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Removal of heavy metal ions from aqueous solutions using chemically (Na_2S) treated granular activated carbon as an adsorbent

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Removal of Cd(II), Pb(II), Hg(II), Mn(II), Ni(II) and Zn(II) by chemically (Na_2S) treated granular activated carbon (GAC) has been found to be concentration, pH, contact time, adsorbent dose and temperature dependent. Adsorption isotherm studies indicated that adsorptive behaviour of metal ions on chemically treated GAC satisfies Langmuir assumptions. Proposed method had potential application for effluent treatment in industries.

Keywords: Adsorbent, Adsorption, Granular activated carbon (GAC), Metal ions, Wastewater

Introduction

Presence of highly toxic heavy metals and synthetic chemicals in ground water, surface water, drinking water and aqueous effluents has impact on human and aquatic life[1]. Wastewaters with heavy metals originate from a large number of industries[2]. In view of toxicity and to meet regulatory safe discharge standards, wastewaters/ effluents need be made free from heavy metals before release into environment. Among a large number of technologies, carbon adsorption is considered the best available technology for eliminating non-biodegradable and toxic organic compounds from aqueous solution.

This study presents feasibility of chemically (Na_2S) treated granular activated carbon (GAC) for maximum removal of heavy metal ions from aqueous solutions with optimized process parameters (initial concentration, adsorbent dose, contact time, temperature and pH).

Experimental Section

Instrumentation

GBC 932 AA atomic adsorption spectrometer (AAS) operating with an air acetylene flame was used to analyze concentration of heavy metals. Three standard solutions with concentrations of copper in linear range of instrument were used to construct each calibration curve. Samples having concentration of heavy metals beyond linear range of references were diluted to appropriate concentrations. All measurements were repeated three times and results with standard deviations above 0.1 mg/l were not accepted. pH measurements were performed with a controlled pH analyser (LABINDIA). pH meter was standardized using buffer solutions (pH values: 4, 7, 9). Micromeritics (ASAP 2010 make) surface area analyzer and a mechanical shaker (WIDSONS SCIENTIFIC make) was used for all adsorption experiments for agitating sample for a desired contact time.

Chemicals

Analytical grade reagents were used for heavy metal solution, ACS reagent grade concentrated nitric acid, NaOH and pH buffer solutions (E. Merck) were used to adjusted pH values of samples. In all experimental work, distilled demineralised water was used.

Adsorbate Solution

Synthetic stock solutions of heavy metals were prepared by dissolving required quantity of Analar grade salts in distilled demineralised water. Stock solution was further diluted with distilled demineralised water to desired concentration for obtaining test solutions.

Adsorbent

Preparation of Treated GAC

Coconut based GAC (99.5 g) was immersed for 24 h in minimum quantity of distilled water containing Na_2S

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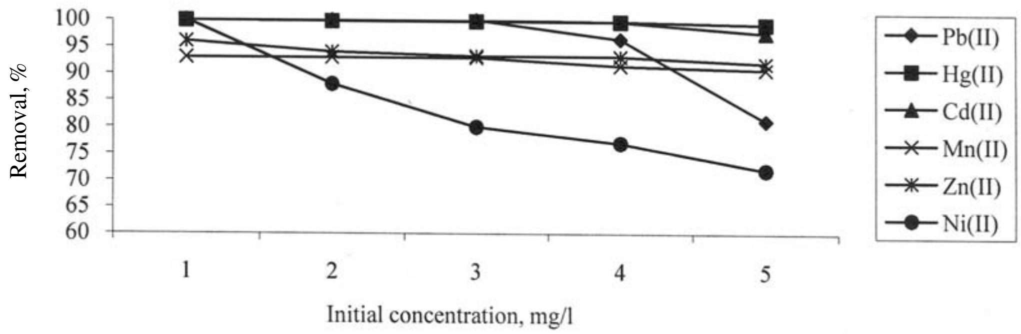

Fig. 1—Effect of initial concentration on % removal of heavy metal ions by treated GAC (adsorbent dose, 1g/100ml; contact time, 48 h)

