Application of dried leaves for the removal of Cadmium from aqueous solution

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Abstract

Water contamination due to heavy metals is associated with various industrial activities. Cadmium enters into the water bodies due to these activities, gets accumulated into organisms and thus is of prime concern. In the present study, we used powdered neem leaves (Azadirachta indica) as a non-conventional biosorbent for the removal of Cd (II). Batch experiments were conducted to study the adsorption of Cd (II) onto powdered neem leaves. The batch experiments were conducted to optimize pH, equilibrium time, adsorbent dose and metalion concentration. Process followed Langmuir isotherm model. The adsorption process obeyed pseudo-second-order reaction. The experiment showed that powdered neem leaves are effective and has a good potential for the removal of Cd (II) from aqueous solution.

Keywords: Adsorption; *Azadirachta indica*; Biosorbent; Cadmium; Isotherms

INTRODUCTION

Environmental contamination due to heavy metals from anthropogenic sources is one of the major areas of concern. Various industries *viz*., power generation, manufacturing, mining etc. significantly contribute to water pollution. Heavy metals forms metal-organic complexes in living organisms and eventually increase their concentration in biological cycles (Rashad et al., 2012). The effluents containing higher concentrations of heavy metals if left untreated contaminate both surface and sub-surface waters. Cadmium is well known for its harmful environmental impacts (Igwe and Abia, 2007), has gained significance due to its persistence and subsequent toxicity in the ecosystem. Sources of cadmium in the environment largely include fertilizers and pesticides, cadmium batteries, smelting processes, electroplating and extensive mining activities. (Othman et al., 2011) Cadmium being toxic, it can be mutagenic, and carcinogenic in nature. Several methods, like precipitation, coagulation/flocculation, chemical reduction, ion exchange, electrodialysis, reverse osmosis, filtration, etc. are used for treating the waste water. However, due to capital investments and operating costs these methods are not used popularly. Adsorption is a physical technique used for the removal of toxic metals and is well established due to its simple usage and availability of wide range of adsorbents.

Adsorbent's affinity towards adsorbate is a function of electrostatic, net dispersion, and functional group interaction (Sharma and Bhattacharyya, 2005 b). Adsorption may result either from the universal van der Waals interactions like physisorption or from chemical processes like chemisorption, but the later occurs only as monolayer (Dabrowski, 2001). Scientists are progressively exploring different adsorbent which are non-conventional and economical. Biosorption involves a two phase system, having a solid phase (dead/live biomass/adsorbent) and a liquid phase (solution/adsorbate) containing metal ions (Das et al., 2008).Adsorption isotherm represents the absorbable solutes distribution between the liquid and adsorbed phase at several equilibrium concentrations (Ng et al., 2002).Sorption of pollutantsfrom the contaminated aqueous solution plays a significant role in treatment of wastewaters. Thus, the study of adsorption kinetics in waste water decontamination process is important as it governs the reaction pathways and the sorption reaction mechanisms (Ho and McKay, 1999a).

Many cost-effective / non-conventional materials have been used as biosorbent for the removal of cadmium and other heavy metals *viz*., sugar beet pulp (Reddad et al., 2002; Pehlivan et al., 2008), coffee residues (Boonamnuayvitaya et al.,2004), neem leaves (Sharma and Bhattacharyya, 2005a), wheat bran (Singh et al., 2006), maize husk (Igwe and Abia, 2007), fruit wastes (Schiewer and Patil, 2008), vegetable biomass (Salem and Allia, 2008), agricultural waste (Othman et al., 2011).Neem leaves has been explored as a low cost potential adsorbent for metal removal (Sharma and Bhattacharyya, 2005a; Sharma and Bhattacharyya, 2005c; Pandhareet al., 2013, Malik et al., 2014, Sulaiman and Garba, 2014). In the present study we used powdered neem leaves as a low cost easily available adsorbent for the removal of Cd (II) from aqueous solutions. Results obtained were fitted intopseudo-first and pseudo-second order equations, and adsorption isotherm models, *viz*., Freundlich and Langmuir. The adsorption characteristics were studied under different batch experiments evaluating the effect of contact time, initial Cd (II) concentration and dosage of adsorbent.

