Characterization of pit coal fly ash as sorbent for Cd(II) ions from aqueous solutions

L.TOFAN, C. PADURARU, R. WENKERT[a*]
Department of Environmental Engineering and Management, Faculty of Chemical Engineering and Environmental Protection, "Gheorghe Asachi" Technical University of Iasi, 73 D.Mangeron Street, 700050 Iasi, Romania
[a]Soroka University Medical Center, Beer-Sheva, Israel

The potential of a fly ash resulted from the combustion of an energy pit coal in a thermal power plant in Iasi, Romania as low- cost sorbent for cadmium (II) ions removal from aqueous solutions has been tested in batch conditions as function of initial pH, metal ion concentration, contact time and temperature. The ability of the tested fly ash for the Cd(II) sorption exhibited a maximum at pH 4.5-5. The amount of Cd(II) retained on the tested pit coal fly ash increased with increasing metal ion concentration, but the Cd(II) sorption percentage decreased. The kinetics of cadmium removal by fly ash presented a shape characterized by a strong capacity of tested metal ion removal by fly ash during the first few minutes, following a slow increase until the state of equilibrium is reached. The Cd(II) sorption by the fly ash under investigation is very well described by both Langmuir and Freundlich isotherm models. The calculated values of the thermodynamic parameters showed that the process of Cd(II) ions sorption by fly ash is spontaneous, endothermic and of chemical nature.

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1. Introduction

The contaminated effluents treatment is a process that is sometimes more complicated that any other manufacturing process, because waters can have a very variable composition in terms of organic or inorganic compounds, extreme acidity or basicity, presence of volatile substances or so on. Therefore, few processes provide clean effluents while fulfilling at the same time, requirements such as economic costs, flexibility in terms of both the amount of effluent to be treated and the pollutant concentration present, continuity of the system, minimal supervision and maintenance and sufficient selectivity regarding the removal of the pollutant considered. In last time, sorption on low cost sorbents has been proposed as one of the most promising technologies for the removal of toxic metals and organic pollutants from wastewaters [1,2].The main attractiveness of the use of this kind of technology is based on three aspects. The first one is the intrinsic low cost of these materials, because they are either natural widely available materials or by–products of agricultural and industrial processes. The second is the wide range of these materials with different origin which can be used either on its raw form or after a previous treatment to enhance their sorption capacity or to improve their mechanical or mass transfer properties [3- 9]. The third is that in the case of reuse of industrial by – products, an added – value is conferred to these materials. Otherwise, they would be considered as wastes, raising the costs in industry, because they have to be transported to the agreed sites for treatment, management or disposal.

The fly ash is produced in growing quantities by burning coal in all coal-fired power stations and other industrial sources. Literature survey indicates that different kinds of fly ashes may be used beneficially for the removal of some pollutant species (heavy metals, organics, dyes) from wastewaters[10 -12]. The sorption of Cu(II), Zn(II) and Pb(II) from very diluted aqueous solutions by an energy pit coal fly ash from a thermal power plant in Iaşi has been reported[13–14]. In this paper, the sorption properties of the the same fly ash with respect to cadmium(II) in aqueous solution are studied. This heavy metal ions were chosen due to their solubility over a wide range of pH and their presence in several industrial wastewaters[15].

2. Experimental

2.1 Sorbent preparation and characterization

In this study, the ash is obtained by burning energy pitcoal in Iasi thermal power plant from Romania.

The ash can be described as a mixture of oxides representing about 95% from its total weight, the elemental composition of the fly ash under study, as oxides (wt.%) is given: $\%SiO_2 = 47.39$; $\%Al_2O_3 = 23.49$; $\%Fe_2O_3 = 8.55$;$\%CaO = 4.67$; $\%Na_2O = 1.36$. The ash was dried at 105^0C and stored in a dessicator before use.

The elemental composition of the investigated pit coal fly ash has been determined by X-ray photoelectron spectroscopy.

