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RESEARCH ARTICLE

2-HBAOT: AN EXCELLENT RESIN ADSORBENT FOR CADMIUM ABETMENT FROM CONTAMINATED WATER

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ABSTRACT

Out of known 104 naturally occurring elements some are very useful, rather essential for human life, while a few others inclusive of cadmium are toxic and dangerous. Cadmium is mainly used in the industries for coating steel, glass, plastics etc. and also for the production of Ni-Cd battery and automotive tyres. Cadmium is much dangerous due to its long half life and it can exert toxic effects on almost all systems of the human body. The intake of cadmium depends on its concentration in natural sources such as air, land and water and should not exceed 20 mg per day. Cadmium would also be shown to be associated with occurrence of Itai-Itai, a kind of disease, under which patient shows a wide range of symptoms such as low grade of bone mineralization, high rate of fractures, increase rate of asteoporosis and intense bone associated pain. In the present investigation, attempt has been made to study the applicability of Terpolymer Resin derived from 2-Hydroxybenzaldehyde (2-HBA), Oxamide (O) and Trioxane (T) as a potential metal adsorbent to remove Cadmium from aqueous solution (contaminated water). A direct proportionality between the percentage of divalent Cadmium removal and adsorbent doses was noted. Maximum removal of Cd(II) was achieved at pH ranges of 6.5 – 9 for this adsorbent. The optimum temperature of 308 K for efficient removal of Cd (II) was observed. The effect of anions like SO_4^{2-}, Cl^-, NO^{3-} and ClO_4^- on divalent Cadmium adsorption has also been investigated. The adsorption isotherm data have been confirmed to Freundlich and Langmuir isotherms. Kinetic studies indicated pseudo second order kinetics. Thus the terpolymer resin (2-HBAOT) under present investigation is found to be successful for the removal of toxic Cadmium from aqueous solution (contaminated water).

INTRODUCTION

It is well known that some metals can have toxic or harmful effects on many forms of the life (KaYrabulut, 2000). Metals which are significantly toxic to human beings and ecological environments, include chromium, copper, lead, mercury, cadmium, nickel and iron, (Bowen, 1979) etc. This problem has received considerable attention in recent years. These heavy metals are toxic to aquatic flora and fauna even in relatively low concentration. Some of these are capable of being assimilated, stored and concentrated by organisms (Yu 2000; Murley 1992). Cadmium is accumulated in the human body causing erythrocyte destruction, nausea, salivation, diarrhea, muscular cramps, renal degradation, chronic pulmonary problems and skeleton deformity (Kadrvelu 2003; Low 1998; Krishnan 2003). Cadmium contamination in drinking water can naturally occur from zinc, lead and copper ores through diffusion. But its main sources are industrial processes such as electroplating, smelting, alloy manufacturing, nickel-cadmium and solar battery production.

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According to the World Health Organization (WHO) guidelines, the permissible concentration of cadmium in drinking water is less than 1 μg/lit. Cadmiumions have little tendency to hydrolyze at Ph< 8 but at Ph> 11, all cadmium ion exists as the hydroxyl-complex (Corapcioglu, 1987).

Various treatment technologies have been developed for the purification of water and wastewater contaminated by heavy metals. The most commonly used methods for the removal of metal ions from industrial effluents include: chemical precipitation, solvent extraction, oxidation, reduction, dialysis/ electro dialysis, electrolytic extraction, reverse osmosis, ion-exchange, adsorption etc. Amongst all the purification methods adsorption is highly effective and economical. Though the use of commercial activated carbon is a well-known as an adsorbent for removal of heavy metals from water and wastewater, the high cost of activated carbon limits its use as an adsorbent in developing countries. Hence, it is a growing need to derive the activated carbon from cheaper and locally available waste materials. Several research workers used different low cost adsorbents obtained from agriculture wastes such as coconut coir pith, sawdust, rice husk, banana pith, cottonseed hulls, apple wastes, sugarcane bagasse pith, peanut hull, etc. for the removal of cadmium from water and wastewater (Marshell P, 1996). In spite of several researchers adopted various low cost adsorbents, there is still a need to develop suitable adsorbents for the removal of cadmium from aqueous solution. In the present investigation, studies have been carried out for the removal of cadmium from polluted (contaminated) water using polymeric Resin derived from 2-Hydroxybenzaldehyde, Oxamide and Trioxane. The terpolymer resin reported in this research paper has been abbreviated as 2-HBAOT.