MATERIALS AND METHODS

All the chemicals used in experiments were of analytical grade. A stock solution was prepared by dissolving 1,000 mg of cadmium nitrate (Merck) in one liter of double distilled water. The stock solution was diluted and used for different concentrations of cadmium ions required for the experiments.

Preparation of powdered neem leaves

Fresh neem leaves were collected from local gardens and washed thoroughly using deionized water and dried under shade and then in microwave for about 10 min in a LG make domestic microwave oven having temperature range 40–80^{0} C. The leaves were then grinded, sieved and allowed to dry under room conditions. The dried powder was stored in plastic bottles for further use.

Batch experiments

Batch experiments were conducted under room temperature and after that the adsorbent was separated from the solution by filtration with whatman filter paper number 41 followed by centrifugation at 3,000 rpm for 10 min. The residual metal ions were analyzed using an atomic adsorption spectrophotometer(GBC Avanta). Adsorption data obtained were applied for testing the applicability of different isotherms equations. Blank samples were also run under similar conditions. Each of the studies was conducted in triplicates and the mean value was used for calculations. Amount of metal adsorbed, qe was calculated by the following equation

$$qe=\frac{(Ci-Ce)V}{W}$$

Where Ci is the initial concentration (mg/l), Ce is the equilibrium concentration (mg/l), V represents the volume (L) of the adsorbate and W represents the adsorbent mass (g).

RESULTS AND DISCUSSION

Effect of pH

pH is one of the most important factor affecting metal adsorption onto adsorbent, as hydrogen ions compete with the adsorbate (Prasanna Kumar et al. 2007). Studies were conducted by using 100 mg/l metal ion concentration and 1 g of adsorbent for 75 minutes at room temperature. The pH of the solutions was adjusted to the desired value by adding 0.1 M HClor0.1 M NaOH solution. The effect of pH (range 2–7) on adsorption of Cd (II) ions is shown in Fig. 1. Adsorption for all the different concentrations of Cd (II) increased with increase in pH and reached a maximum 91.2 % at pH 6.It may be due to the fact that active adsorption sites remain protonated at low pH, and become less available for metal ion adsorption. Optimum pH was found to be 6 and used for further experiments. At higher pH cadmium hydroxide starts precipitating from the solution. Results confirm the adsorption is pH-dependent (Pavasant et al. 2006).

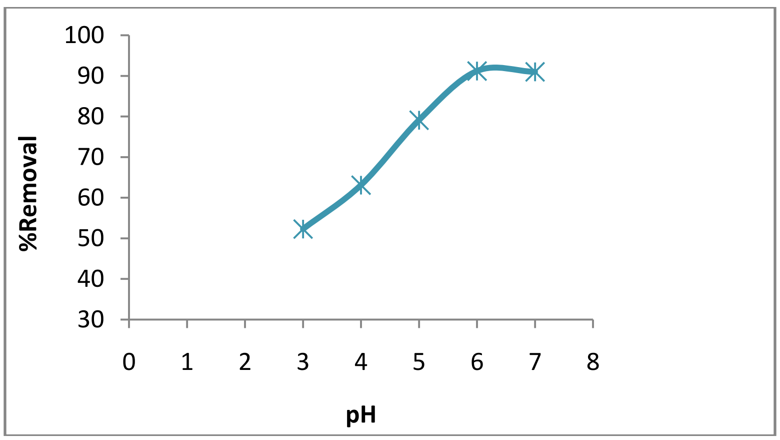

Figure: 1 Effect of pH

Effect of contact time and initial metal ion concentration

Contact time highly influenced the adsorption rate of Cd (II). Removal was fast (80.4%) initially due to higher concentration of Cd (II) ions in 15 min and reached the peak at 60 min (91.3%).Changes were not significant beyond 75 min (Figure 1).

