

Comparative studies on removal of Cadmium metal ions from effluents using Coconut Shell Coke and Commercial Activated Charcoal

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This study investigated the effect of various parameters on the removal of cadmium metal ions by adsorption using coconut shell coke (CSC) and commercial activated charcoal (CAC). The time of contact, initial metal ion concentration, adsorbent dosage, and volume of the adsorbate solution are the parameters studied. The adsorption isotherms so obtained in this study followed the Freundlich and Langmuir equations showing a marginal average deviation.

Keywords: Adsorption, Adsorbate, Adsorbent, Activated charcoal, Cadmium.

Introduction

Water is the elixir of life. It plays various roles like biological fluid, solvent, waste carrier, in short - it supports life itself. Availability of good clean water is diminishing day by day due to increased industrial activities. Purification and recycling of industrial wastewater have become imperative in view of reduced availability and deterioration of the quality of water. Water pollution is mainly due to the presence of organic materials such as proteins, fats, carbohydrates and other substances found in domestic and industrial waters and inorganic chemicals such as free chlorine, ammonia, hydrogen sulfide, salts of metals like Ag, Cd, Co, Cr, Cu, Fe, Ni, Zn etc. Most of them are toxic which cause potential health hazards and can be tolerated only at micro levels. Chemical precipitation, coagulation with alum or iron salts, membrane filtration, ion exchange, reverse osmosis and adsorption are some of the most commonly used methods for the treatment of metallic pollutants from wastewater. The present work is emphasized on removal of metallic ions by adsorption technique using coconut shell coke (CSC) and commercial activated charcoal (CAC). Several investigations (1-9) are reported in the literature on the treatment of metallic pollutants by adsorption technique. The present study envisages on investigating the effect of various parameters like time of contact, volume of sample, initial concentration, and amount of adsorbent on removal of cadmium ions using CSC and CAC. The adsorption isotherms are plotted for adsorption of cadmium verified for the validity with the Freundlich and Langmuir equations.

Experimental Procedure

The various steps involved in the experimental procedure are: (i) Preparation of coconut shell coke adsorbent (ii) Preparation of synthetic samples of CdSO₄ and (iii) Effective contact of the adsorbent with adsorbate for the removal of cadmium metal ions and analysis of the samples to estimate the percent removal.

Preparation of coconut shell coke (CSC)

The coconut shells are surface treated to remove all the fibers on its surface, broken into small pieces to allow insertion into a muffle furnace (KW=0.3, AMP=13,

Type-MFRA, Phase-single) and are subjected to destructive distillation. The temperature of the furnace is allowed to increase to a maximum of 400°C. The shells are left in the furnace for about 1 hr to avoid reactions with

atmospheric oxygen and thereby preventing the formation of ash, before they are cooled to the room temperature. The final material is crushed in a ball mill and then subjected to sieving to obtain samples of -7+8 mesh, -8+12 mesh, -12+14 mesh, -16+18 mesh and -30+36 mesh. Delignification is carried out for the coke and the treated adsorbent materials are dried in sunlight and stored in desiccators. The characteristics of coconut shell coke in comparison with commercially available activated charcoal are summarized in Table 1.

Table 1: Characteristics of coconut shell coke and activated charcoal

Characteristic	Activated Charcoal	Coconut shell coke
Bulk density, g/cc	0.49	0.68
Moisture, %	2.32	5.08
Ash, %	5.41	2.54
Decolorizing power, mg/g	89.00	58.00
B.E.T-Surface area, m ² /g	963.00	388.00
pH	7.20	6.20

Preparation of synthetic samples

Five samples of CdSO₄ Solution, concentrations ranging from 2.5ppm to 100ppm are prepared by dissolving known quantities of cadmium sulfate in distilled water.

Effective contact of the adsorbent with adsorbate in the removal of cadmium metal ions and analysis

The adsorbate (known volume) is allowed to be in contact continuously with adsorbent (known weight) for intervals ranging from 15mins to 8hrs with continuous shaking of the flasks in a rotary shaker. The clear liquid is then separated and analyzed using atomic absorption spectrophotometer (Perkin Elmer model-31101).

Results and discussions

All the experiments are carried out in batch wise by varying the contact time, the concentration of cadmium, and by varying the adsorbent dosage.