(0.5 g). Mixture was heated almost to dryness and then dried in an oven for 4 h at 110°C. Dried sample was washed with distilled water several times till it gave negative test for sulphide. Washed sample was again dried at 110°C for 4 h and stored in a dessicator for use. Coconut shell based GAC (ACG-50), procured from Active Carbon Ltd., Hyderabad, India, had physico-chemical characteristics of carbon as follows: pH, alkaline; conductivity, 102 μscm^{-1}; salanity, 0; bulk density, 0.48 g/ml; moisture, 4%; BET surface area, 1200 m^2/g; iodine number, 950; $CCl_{4,}$ 50%; hydrogen number, 95%; ash content, 9.0%; particle size, 8-20 mesh. Element analysis of GAC, performed with an elemenatar analyse system GmbH, gave following values: C, 66.0; H, 3.5; N, 0.331; O, 29.1; and S, 0.58% (by wt). Other values were: carboxylic functional groups, 0.105 meq/gCA; lactonic functional group, 0.003 meq/gCA; and phenolic functional group, 0.006 meq/gCA.

Batch Mode Adsorption Studies

Effect of several parameters (pH, concentrations, contact time and adsorbent dose) on adsorption of heavy metals on chemically treated GAC was studied by batch technique. pH of adsorptive solutions was adjusted using HNO_3, NaOH and buffer solutions. Adsorption of copper on walls of glass flasks, determined by running blank experiments, was found negligible. Results were used to get optimum conditions for maximum heavy metals removal from aqueous solution.

Results and Discussion

Effect of Initial Concentration of Heavy Metal

At constant adsorbent dose (1 g/100 ml) and a contact time (48 h), removal (%) of heavy metals by chemically treated GAC (Fig. 1) decreased with increase in initial heavy metal concentration. For Hg (II), removal was almost complete (100%) throughout initial concentration (1-5 mg/l). For Cd (II) and Pb (II), there was slight drop in removal at higher initial concentration, whereas for Ni (II), removal was highly effective up to 1 mg/l initial concentration, after which removal decreased gradually to below 75%. At higher initial concentrations, Mn (II) and Zn (II) showed greater removal than Ni (II). Therefore, fractional adsorption was independent of initial concentration. However, at higher concentrations, numbers of heavy metal ions were relatively higher compared to availability of adsorption sites. Hence removal (%) of heavy metals depended on initial concentration.

Effect of Adsorbent Dose

At constant initial concentration (3 mg/l) and a contact time (48 h), removal of Hg (II) ions with respect to adsorbent dose was 100% (Fig. 2). There was a sharp increase in removal with adsorbent dose for Mn (II), Zn (II), Cd (II), and Pb (II) ions. There was slight and gradual increase in removal with increasing dose of Ni (II) ions. Removal (%) of heavy metals increased rapidly with increase in adsorbent dose due to greater availability of exchangeable sites or surface area.

Effect of Contact Time

At constant adsorbent dose (1 g/100 ml) and initial concentration (3 mg/l), removal for Hg (II) ions using chemically treated GAC (1 g) for varying initial concentration (1-5 mg/l) was nearly 100% (Fig. 3) for all contact times. In cases of Cd (II), Pb (II) and Hg (II) ions, removal was nearly 100% for all contact times, with increasing removal efficiencies at higher contact time. In case of Ni (II) ions, sharp rise in removal with

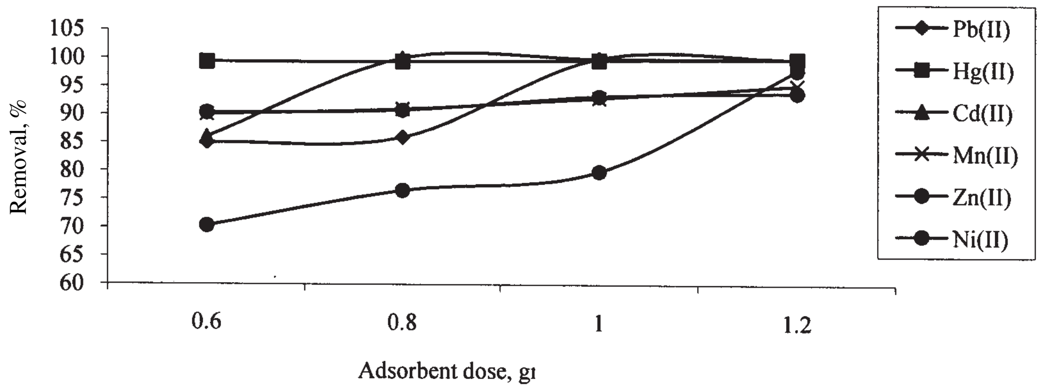

Fig. 2—Effect of adsorbent dosage on % removal of heavy metal ions by treated GAC (contact time, 48 h; initial concentration, 3 mg/l)