MATERIALS AND METHODS

All the chemicals used were of analytical grade and obtained from E. Merck, Mumbai, India. Stock solution of cadmium was prepared using cadmium nitrate in deionsed water. Double distilled water or deionized water (DI) was used throughout the investigations. AR grade HCl and NaOH etc. were used in the experiments. A pH meter (Systronic made) was used for the pH measurements. Atomic absorption spectrophotometer (AAS) with cadmium hallow cathode lamp and air acetylene flame was use for determining cadmium concentration.

Synthesis and characterization of 2-HBAOT terpolymer

The 2-HBAOT terpolymer was synthesized by condensing 2-hydroxybenzadehyde, Oxamide and Trioxane in the molar ratio of 3:3:2. Hydrochloric acid (2M) was used as a catalyst. The reaction mixture was heated at 382 K in an electrically heated oil bath for about 5 h. Voltage regulator was applied to maintain constant temperature of the bath. The solid mass obtained was immediately removed from the flask as soon as the reaction was complete. The separated polymeric mass, having resinous texture, was washed repeatedly with DI hot water and dried. The dried mass was washed with petroleum either to remove the unreacted starting materials or 2-HBA-trioxane copolymer formed if any. The terpolymer was purified by dissolving it in 2·5 N sodium hydroxide solution and reprecipitating it by dropwise addition of 1:1 (v/v) hydrochloric acid/DI water. The purification by precipitation process was repeated twice. The resulting terpolymer sample was washed with boiling water several times, filtered and dried in vacuum at room temperature. The purified terpolymer was finally ground well to pass through a 300 mesh sieve and kept in vacuum over silica. The yield of terpolymer was found to be 70%. The purity of terpolymer was tested and confirmed by thin layer chromatography method. The terpolymer was characterized in light of studies such as IR and SEM analysis.

Adsorption studies

Working standards were prepared by progressive dilution of stock solution of cadmium salt. AR grade HCl, NaOH and buffer solution was used to adjust pH of the solutions. Removal of Cd(II) using 2-HBAOT was carried out by batch equilibration method. The influence of various parameters such as effect of pH, contact (agitation) time, adsorbent dose and initial metal ion concentration etc. were studied. For each experimental run, 100ml of waste water of known concentration of metal ion was taken in 250 ml stoppered polyethylene reagent bottles. pH was adjusted to the desired value and a known amount of the 2-HBAOT was introduced into the solutions. The bottles were agitated at temp. (308$\pm$ 1K) using a mechanical shaker for a prescribed time to attain equilibrium. At the end of the predetermined time intervals, the samples were taken out, solutions were separated from the 2-HBAOT by filtration using Whatman filter paper No. 41 and the final concentration of metal ions were determined in the filtrate by atomic absorption spectrophotometer. Blank solution was treated similarly (without adding 2-HBAOT) and the concentration was taken as initial concentration. The batch adsorption study was replicated twice to confirm the reproducible results. The experimental conditions are tabulated in Table 1.

Sorption isotherm models

The sorption equilibrium data of cadmium on 2-HBAOT was analyzed in terms of Freundlich and Langmuir isotherm model. Freundlich isotherm equation $X/m = K_F\ C_e^{1/n}$ can be written in the liner form as given below.

$$Log\ {}^{X}\!/_{m} = LcgK_F\ + {}^{1}\!/_{n}\ Log C_e$$

Where X/m and Ce are the equilibrium concentration of cadmium in the adsorbed and liquid phases in mg/g and mg/l respectively. K_F and n are the Freundlich constants that are related to the sorption capacity and intensity respectively. Freundlich constant K_F and n can be calculated from the slop and intercept of the linear plot with log(X/m) versus log Ce.

The Langmuir sorption isotherm equation ${}^{X}\!/_{m} = Q_m K_L C_e/(1 + K_L C_e)$ on linearization becomes

Table 1. Experimental conditions for batch adsorption studies for 2-HBAOT

S.No.	Optimization study	Constants	Variables
1	Agitation time	i) Metal ion conc.=70 mg dm^{-3} ii) Adsorbent weight=500mg per 0.1 mg dm^{-3} iii) pH=8$\pm$ 0.2	Time (min) 10,20,30,40 50 & 60 min
2	pH	i) Metal ion conc.=70 mg dm^{-3} ii) Adsorbent weight=500mg per 0.1 mg dm^{-3} iii) Agitation t time =60 min.	pH ranges from 3-10$\pm$ 0.2
3	Initial metal ion concentration	i) Adsorbent weight=500mg per 0.1 mg dm^{-3} ii) pH=8$\pm$ 0.2 iii) Agitation time =60 min.	Concentration of metal ions 60,50,40,30,20 mg dm^{-3}
4	Adsorbent weight	i) Metal ion conc.=70 mg dm^{-3} ii) pH=8$\pm$ 0.2 iii) Agitation t time =60 min.	Adsorbent weight 0.1,0.25,0.5,0.75,1.0,1.25 & 1.50 g per 0.1 dm^{-3}