Effect of contact time

The effect of contact time is evaluated by keeping all other variables constant such as initial concentration of metal ion (C_i), adsorbent dosage (W), volume of the solution (V) (C_i=100ppm, W=5g, V= 50ml). The samples are collected at different time intervals varying from 15min to 480 min. They are analyzed for residual metal ion concentration. The variation of percent removal of cadmium with increase in the time of contact is plotted as shown in Figure 1. From the plot, it is observed that the percent adsorption of cadmium increased continuously up to 3hrs and thereafter no significant increase in percent adsorption is noticed. This asymptotic approach indicates that the state of equilibrium is attained after a contact time of 3hrs. Therefore this contact time of 3hrs is fixed for evaluating the effect of other variables in subsequent experiments

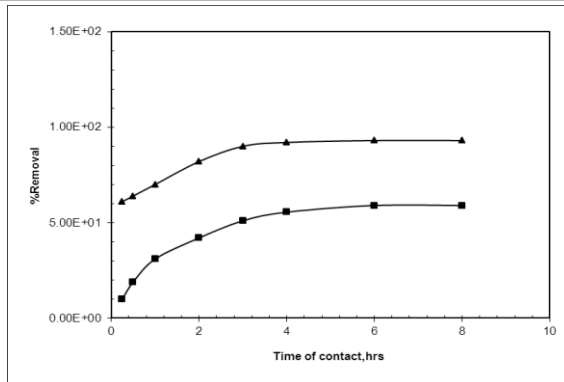


Figure 1: Effect of time of contact on % removal of cadmium on activated charcoal & Coconut shell coke.

Effect of initial concentration of metal ion

Figure 2 shows the variation of percent removal of metal ions with initial concentration. Keeping a contact time of 3hrs and varying the concentration of metal ions from 5ppm to 100ppm, it is observed that adsorption is greatly influenced by varying initial concentration and the rate of adsorption increases from (on CSC) and 90% to 97% (on CAC) for an increase in the initial concentration from 5ppm to 100ppm. With the increase in the initial concentration of metal ions in the solution, the amount of adsorption of cadmium on both adsorbents increased, and hence the increase in percent removal. However the adsorption of on CSC is found to be less compared to the adsorption on CAC, which might be due to less active sites on CSC.

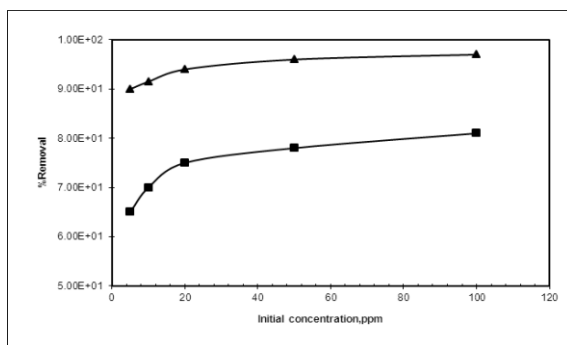


Figure 2: Effect of initial concentration on % removal of cadmium on activated charcoal & coconut shell coke.

Effect of adsorbent dosage

The variation in percent removal of metal ion with adsorbent dosage is shown in the Figures 3. The dosage of the adsorbent is varied from 7.41 to 28.57 wt%, the other parameters fixed at $t=3$ hrs, $C_i=20$ ppm, $V=50$ ml. The amount of adsorbent is a key factor as the adsorption mainly depends upon the surface area of the adsorbent available for the contact of pollutant at the interface. It is noticed that an increase in the adsorbent dosage, resulted in an increase in the amount of metal ion adsorbed. The percentage of adsorption increases from (on CSC), and from 92.8% to 94.5% (on CAC) for an adsorption dosage increases from 7.41 to 28.57 wt%. Seco et al., (2) reported the same observation on increase of activated carbon concentration. The effect of adsorbent dosage on metal adsorption for both adsorbents showed a similar trend, but exhibited slightly lower values of adsorption on CSC compared to CAC.