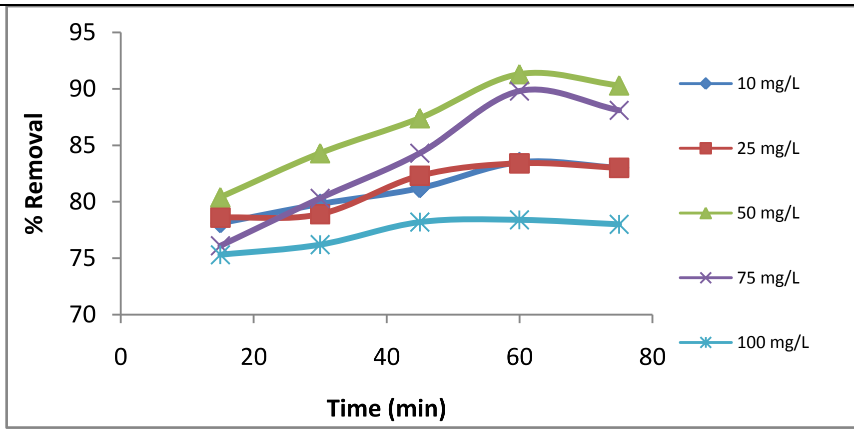

Figure: 2Effect of contact time & initial metal ion concentration

The rate of adsorption is controlled by the concentration gradient between the liquid layer surrounding the adsorbent particles and the active sites available for binding Cd (II). Thus, after equilibrium only lesser number of active sites participated in metal ions adsorption (Anirudhan, 2013) and the uptake rate was governed by the rate of transport of ions from the outer to the inner sites of adsorbent.

The effect of initial concentration was determined by taking the equilibrium time 60 min and equilibrium dosage of adsorbent 1 g under varying Cd(II) concentrations 15-100 mg/l. The Cd(II) adsorption was highest (91.2.6%) which gradually decreased to 87.2% at 200 mg/l of Cd(II)(Figure 2). Increased initial concentration results in significant decrease in removal because at lower concentrations, higher numbers of unsaturated sites are present on the adsorbent surface, and adsorption kinetics is dependent on the adsorbent's surface area. Further, higher metal concentrations adversely affect the adsorption because the moles of available ions on the surface of adsorbent remain high (Tangjuank et al., 2009) and eventually these binding sites become saturated (Gupta and Babu, 2009; Raju et al., 2012) thus leading to reduced adsorption.

Effect of adsorbent dosage

The amount of Cd (II) removed from the solution increased with increase in powdered neem leaves dosage (0.2 g to 1.5 g). No significant increase in adsorption was recorded with further addition of adsorbent (Figure 3). With adsorbent dosage the percentage removal of Cd (II) increased from 87.8% to 91.4%. The increased adsorption in the present case is due to the increase in the available sites for Cd (II). This is due to the fact that, at a given concentration, if the dose of adsorbent increases, the uptake of metal gradually lowers as lesser number of Cd (II) ions are available to bind (Shukla et al., 2002; Anirudhan, 2011).

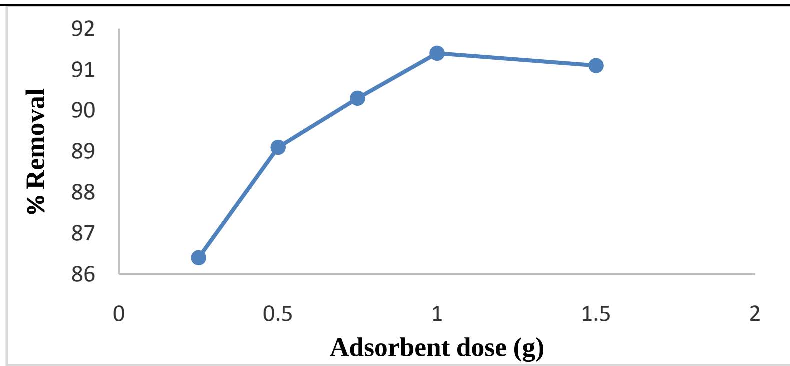

Figure: 3 Effect of adsorbent dose

Kinetics of adsorption

The kinetics of Cd (II) adsorption was studied using pseudo-first and pseudo-second order equations.