$$\frac{Ce}{X/m} = \frac{Ce}{Q_m} + \frac{1}{Q_m\ K_L}$$

Where Q_m and K_L are Langmuir constants which are related to sorption capacity and energy of sorption respectively and can be calculated from the intercept and slope of the linear plot with C_e /(X/m) Vs C_e.

Kinetics

The kinetics of the interactions was studied by determining the amount of metal ions adsorbed at different agitation times for various concentrations of the metalions (20, 15, 10 and 5 mg dm^{-3}) and the optimum pH. Pseudo second order kinetics have been applied for the experimental data to predict the adsorption, which can be expressed as

$$t/q_t = 1/K_2 q^2{}_e + 1/q_e\, t.$$

Where K_2 is the rate const. K_2 and q_e can be obtained from the intercept and slope by plotting t/q_t versus t. The experimental results are tabulated in Table 2.

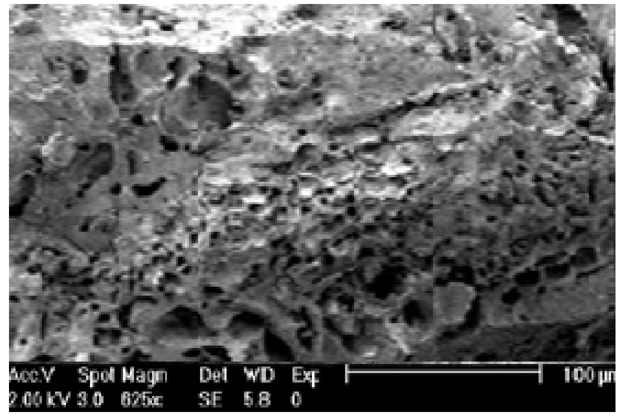

Fig. 2. Scanning electron micrographs of 2-HBAOT at 625 x

Effect of pH

The effect of pH on removal of Cd (II) by adsorbent was carried out in the pH range 3.0-10.0 ± 0.2 and the results are given in Table 3. It can be noted that the removal of Cd (II) ions increased with increasing pH of aqueous solution and reached maximum value at pH 9. It is evident that the2-HBAOT is effective for maximum removal of Cadmium over the pH range 6.5- 9. Studies were carried out up to pH 9. At the pH beyond 9 the tendency of metal ions to precipitate as metal hydroxide was predominant and hence further studies beyond pH 9 were not conducted.

Table 2. Adsorption kinetics for removal of Cadmium on to 2-HBAOT for pseudo second order kinetics

Meta lion	Concentration (mg/g)	q_e (Exp) mg/g	Kinetic parameters		
			K_2	R^2 x 10^{-4}	q_e(Theo.)(mg/g)
	60	20.45	0.130	9945	18.02
	50	18,89	0.172	9823	13.53
	40	10.32	0.281	9650	8.50
	30	5.20	0.390	9521	3.47

Table 3. Effect of pH on removal of Cadmium by2-HBAOT

% removal	60	63	65	69	85	91	95
pH	3	4	5	6	7	8	9

RESULT AND DISCUSSION

Characterization of the Adsorbent Material

FTIR (Fig.3) analysis was performed to examine the functional groups present on adsorbent material. FTIR spectrum of 2-HBAOT displays number of absorption peaks. The broad peak around 3300-3200 cm^{-1} is due to existence of hydroxyl group. The absorption peak at 1760 cm^{-1} represents the stretching band of carbon oxygen double bond of the carboxyl functional group. The peak around 1610 cm^{-1} may be assigned due to stretching of C=O bond.

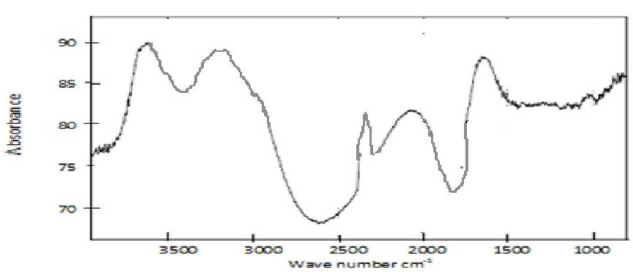

Fig. 1. IR Spectrum of 2-HBAOT terpolymer resin

The scanning electron microscopy of 2-HBAOT shows that the surface of the material was rough, uneven and with numerous gaps. The porous surface is indicative of high surface area (Fig. 2).