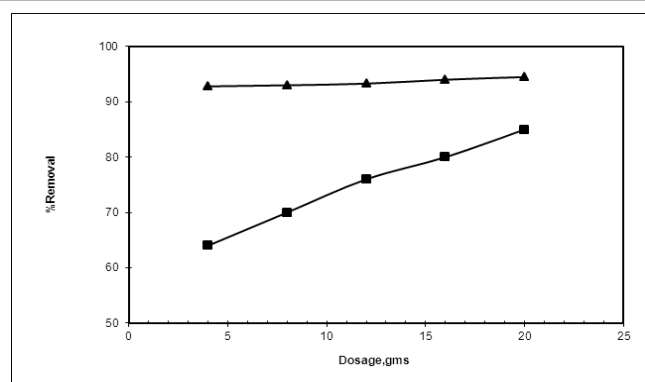


Figure 3: Effect of adsorbent dosage on % removal of cadmium on activated charcoal & Coconut shell coke.

Effect of volume of the solution

The effect of volume of the solution on adsorption of cadmium metal ion is studied keeping other conditions constant (i.e. $t=3$ hrs, $W=5$ grms, $C_i=20$ ppm). From the Figure 4, it was observed that the rate of adsorption decreases from (on CSC), 94.5% to 92.8% (on CAC), for an increase in the volume of solution from 50ml to 125ml. The percent removal of pollutants is seems to be marginal and hence it may require a combination of other treatment processes for treating the effluents at industrial level.

Adsorption equilibrium

The equilibrium between the concentration of the adsorbate in the fluid phase and the concentration of adsorbate held by a particular adsorbent is generally known as the isotherm for solute-adsorbent system at a given temperature. There are many equations, which represent equilibrium adsorption data. Of these, two are widely used viz., the Freundlich equation(10) and the Langmuir equation(11). Since the total adsorption cannot be measured, the relative or apparent adsorption of solute is determined instead

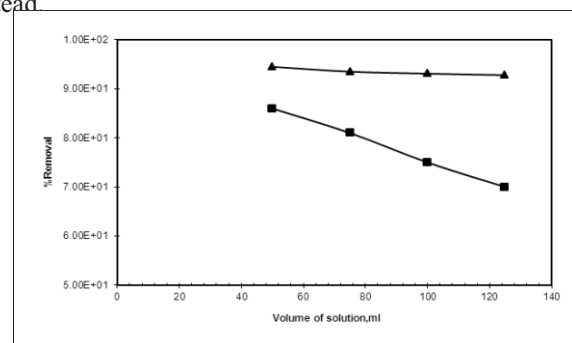


Figure 4: Effect of volume of solution on % removal of cadmium on activated charcoal & coconut shell coke.

The customary procedure is to treat a known volume of solution with a known weight of adsorbent, volume of solution/ mass of adsorbent. As a result of preferential adsorption of solute, the solute concentration is observed to fall from initial value (C_i) to a final equilibrium value (C_E), mass solute/volume liquid. The apparent adsorption of solute neglecting any volume change in the solution is then $V(C_i - C_E)$, mass solute adsorbed/mass adsorbent (q_E). This is satisfactory for dilute solutions when the fraction of original solvent, which can be adsorbed, is small.

The adsorption isotherms, over small concentration gradients, particularly for dilute solutions can be frequently given by an empirical expression by Freundlich as $q_E = K[C_E]^{1/n}$, where C_E is the equilibrium concentration and K and n are constants. The Langmuir equation is $q_E =$

($bCE/(1+aCE)$), where 'a' and 'b' are the Langmuir constants (7). This equation is theoretical but does not hold for many substances. It is applicable to chemisorption on active centers besides physical monolayer adsorption. The adsorption isotherms were plotted for adsorption of cadmium on both adsorbents, to verify whether they follow the Freundlich and Langmuir equations as shown in the Figures 5-6. The plots indicated a marginal average deviation of 5%. Gupta et al (5) reported the adsorption of zinc and copper on bagasse fly ash to be endothermic in nature and followed both Freundlich and Langmuir models. Rao and Bhole (8) correlated their data on removal of organic matter from dairy industry wastewater using low cost adsorbents with both Langmuir and Freundlich adsorption isotherm models. Sangita and Pal (7) computed the Langmuir adsorption isotherm for their experimental data of studies on adsorption characteristics of drug removal by activated charcoal. On regression analysis, the entire data covered in the present study is represented by the following equations:

Freundlich isotherm

On CSC	$q_E = 1.3328 (C_E)^{1.77}$
On CAC	$q_E = 1.726(C_E)^{0.6554}$

Langmuir isotherm

On CSC	$q_E = -0.258C_E/(1-0.069C_E)$
On CAC	$q_E = -0.118C_E/(1-0.708C_E)$

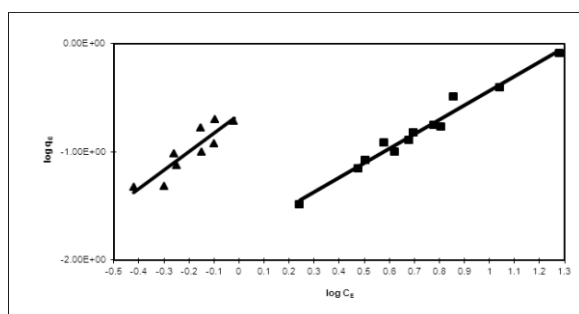


Figure 5: Freundlich isotherms for Cadmium adsorption on activated charcoal & Coconut shell coke

Figure 5: Freundlich isotherms for Cadmium adsorption on activated charcoal & Coconut shell coke

Activated carbon
Coconut shell coke

Figure 6: Langmuir isotherm for Cadmium adsorption on activated charcoal & Coconut shell coke.

Conclusions

The following conclusions were drawn from the present study: (1) the adsorption of cadmium was found to increase continuously with increase in time up to 3hrs and thereafter not much significant change was found with further increase in contact time. Hence, the time of contact is found to be optimum at 3hrs for adsorption of cadmium (2) with increase in initial concentration of cadmium metals in solution, the percent adsorption was found to increase for both the cases on CSC and CAC. (3) The increase in adsorbent dosage has resulted in an increase in the removal of metallic ions in both the cases. (4) With increase in the volume of the solution, the percent removal of the metallic ions was observed to decrease. From the experimental data, it

was concluded that the adsorption of metal ions was found to be more compare on CSC to that on CAC.

Nomenclature:

a = Langmuir constant
b = Langmuir constant
CE = Equilibrium adsorption concentration, mg/l
CI = Initial metal ion concentration, mg/l
K = Freundlich constant
n = Freundlich constant
qE = Amount adsorbed per unit weight of adsorbent at equilibrium, mg/gm
t = Time in hours/minutes
V = volume of solution, ml
W = Adsorbent dosage, gm

References:

1. Al Asesh et al., "Adsorption of heavy metals from industrial waste waters using plant material", Water quality Res. J can (1999).
2. Seco et al., "Study of adsorption of cadmium and zinc on to an activated carbon, Influence of pH, cation concentration and adsorbent concentration", Sep Science Technol (1999).
3. V. Ramachandran and T. J. D' Souza, "Adsorption of cadmium by Indian soils", Water, Air and Soil Pollution 111-225-234 (1999)
4. Irena Atanassova and N. Poushkarov, "Competitive effect of copper and nickel on Ion adsorption and desorption by soil clays", Water, Air and Soil Pollution 113-115-125 (1999)
5. Gupta et al., "Utilization of bagasse fly ash for the removal of copper and zinc from waste water", Sep Purif Technol, 18(2), 130-140(eng), Elsevier Science B.V (2000).
6. Benerjee et al., "Cadmium and Copper removal by a granular activated carbon in laboratory column systems", Sep Science Technol (2000).
7. Sangita Agarwal and T. K. Pal., "Studies on adsorption characteristics of drug removal by activated charcoal", Indian Chem. Engr., Section A., Vol. 43, No. 3 (2001).
8. M. Rao and A. G. Bhole, "Removal of organic matter from dairy industry waste water using low cost adsorbents", Indian Chem. Engr., Section A, Vol.44, No.1. (2002).
9. B. S. Inbaraj and N. Sulochana, "Basic dye adsorption on a low cost carbonaceous sorbent – kinetic and equilibrium studies", Indian Journal of Chemical Technology, Vol.9, pp. 201-208(2002).
10. H. Freundlich, "Colloid and Capillary chemistry", E. P. Dutton and Company, New York (1922).
11. I. Langmuir, "The adsorption of gases on plane surfaces of glass, mica and platinum", J. Am. Chem. Soc., 40,1361-1403 (1918).