The general form of pseudo-first order is expressed as

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (1)$$

q_e and q_t are amount of metal ion (mg/g) at time t and at equilibrium respectively. k_1 is the rate constant of pseudo first-order adsorption. Integrated form of equation is

$$\frac{q_t}{q_e} = 1 - e^{(-k_1 t)} \quad \textbf{Or} \quad \log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (2)$$

The pseudo-second-order kinetic expression was developed by (Lagergren, 1898) to describe the biosorption of metal ions. The pseudo second order model (Ho and McKay, 1999) is based on sorption capacity of solid phase.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (3)$$

Where k_2 is rate constant of pseudo second-order adsorption. Integrated linear form of equation is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (4)$$

The applicability of the above two models were examined by each linear plot of *ln* (qe-q) vs. t, and (t/q_t) *vs*. t, respectively. The validity of the kinetic models is tested by the magnitude of the regression coefficient R^2. The kinetics of interaction was studied by taking a definite amount of adsorbent 1 g and 100 mg /l of Cd (II) under varying contact times 15-75 minutes.

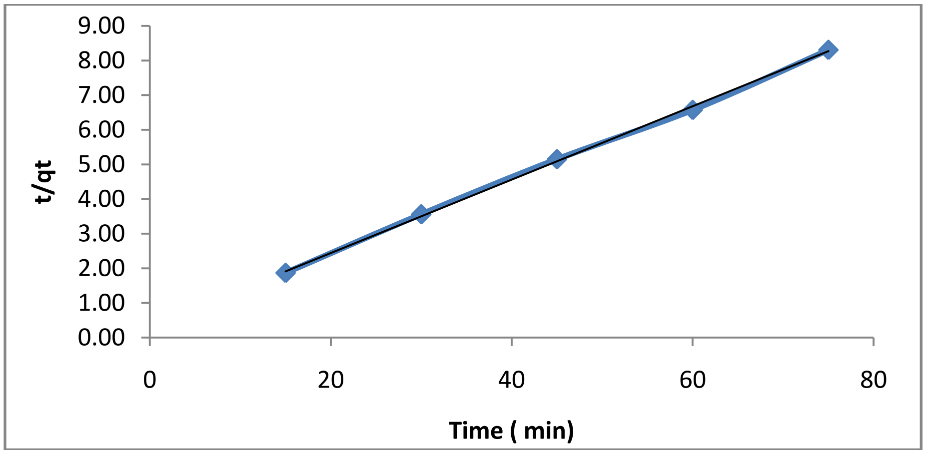

Figure: 5 Pseudo second order kinetics plot

The adsorption process in the current study can be best explained by pseudo-second order equation (Figure 5) with high regression value R^2.999. Here chemisorption played significant role by involving covalent forces during the sharing of electrons (Robati,2013) between adsorbent and the Cd (II) ions. Thus, in pseudo-second order kinetics, chemisorption is the rate controlling / limiting step, where the removal from a solution is due to physico-chemical interactions between two phases (Wang et al., 2007).

Adsorption isotherms

The adsorption process can be best understood by considering its behaviour with different isotherm models. The Langmuir model (Langmuir 1916) is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane. The Langmuir isotherm is given by

$$\frac{1}{Q_e} = \frac{1}{qbC_e} + \frac{1}{q} \qquad (5)$$

Q_e = Cd(II) ions concentration at equilibrium (mg /g),

q = maximum metal uptake per unit mass of adsorbent adsorption capacity

b = Langmuir constant (L) related to energy of sorption

C_e = Concentration of Cd (II) ions in aqueous phase

The Freundlich isotherm model (Freundlich 1906) is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved.

Freundlich isotherm: $Q_e = KC_e^{1/n}$ (9)

K= Freundlich constant indicating the adsorption capacity

n= Freundlich constant, indicating the adsorption intensity

The above equation is rearranged in linear form to give:

$\log Q_e = \log K + 1/n \log C_e$ (10)

Freundlich constants K and n, were calculated from the intercept and slope of the plot of log Qe versus log *C*e.

The Langmuir correlation coefficient (R^2) was very high 0.999, thus, in the present study Langmuir isotherm is suitable with maximum adsorption capacity qe is 86.923mg/g. R_L was found to be 0.010 from this value it is confirmed that powdered neem leaves are favourable biosorbent for Cd (II) ions.