Effect of contact time on the removal cadmium by 2-HBAOT

Equilibrium time is considered as one of the important parameters for economical waste water treatment plant applications. The experimental results for removal of Cd(II) by the 2-HBAOT as a function of contact time at initial concentration of Cd^{+2} is 80 mg dm^{-3} is presented in Table 4. Equilibrium adsorption was established within 60 min for Cd (II). It could be seen that the removal was found to 95 % for Cd(II) at optimum pH conditions. According to these results the agitation time was fixed at 60 minute for rest of batch experiments to make sure that the equilibrium was reached in every experiment.

Table 4. Effect of contact time on the removal of cadmium by 2-HBAOT

Contact time (min)	10	20	30	40	50	60
% removal	52	63	67	80	91	95

Effect of Anions

The effect of ions like sulphate, nitrate, chloride, perchlorate, etc. on the adsorption of Cadmium (II) are tabulated in Table 5 .The inhibition on adsorption by monovalent Cl^- is less than that of divalent SO_4^{-2}. As can be expected, similar conclusion can be drawn for the effect of perchlorate, nitrate anions. The ionic or electrostatic attraction between sorbent and sorbet is the ordinate mechanism, but other mechanism at low and high pH would be responsible for adsorption.

Table 5. Evaluation of the effect of different electrolytes on the uptake of Cd(II) ion at 308 K

Concentration of Electrolyte mg./dm^3	Amount of Cd(II) adsorbed per g of 2-HBAOT (mg per g)			
	$NaClO_4$	NaCl	$NaNO_3$	Na_2SO_4
20	3.6	3.4	3.9	2.8
40	6.5	6.6	6.2	4.7
60	10.1	7.5	8.9	6.1
80	12.2	11.0	11.7	9.3

Adsorption Isotherms

The analysis of the isotherms data is important to develop an equation which accurately represent the results and could be used for designing purpose. The sorption data was analyzed in terms of Freundlich and Langmuir isotherms models. The fitted constants for Freundlich and Langmuir model along with regression coefficient are summarized in Table 6.

Table 6. Freundlich and Langmuir constants for Cadmium adsorbate

	Cadmium
Freundlich	
k_F	7.32
n	3.10
R^2	0.9945
Langmuir	
Q_m	16.45
k_L	0.55
R^2	0.9432

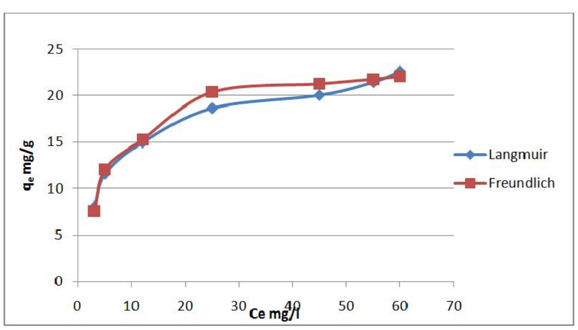

Fig.3. Adsorption isotherm of Cadmium

The Freundlich and Langmuir isotherms are shown in Fig. 3. As can be seen from isotherms and regression coefficients, the fit is better with Freundlich than Langmuir model. The essential characteristics of the Langmuir isotherms can be expressed in terms of dimensionless constant i.e. separation factor or equilibrium parameter R_L which is defined as

$$R_L - \frac{1}{(1 + K_L C_e)}$$

Conclusion

Removal of poisonous Cadmium from aqueous solution is possible using 2-HBAOT terpolymer resin which effectively removes more than 95 % of Cd(II) at 308 K. Adsorption of Cd (II) was highly pH-dependent and shown the optimum at pH 8 for the removal of Cadmium at which Cd(II) exists in the most easily adsorbable form. Increase in the dose of adsorbent, initial concentration of Cd (II) and contact time up to 1h, results in the increased percentage of removal of Cd(II). The adsorption data satisfactorily explained by Freundlich and Langmuir isotherms (Table 6). Sorption of Cd(II) follows pseudo second order kinetics. The values of R_L factor ranging from 0 to 1 indicate the favorable adsorption situation. Thus the newly generated 2-HBAOT has been proved to be an excellent adsorbent which can employed for removal of Cd (II) from polluted water. Thus it proves the practical applicability of the sorbent under investigation for control of cadmium pollution in contaminated water.

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