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Removal of Cadmium from Wastewater Using Coal Fly Ash

KEYWORDS
Adsorption,coal fly ash, Cadmium,Freundlich and Langmuir Isotherm

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ABSTRACT *This paper deals with the utilization of coal fly ash as a low cost adsorbent for the removal of cadmium from wastewater. As much as 80% removal of cadmium is possible in about 5 hours under the batch test conditions. Effect of various operating variables, viz., solution pH, adsorbent dose, adsorbate concentration,temperature on the removal of cadmium has been studied. A dose of 10 g/L of adsorbent was sufficient for the optimum removal of metal ion. The material exhibits good adsorption capacity and the adsorption data follow the Langmuir model better then the Freundlich model. The adsorption of metal ion decreased with increasing temperature indicating exothermic nature of the adsorption process. Isotherms have been used to determine thermodynamic parameters of the process, viz., free energy change, enthalpy change and entropy change.*

Introduction

The presence of heavy metals in the aquatic environment has been of great concern due to their toxicity and non-biodegradable nature (1-3). Cadmium is toxic and relatively widespread in the environment (4). The metal is used in a wide variety of industries such as plating and cadmium–nickel battery, phosphate fertilizers, mining, pigments, stabilizers and alloys and finds its way to the aquatic environment through wastewater discharges. Therefore, a systematic study on the removal of cadmium from wastewater is of considerable significance from an environmental point of view. Fly ash is by- product from coal based thermal power plants. It has been found to be a better option in place of high cost adsorbents. Worldwide, more than 65% of fly ash produced from coal power stations is disposed of in landfills and ash ponds.

This study aims at investigating the utilization of fly ash as an adsorbent to remove cadmium ions from aqueous solution, such as wastewater. Fly ash is strong alkali material, and its pH value normally varied from 10 to 13 when added to water. Thereby, it can be expected that cadmium ions can be removed from aqueous solutions by adsorption [5]. Therefore, a number of studies were undertaken to verify the Influence of fly ash in the removal of heavy metal ions from aqueous solutions [6]. However, the results appeared to less comprehensive, and more practical factors should be chosen to test the effectiveness of fly ash to remove cadmium ions from aqueous solution.

In this paper, batch experiments were designed for the sorption process, and the effects of temperature, pH value, initial concentrations of cadmium ions and fly ash dosages on adsorption were evaluated. The optimum condition was also discussed for cadmium ion removal.

Experimental methodology

Chemicals and Instruments

Fly ash sample was collected from Unchahar Thermal Power Station ,Singrauli (MP).It was sieved, and the particle size less than 100 mesh was collected and dried at 105°C. Chemical composition of the ash is listed in Table 1.

All chemicals and reagents used were of analytical grade and were obtained from E. Merck, India. Stock solution of cadmium was prepared using cadmium nitrate in deionized water. A pH meter (Systronic) was used for pH measurements. X-ray measurements were made using a Phillips X-ray diffractometer employing nickel-filtered CuKa radiations. The surface area of the adsorbent was measured by a surface area analyser (Quantasorb Model QS-7). IR spectra of the samples were recorded on an infrared spectrophotometer (FTIR Perkin Elmer Model 1600).

Table-1. Chemical constituents of the fly ash

Constituents	%
SiO_2	61.10
Al_2O_3	25.02
C_aO	1.69
Fe_2O_3	6.92
MgO	0.53
Others	4.94
LOI	2.6

Adsorption studies

Batch adsorption experiments were carried out in a series of Erlenmeyer flasks of 100 ml capacity covered with Teflon sheets to prevent contamination. The effect of contact time (0–360 min), concentration (10.0-70.0 mg/L), solution pH (2.0–12.0), adsorbent dose (5.0-25.0 g /L), and temperature (303 K, 313 K, and 323 K) were studied. Isotherms were obtained by adsorbing different concentrations of metal ions after prescribed contact time, the solutions were filtered and the concentrations of metal ion were determined by atomic absorption spectrophotometer. The concentrations of metal ion were determined by atomic absorption spectrometer (Perkin Elmer Model 3110) using air acetylene flame.