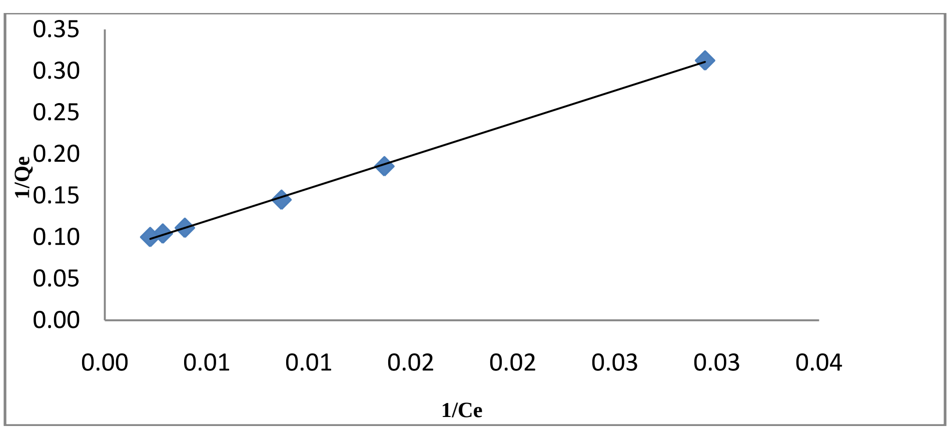

Figure: 6 Langmuir isotherm model

CONCLUSION

The powdered neem leaves can be effectively used for the removal of Cd (II) ions. The adsorption process is influenced by factors *viz*., pH, contact time, Cd (II) concentration and adsorbent dosage. Thus, it is prerequisite to attain desired conditions for maximum efficiency prior to its application for Cd (II) powdered neem leaves decontamination from waste water at large scale. The adsorption process was best fitted with the pseudo second order kinetic equation and Freundlich isotherm model. Use of *Azadirachta indica* for removing Cd(II)from waste waters is economically viable, eco-friendly and a sustainable approach.

REFERENCES

1. Anirudhan, T.S., 2011. Adsorptive characteristics of chromium (VI) ions from aqueous phase by iron (III)coordinated Amino-Functionalized Poly(glycidyl methacrylate)-Grafted Cellulose: EquilibriumKinetics and Thermodynamics study. Sep. Sci. Technol. 46(9), 1430–1442.
2. Anirudhan, T.S., 2013. Adsorptive removal of mercury(II) ions from water and wastewater by Polymerized Tamarind Fruit Shell. Sep. Sci. Technol. 43(13), 3522–3544.
3. Babu, B.V., Gupta, S., 2008. Adsorption of Cr(VI) using activated neem leaves. Adsorption 14, 85–92.
4. Boonamnuayvitaya, V., Chaiya, C., Tanthapanichakoon, W., Tarudilokkul, S., 2004. Removal of heavy metals by adsorbent prepared from pyrolyzed coffee residue and clay. Sep. Purif. Technol. 35, 11–12.
5. Dabrowski, A., 2001. Adsorption – from theory to practice Adv. Colloid. Int. Sci. 93, 135–224.
6. Das, N., Vimala, R., Karthika, P., 2008. Biosorption of heavy metals-an overview. Indian J. Biotechnol. 7,159–169.
7. Gupta, S., Babu, B.V., 2009. Utilization of waste product (tamarind seeds) for removal of Cr(VI) fromaqueous solutions: Equilibrium, kinetics, and regeneration studies. J. Environ. Manage. 90, 3013–3022.
8. Ho, Y.S., McKay, G., 1999a. Pseudo-second order model for sorption processes. Process Biochem. 34, 451–465.
9. Igwe, J.C., Abia, A.A., 2007. Equilibrium sorption isotherm studies of Cd(II), Pb(II), and Zn(II) ions detoxification from waste water using unmodified and EDTA-modified maize husk. Electron. J.Biotechnol. 10 (4), 536–548.
10. Lagergren, S., 1898. Zurtheorie der sogenannten adsorption gelˆsterstoffe, KungligaSvenskaVetenskapsakademiens. Handlingar 24(4), 1–39.
11. Malik, R., Lata, S., Singhal, S., 2014. Neem leaf utilization for copper and zinc ions removal from aqueoussolution. Int. J. Sci. Res. 3(5), 695–705.
12. Ng, C., Loss, J.N., Marshall, W.E., Rao, R.M., 2002 Freundlich adsorption isotherms of agricultural byproduct-based powdered activated carbons in a geosmin-water system Biores. Technol. 85(2), 132–135.
13. Othman, Z.A.A., Hashem, A., Habila, M.A., 2011. Kinetic, equilibrium and thermodynamic studies ofcadmium(II) adsorption by modified agricultural wastes. Molecules 16, 10443–10456.