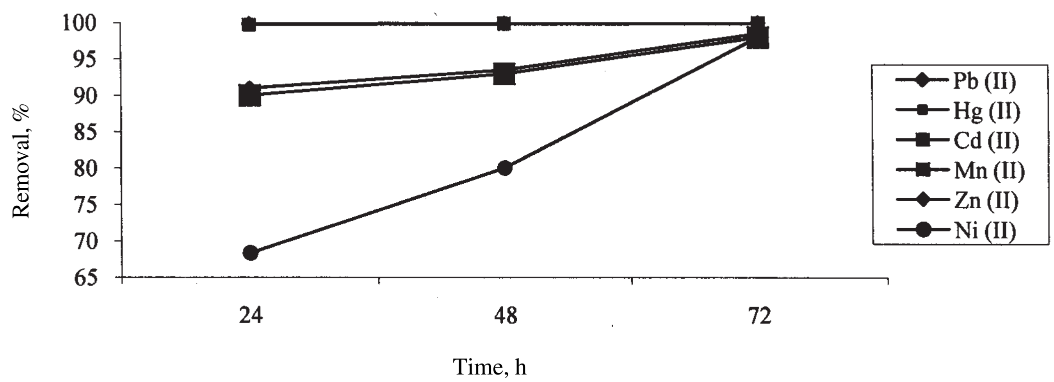

Fig. 3—Effect of contact time on % removal of heavy metals by treated GAC (adsorbent dose, 1 g/100 ml; initial concentration, 3 mg/l)

increasing contact time was observed. Removal of Mn (II) and Zn (II) increased gradually with contact time, reaching nearly 99% at 72 h. Optimum contact time to attain equilibrium with chemically treated GAC was found to be 48 h.

Effect of pH

Effect of pH on heavy metals removal efficiencies of treated GAC was studied (Fig. 4) at a constant initial concentration (3 mg/l), adsorbent dose (1g/100 ml solution) and agitation period (48 h). Adsorption (%) increased with pH to attain a maximum at pH 4-8 and thereafter it decreased with further increase in pH. Maximum removal at pH 4 was found for: Hg (II), 99.9; Mn (II), 98.5; and Cd (II), 99.9%. Whereas, at pH 8, maximum removal was found for: Pb (II), 99.9; Ni (II), 80; and Zn (II), 93.3%.

Presence of dominant metal ion M(II) species at pH >6.0 is $M(OH)_2$ and at pH< 6.0 is M^{2+} and $M(OH)^+$. Increase in metal ion adsorption >pH 6.0 for sulphurised carbon may be due to retention of $M(OH)_2$ species in micropores of carbon particles. Maximum sorption efficiency at pH 4.0-6.0 for sulphurised carbon may be due to interaction of metal ion or $M(OH)^+$ with surface sulphur groups present in sulphurised carbon. During acid-base reaction, hard acids prefer to coordinate with hard base and soft acids to soft acids and as a rule interaction of metal ion or M $(OH)^+$ with surface sulphur groups (soft bases) is likely to favour at pH 4.0-6.0. Sites responsible for adsorption process are not exclusively due to sulphur groups; other sites on carbon surface can also contribute to adsorption process. At low pH, particularly below pH of zero point charge, positively charged metal ion (M^{2+}) or $M(OH)^+$ species present in solution may exchange with H^+ from – COOH groups of carbon.