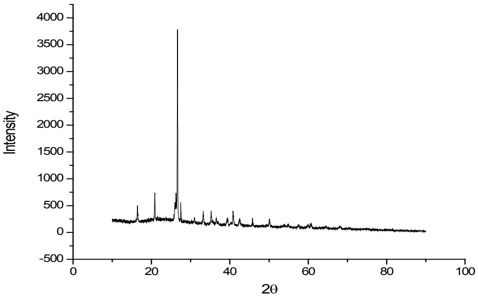
Results and discussion

Characteristics of Fly Ash

The x-ray diffraction pattern of fly ash sample was shown in Figure 1. It can be observed from the figure that fly ash consists mostly of Quartz, mullite,and Small amount of hematite and calcium oxide with large characteristic peaks of quartz (SiO_2).

The intensity of quartz is very strong with mullite forming a chemically stable and dense glossy surface layer. The low calcium oxide intensity is characteristic of low-Ca Class-F fly ash.

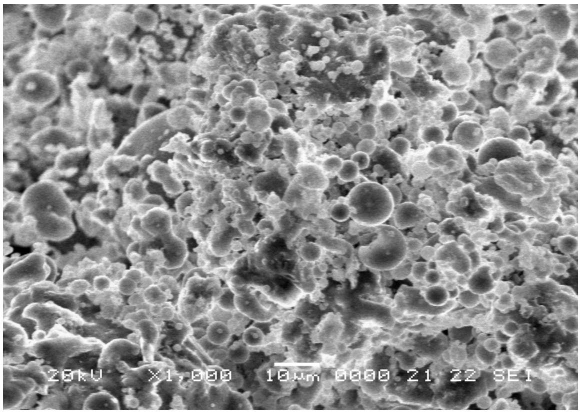
Figure 1: XRD Spectra of Fly ash



SEM Analysis:

SEM stands for scanning electron microscopy, which is used for studying the surface morphology of substances due to its high magnification imaging capability. The scanning electron micrograph is given in figure 2.The image reveals that the fly ash particles mainly composed of irregular and porous particles.

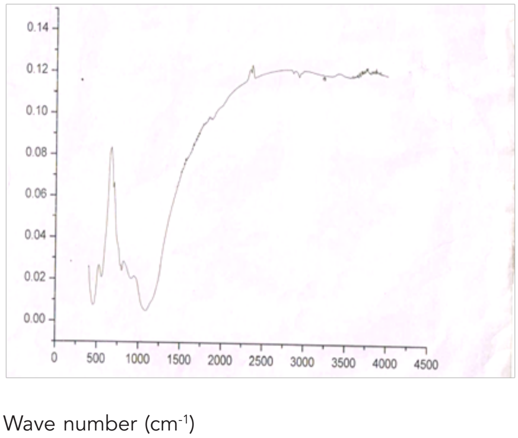
Figure 2. SEM micrograph of Coal Fly Ash



FTIR Analysis

IR spectroscopy of the powder sample was applied using Perkin Elmer FTIR system. The sample was scanned in the region 4000 – 400 cm-1 and shown in Figure 3. The peaks in IR spectra indicate the presence of Al–O, Si–O and Fe-O bonding.

Figure- 3. FTIR Spectra of fly ash

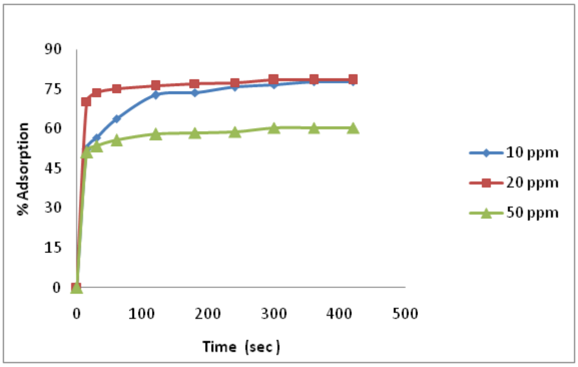


Effect of operating variables

Effect of contact time:

In the adsorption system contact time plays a vital role, irrespective of the other experimental parameters affecting the adsorption kinetics

