, N.B., 1982. The effects of chromium on the skin. Biological and environmental aspects of chromium, Amsterdam, Elsevier Biomedical Press, pp: 249-275.
7. Sarin, V. and K.K. Pant, 2006. Removal of chromium from industrial waste by using eucalyptus bark. Bioresource Technology, 97: 15-20.
8. Kim, D., J. Om and C. Kim, 2012. Hexavalent chromium reduction by water soluble anti-oxidants. Chemical Sciences Journal, pp: 88.
9. Dong, X., L.Q. Ma and Y. Li, 2011.Characteristics and Mechanisms of hexavalent chromium removal by biochar from sugar beet tailing. Journal of hazardous Materials, 190(1-3): 909-915.
10. Garg, U.K., M.P. Kaur, V.K. Garg and D. Sud, 2007. Removal of hexavalent chromium from aqueous solution using agriculture waste biomass. Journal of Hazardous Materials, 140: 1-2.
11. Selvi, K., S. Pattabhi and K. Kadirvelu, 2001. Removal of Cr (VI) from aqueous solution by adsorption onto activated carbon. Bioresource Technology, 80: 87-89.
12. Ahalya, N., R.D. Kanamadi and T.V. Ramachandra, 2010. Removal of hexavalent chromium using coffee husk. Int. J. Environment and Pollution, 43: 106-116.
13. Chakravathi, A.K., S.B. Chowadary, S. Chakrabarty, T. Chakrabarty and D.C. Mukherjee, 1995. Liquid membrane multiple emulsion process of chromium (VI) separation from waste waters. Colloids and Surfaces A, 103: 59-71.
14. Aksu, Z., D. Ozer, H.I. Ekiz., T. Kutsal and A. Calar, 1996. Investigation of biosorption of chromium (VI) on Cladophora crispata in two-staged batch reactor. Environmental Technology, 17: 215-220.
15. Kumar, R., N.R. Bishnoi, Garima and K. Bishnoi, 2008. Biosorption of Cr (VI) from aqueous solution and electro plating wastewater using fungal biomass, Chemical Engineering Journal, 135(3): 202-208.
16. Pilli, S.R., V.V. Goud and K. Mohanty, 2010. Biosorption of Cr (VI) from aqueous solutions onto Hydrilla verticillata weed. Equilibrium, Kinetics and Thermodynamic Studies. Environmental Engineering and Management Journal, 9(1): 1715-1726.
17. Mohanty, K., M. Jha and B.C. and M.N. Biswas, 2005. Removal of chromium (VI) from dilute aqueous solutions by activated carbon developed from Terminalia arjuna nuts activated with zinc chloride. Chemical Engineering Science, 60(11): 3049-3059.
18. Abbas, M.M.A., M. Farooq and Z. Ilyas, 2010. Removal of chromium (III) ions from aqueous solution by natural clays. Middle-East Journal of Scientific Research, 6(4): 377-381.
19. Hossein Berenjeian Tabrizi, Ali Abbasi and Hajar Jahadian Sarvestani, 2013. Comparing the Static and Dynamic Balances and Their Relationship with the Anthropometrical Characteristics in the Athletes of Selected Sports, Middle-East Journal of Scientific Research, 15(2): 216-221.
20. Anatoliy Viktorovich Molodchik, 2013. Leadership Development: A Case of a Russian Business School, Middle-East Journal of Scientific Research, 15(2): 222-228.
21. Meruert Kylyshbaevna Bissenova and Ermek Talantuly Nurmaganbet, The Notion of Guilt and Problems of Legislative Regulations of its Forms: The Notion of Guilt in the Criminal Law of Kazakstan, Middle-East Journal of S cientific Research, 15(2): 229-236.