14. Pandhare, G.G., Trivedi, N., Pathrabe, R., Dawande, D., 2013. Adsorption of cadmium(II) and lead(II) from astock solution using neem leaves powder as a low-cost adsorbent. Int. J. Innov. Res. Sci. 2(10), 5752–5761.
15. Pasavant, P., Apiratikul, R., Sungkhum, V., Suthiparinyanont, P., Wattanachira, S., Marhaba, T.F., 2006.Biosorption of Cu^{2+}, Cd^{2+}, Pb^{2+}, and Zn^{2+} using dried marine green macroalga *Caulerpalentillifera.*Biores. Technol. 97, 2321–2329.
16. Pehlivan, E., Yanik, B.H., Ahmetli, G., Pehlivan, M., 2008. Equilibrium isotherm studies for the uptake of cadmium and lead ions onto sugar beet pulp. Biores. Technol. 99, 3520–3527.
17. Prasanna Kumar Y, King P, Prasad VSRK (2007) Adsorption of zinc from aqueous solution using marine green algae-Ulva fasciata sp. Chem Eng J 129:161–166

18. Rashad, M., Selim, E.M., Asaad, F.F., 2012. Removal of some environmental pollutants from aqueoussolutions by linde-zeolite: adsorption and kinetic study. Adv. Environ. Biol. 6(5), 1716–1724.
19. Reddad, Z., Gerente, C., Andres, Y., Cloirec, P.L., 2002. Adsorption of several metal ions onto a low-costbiosorbent: kinetic and equilibrium studies. Env. Sci. Technol 36(9), 2067–2073.
20. Robati, D., 2013. Pseudo-second-order kinetic equations for modelling adsorption systems for removal of leadions using multi-walled carbon nanotube. J. Nanostructure Chem. 3(1), 1–6
21. Schiewer, S., Patil, S.B., 2008. Pectin-rich fruit wastes as biosorbents for heavy metal removal: equilibriumand kinetics. Biores, Technol. 99, 1896–1903.

22. Sharma, A., Bhattacharyya, K.G., 2005a. Adsorption of chromium (VI) on *Azadirachta indica*(Neem) leafpowder. Adsorption 10, 327–338.

23. Sharma, A., Bharttacharyya, K.G., 2005b. *Azadirachta indica* (Neem) leaf powder as biosorbents for removal of Cd(II) from aqueous medium. J. Hazard. Mater. B. 125, 102–112.

24. Sharma, A., Bhattacharyya, K.G., 2005c. Utilization of biosorbents based on *Azadirachta indica*(Neem)leaves for removal of water-soluble dyes. Ind. J. Chem. Technol. 12, 285–295.

25. Shukla, A., Zhang, T.H., Dubey, P., Margrave, J.L., Shukla, S.S., 2002. The role of sawdust in the removal of unwanted materials from water J. Hazard. Mater. B. 95, 137–152.

26. Singh, K.K., Singh, A.K., Hasan, S.H., 2006. Low cost bio-sorbent 'wheat bran' for the removal of cadmium from waste water: Kinetic and equilibrium studies. Biores. Technol. 97, 994–1001

27. Sulaiman, M.S., Garba, M.D., 2014. Biosorption of Cu(ii) ions from aqueous solution using *Azadirachta indica*(Neem) leaf powder. Chem. Process. Eng. Res. 27, 1–11.

28. Wang, H., Zhou, A., Peng, F., Yu, H., Yang, J., 2007 Mechanism study on adsorption of acidified multi walled carbon nano tubes to Pb (II). J. Colloid. Interface. Sci. 316, 277–283.