Increases in metal removal with increased pH can be explained on the basis of a decrease in competition between proton and metal cations for same functional

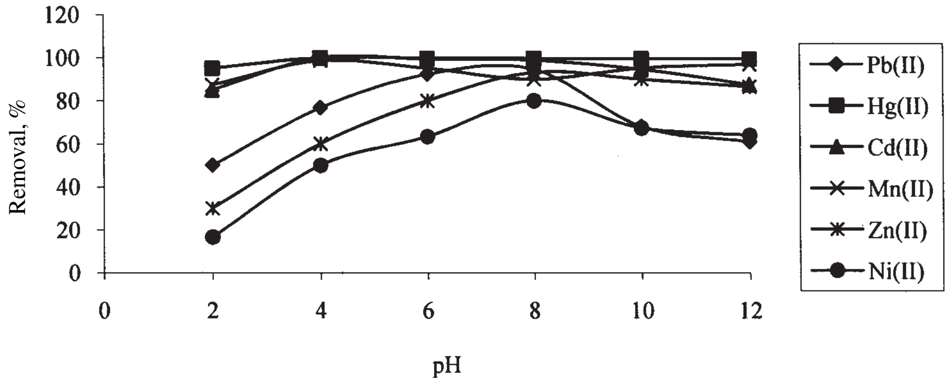

Fig. 4—Effect of pH on % removal of heavy metal ions by treated GAC (initial concentration, 3mg/l; adsorbent dose, 1 g /100ml; contact time, 48 h)

groups and by decrease in positive surface charge, which results in a lower electrostatic repulsion between surface and metal ions. Decrease in adsorption at higher pH (> pH 6) is due to formation of soluble hydroxy complexes[3].

Effect of Temperature

Metal ions adsorption (initial concentration, 3 mg/l; pH, 6-8) has been found to increase with an increase in temperature from 20 to 60°C. Increase in adsorption capacity of chemically treated GAC with temperature indicates an endothermic process. At higher temperature, possibility of diffusion of solute within pores of adsorbent may not be ruled out. Results were further substantiated by thermodynamic parameters [free energy (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°)] determined as

$$K_c = C_{Ac}/ C_e \quad \ldots(1)$$

where, K_c is equilibrium constant, C_{Ac} and C_e are equilibrium concentration (mg/g) of metal ion on adsorbent and in solution respectively. Free energy change (ΔG°) was calculated as

$$\Delta G = -RT \ln K_c \quad \ldots(2)$$

where, T is temperature (K) and R is gas constant ($8.314 * 10^{-3}$ KJ/ mol K).

Enthalpy change (ΔH°) was calculated as

$$\Delta G = \Delta H - T\Delta S \quad \ldots(3)$$

$$\log K_c = \Delta S/2.303R - \Delta H/2.303RT \quad \ldots(4)$$

ΔH° and ΔS° were obtained from slope and intercept of Vant Hoff plots[4,5] of log K_c Vs 1/T. Positive values of ΔH° thermodynamically substantiate assumption that adsorption of metal ions on chemically treated GAC is endothermic. Negative values of ΔG° indicate feasibility and spontaneous nature of adsorption of metal ions on adsorbent. ΔS° is estimated to be very small in experimental conditions. Therefore, entropic change occurring from adsorption is thought to be negligible.

Adsorption Kinetics

Kinetic constants of metal adsorption, which could be used to optimize residence time of an industrial wastewater chemically treated GAC, were computed using experimental data[5,6]. Adsorption kinetics of heavy metal ion adsorption on chemically treated GAC follows first order rate expression[7] as

$$\text{Log}_{10}(q_e - q) = \log_{10} q_e - K_{ad}\, t/ 2.303 \quad \ldots(5)$$

$$Q_e = (C_0 - C_e)\, V/m \quad \ldots(6)$$

where, K_{ad} (1/ h) is rate constant of adsorbent, q and q_e are amounts of heavy metal ions adsorbed (mg/l) at time t (h) and equilibrium time, respectively.

Initial adsorption kinetic coefficient, γ (1/mg h) was computed [7] as

$$\gamma = (dC/dt)_{t-0}\, V/ mC_0 \quad \ldots(7)$$

where t is time (h), C is metal ion concentration at time (t), V is solution volume (l), m is chemically treated GAC weight (mg), C_0 is initial concentration (mg/l).