Figure- 4. Effect of contact time on adsorption of cadmium

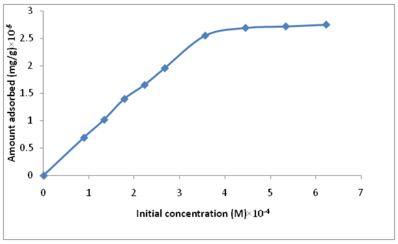


The adsorption data for the uptake of cadmium versus contact time for a fixed adsorbent dose of 10 g /L are shown in Fig. 4. The plots indicate that the remaining concentration of metal ions becomes asymptotic to the time axis such that there is no appreciable change in the remaining metal ion concentration after 360 min in. This represents the equilibrium time at which an equilibrium metal ion concentration is presumed to have been attained

Effect of Initial cadmium(II) Concentration

The plot showing the effect of initial concentration on the adsorption of metal ion is shown in Fig. 5. The plot showed that the total metal ion adsorbed increased sharply in the beginning and then slowly towards the end of the run.

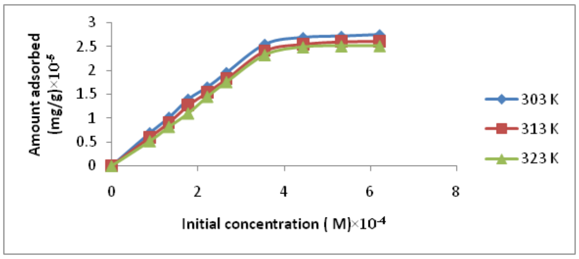
Figure 5. Effect of Initial concentration on adsorption of cadmium.



Influence of temperature:

The effect of temperature on the removal efficiency was investigated in the temperature of 30^0 and 40^{0}C. The experiment were carried out with fixed adsorbent dose of 10 g/l of fly ash and initial Cadmium concentration of 20ppm and pH 6. The adsorption data for the uptake of Cadmium versus temperature is represented in figure 6. Results indicate that Cadmium uptake was favored at lower temperature. The decrease in adsorption with the rise of temperature may be due to the weakening of adsorptive forces between the active sites of the adsorbent and adsorbate.

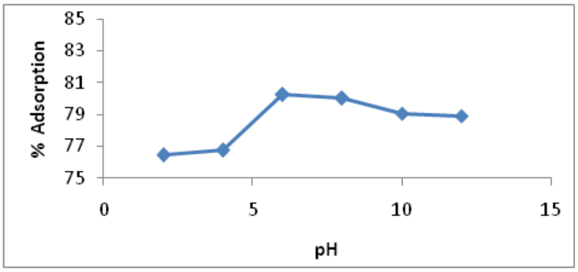
Figure- 6. Effect of temperature on adsorption of cadmium



The pH of the solution was found to influence the adsorption of the adsorbate on fly ash. The degree of adsorption of this adsorbate onto the CFA surface is primarily influenced by the surface charge on the CFA, which in turn is influenced by the solution pH.

The effect of initial pH on the adsorption of Cadmium was also evaluated at 30^{o}C at different initial pH values in the range of 2–12 for initial concentration of 20 ppm for Cadmium solution adjusted by adding either 0.1M HCl or 0.1M NaOH. The variation of adsorption with different values of pH is shown in Figure 7. The percent adsorption increases as pH increases from 2 to 6. The maximum adsorption accured at pH 6. After that pH 6, percent adsorption decreases up to pH 12.

Figure -7.Effect of PH on the adsorption of coal fly ash

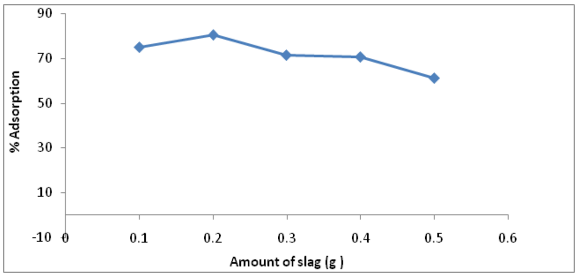


Influence of adsorbent dosage:

In order to investigate the effect of mass of adsorbent on the adsorption of Cadmium, a series of adsorption experiments was carried out with different adsorbent dosage at an initial Cadmium concentration of 20 ppm. Figure 8. shows the effect of adsorbent dosage on the removal of Cadmium.