Adsorption Isotherms

Equilibrium data obtained were analyzed using Freundlich[8] and Langmuir[9] isotherms as

Freundlich equation, $x/m = K\, C_e^{1/n}$ …(8)

Langmuir equation, $x/m = (1/ab)\,(1/C_{e)} + 1/a$ …(9)

where, *x/m* is amount of heavy metal ions adsorbed per unit mass of adsorbent in mg/g, C_e is equilibrium concentration of heavy metal ions in mg/l, K_e and *n* are Freundlich constants, *a* is a Langmuir constant and measure of adsorption capacity in mg/g, and *b* is also Langmuir constant and a measure of energy of adsorption in l/mg. *a* and *b* were calculated from slope and intercept of plots from Eqs (8) and (9).

Adsorption capacity (*a*) was maximum for chemically treated GAC as follows: Pb(II), 464.5; Hg(II), 377; Cd (II), 320; Zn(II), 4.58; Ni(II), 2.58; and Mn(II), 1.27 mg/g. Energies of adsorption (*b*) were highest for: Mn(II), 1.02; Zn(II), 0.61; Ni(II), 0.45; Cd(II), 0.41; Hg(II), 0.36; and Pb(II), 0.31 l/mg. A comparison of Freundlich adsorption isotherms for metal ions showed that *n* is in the order: Pb(II) >Cd (II) > Hg(II) >Ni(II) > Zn(II) and Mn(II). Values of n (1-10) indicated favourable adsorption[10]. K_e seen to be: Ni(II) > Pb(II) > Mn(II) >Cd(II) > Hg(II) and Zn(II). This gives a similar inference as that obtained from Langmuir isotherms. On the basis of regression analysis of experimental data on adsorptive behavior of metal ions on chemically treated GAC, it may be inferred that adsorption behavior of metal ions on chemically treated GAC was in good agreement with Langmuir model.

Conclusions

Chemically treated GAC showed nearly 100% adsorptive removal of heavy metal ions under optimized conditions (dosage, 1 g/100 ml; metal ions conc., 3 mg/l; contact time, 48 h). Langmuir model was found to be in good agreement with experimental data on adsorptive behaviour of cadmium on mustard husk, and chemically treated GAC followed both Freundlich and Langmuir models. Adsorption followed first order kinetics. pH was found to be a most effective variable, controlling adsorption of metal ions on chemically treated GAC surface. Experimental studies would be quite useful in developing an appropriate technology for removal of heavy metal ions from contaminated industrial effluents.

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References

1 Meena A K, Studies on treatment of contaminated water containing heavy metals in Jaipur & Pali, Ph D Thesis, University of Rajasthan, Jaipur, 2005.

2 Namasivayam C & Periasamy K, Bicarbonate treated peanut hull carbon for the removal of Hg(II) from aqueous solution, *Water Res*, **27** (1993) 1663-1668.

3 Meena A K, Mishra G K, Kumar S, Rajagopal C & Nagar P N, Adsorption of Ni (II) and Zn (II) from aqueous solution by chemically treated activated carbon, in *Nat Conf on carbon (Indo – carbon 2003)* (DMSRDE, Kanpur) 2003, 31-140.

4 Meena A K, Kadirvelu K, Mishra G K, Rajagopal C & Nagar P N, Adsorptive removal of heavy metals from aqueous solution by treated sawdust (*Acacia arabica*), *J Haz Mater*, **150** (2008) 604-611.

5 Ansari K R & Omidvari R, Adsorption of mercuric ion from aqueous solutions using activated carbon, *Polish J Environ Stud*, **14** (2005) 185-188.

6 Corupcioglu M O & Huang C P, The adsorption of heavy metals onto hydrous activated carbon, *J Water Res*, *21* (1987) 1031-1036.

7 Lagergren B & Svenka V P, Sorption of Cr(VI) from dilute solutions and wastewater by live and pretreated biomass of *Aspergillus flavus*, *Environ Poly*, **9** (1973) 525.

8 Freundlich H & Heller W, Rubber die adsorption in lusungen, *J Am Chem Soc*, **61** (1939) 2228-2230.

9 Langmuir, The adsorption of gases on plane surface of glass, mica and platinum, *J Am Chem Soc*, **40** (1918) 1361-1403.

10 Hall K R, Eagleton L C, Acrivos A & Vermeulen T, Pore and solid diffusion kinetics in fixed bed adsorption under constant pattern conditions, *Ind Eng Chem Fund*, **5** (1966) 212-223.