The percentage removal of Cadmium increased with the increase in adsorbent dose initially from 0.1 to 0.2g. This can be attributed to increased adsorbent surface area and availability of more adsorption sites resulting from the increase adsorbent dosage. With the increase in the amount of adsorbent, the sites for adsorption increase initially. But on increasing it further the adsorption efficiency is reduced.

Figure-8 Effect of adsorbent dosage on adsorption of cadmium



Adsorption isotherms

The results obtained on the adsorption of cadmium and nickel were analysed by the well-known models given by Langmuir and Freundlich.

Langmuir isotherm

The Langmuir isotherm has been used by various workers for the sorption of variety of compounds. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The rearranged Langmuir isotherm equation can be described as:

$$\frac{1}{Q} = \frac{1}{Qm} + \left(\frac{1}{bQm}\right)\left(\frac{1}{Ce}\right)$$

Q_m and b are the Langmuir constants related to maximum adsorption capacity and energy of adsorption, respectively. The plots of $1/Q_e$ vs. $1/C_e$ yielding straight line (Fig. 9,10), which show that the adsorption of cadmium followed the Langmuir isotherm. The Langmuir constants, b and Q_m were calculated and the values of these were given in Table 2. The values of constants indicate favourable conditions for adsorption.

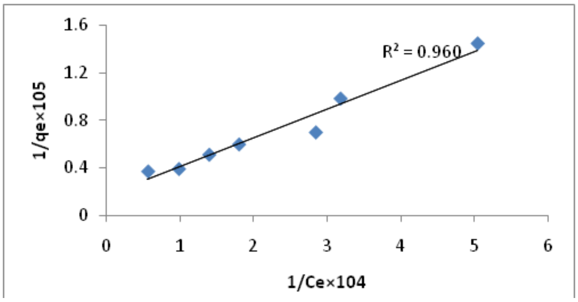


Figure- 9. Langmuir isotherm plot of Cadmium -CFA adsorption system at 303 K

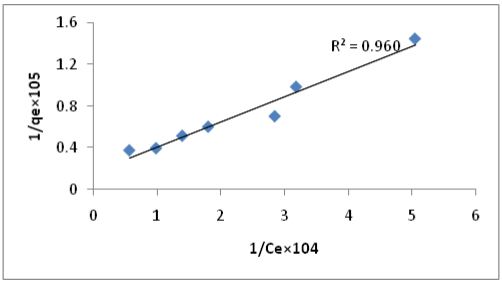
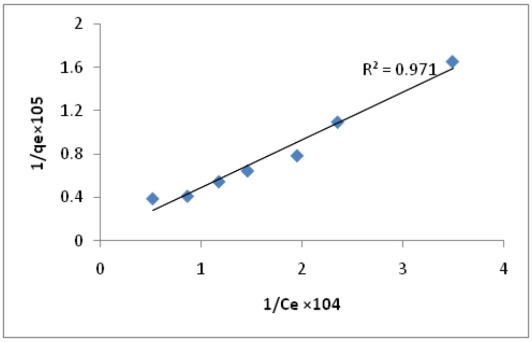


Figure- 10. Langmuir isotherm plot of Cadmium -CFA adsorption system at 313 K



Freundlich isotherm

The adsorption data of cadmium is also analyzed by Freundlich model. The linearized form of Freundlich isotherm is given below:

$$\log Q_e = \log K_f + \frac{1}{n}\log C_e$$

The value of K_f and n can be calculated by plotting log Qe versus log Ce. Where, K_f is a freundlich constant related to the adsorption capacity (mg/g) and n is adsorption intensity respectively (12).

The plots of log qe against log Ce for the adsorption data of cadmium are given in Fig.11,12, which clearly show that the data is not fitting very well to the Freundlich model. However, the Freundlich constants K_f and n were calculated from the best-fit lines and the values of these at two different temperatures are given in Table 3.

Figure- 11. Freundlich isotherm plot of Cadmium -CFA adsorption system at 303 K

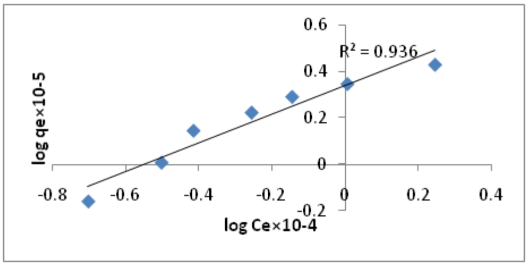


Figure- 12. Freundlich isotherm plot of Cadmium -CFA adsorption system at 313 K

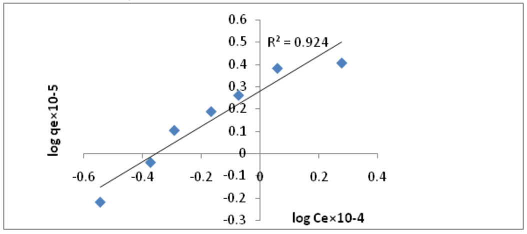


Table 2- Langmuir isotherm parameters of Cadmium-CFA adsorption system

Temperature	Q_m (mg/g)	b	R^2
303 K	6.0277	.6835	.9608
313 K	22.22	.1019	.9715

Table 3- Freundlich isotherm parameters of Cadmium-CFA adsorption system

Temperature	K_f	n	R^2
303 K	0.2344	1.6226	0.9336
313 K	0.1995	1.2668	0.9245

Kinetic studies

The thermodynamic parameters for the adsorption of cadmium were calculated by using the following equations :

$\Delta G^0 = -RT\ln K'$ ----------------(1)

$\Delta H^0 = \Delta G^0 + T\Delta S^0$ ----------------(2)

Therefore, $\ln K' = -\Delta H/RT + \Delta S/R$ ----------------(3)

Where, K′ the equilibrium constant is defined as,

$K' = C_{Ac} / C_e$ ----------------(4)

Ce is equilibrium adsorbate concentration in solution (mg L^{-1}),

C_{Ac} is the equilibrium concentration on the adsorbent (mg g^{-1}),

R is the universal gas constant and

T is the absolute temperature.

The values of thermodynamic parameters are given in Table 4. A perusal of data indicated that the free energy decreased with an increase in temperature thereby indicating decrease in adsorption at higher temperature and exothermic nature of the adsorption.

Table 4-Thermodynamic Parameters

ΔG^0		ΔH^0	ΔS^0	
303 K	313 K		303 K	313 K
-22.24	-18.02	-15.00	0.024	0.010

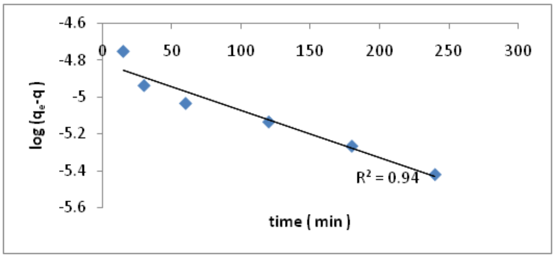
Specific Rate Constant of Adsorption

The rate constant of adsorption for cadmium is determined from the following first order rate expression given by Lagergren

$$\log(q_e - q) = \log q_e - \frac{K_{ad}}{2.303}t \quad \text{------------(5)}$$

Where q and q_e are amounts of metal adsorbed (moles g^{-1}) at time, t and at equilibrium respectively and K_{ad} is the rate constant for adsorption (min^{-1}). A straight line plot of log (q_e-q) versus't' suggested the applicability of Lagergren equation. The rate constant of adsorption (K_{ad}) was calculated from the slope of the plot and is found to be 0.0059 min^{-1}

Figure- 13.Lagergren 'plot for removal of cadmium by adsorption on fly ash



Conclusion:

Coal fly ash obtained from thermal power station is an inexpensive and effective adsorbent for the removal of cadmium from wastewater. Higher removal (%) is observed at low concentration. P^H has a pronounced on the removal of cadmium by adsorption on fly ash with maximum removal (80.27 %) at P^H 6.0.Adsorption data fit very well to the Langmuir model in comparison to the Freundlich model. The adsorption was found to be exothermic in nature.

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