2.2 Chemicals

Stock solution of 1200 mg/Lwere prepared by dissolution of analytical grade reagents $CdSO_4 \cdot 8H_2O$ in deionised water and were complexonometrically standardized. Working solutions of Cd(II) were prepared by the appropriate dilutions of the stock solution.

In order to study the effect of medium acidity on the sorption process, a solution of H_2SO_4 with concentration of 10^{-2} mol / L has been used. (340–A /SET 1 pH-meter).

2.3 Sorption procedure

The sorption experiments were performed by in batch conditions.

For this purpose, samples of about 0.5g ash were equilibrated with 50mL of each aqueous solution containing defined amount of metal ion. The mixture was then filtrated and the solution was analyzed for the cation content. The Cd(II) concentrations in solutions have been determined by atomic absorption spectrometry. (210VGB Buck Scientific atomic absorption spectrometer).

The amount of metal ions sorbed on ash was calculated from the difference between the initial and final concentrations of the solutions.

3. Results and discussion

3.1 Effect of initial pH

The effect of the initial solution pH on the Cd(II) sorption by the tested pit coal fly ash was studied in the initial pH range of 1–5 (Fig. 1).

As can be seen from Fig. 1, the smallest sorption of Cd(II) on the tested fly ash was found at initial pH of 1 (reached by acidification with H_2SO_4 solution).

This effect may be explained on the basis of the repulsion between the positive surface charge of the fly ash(equation 1[16]):

$$\equiv SiOH + H^+ \rightarrow \equiv SiOH_2^+ \quad (1)$$

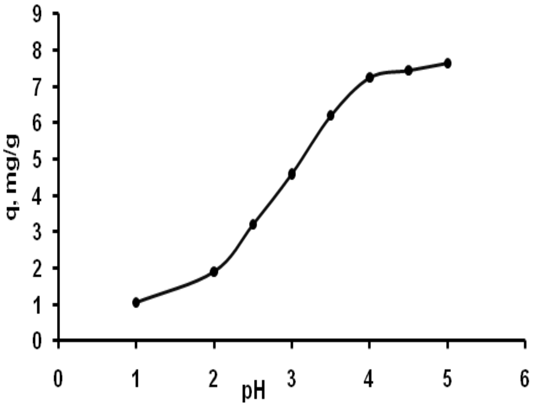

Fig.1. The influence of initial pH on the Cd(II)sorption by the fly ash of Iasi thermal power plant station (C_0 = 80 mg Cd(II) /L; ash dose = 10g/L, time = 24h, t=25^{0}C).

and the double positively charged form of cadmium which is predominant at initial pH =1- 5 [17].

Subsequently, with initial pH increasing from 1 to 3.5, the Cd(II) sorption abilily of the tested fly ash rapidly increased. At initial pH values higher than 3.5, the amount of the sorbed cation did not increase further. This trend is in good agreement with Cd(II) sorption on other kinds of fly ash and is due to the increasing total net negative charges of fly ash surface, resulting in intensified electrostatic forces in the Cd(II) retention process [16- 17]. Thus, this behavior is the consequence of the following processes taking place in the initial aqueous solution with pH
2 – 5 [16]:

- the hydrolysis of cadmium ions:

$$Cd^{2+} + H_2O \leftrightarrow CdOH^+ \quad (2)$$

- the dissociation of the superficial hydroxyl groups, resulting in negative charges at the active sites on the pit coal fly ash surface:

$$\equiv SiOH \rightarrow \equiv SiO^- + H^+ \quad (3)$$

$$\equiv AlOH \rightarrow \equiv AlO^- + H^+ \quad (4)$$

- the chemisorption of Cd(II) ions:

$$2(\equiv SiO^-) + Cd^{2+} \rightarrow (\equiv SiO)_2Cd \quad (5)$$

$$2(\equiv AlO^-) + Cd^{2+} \rightarrow (\equiv AlO)_2Cd \quad (6)$$

In this context, the influence of contact time, Cd(II) initial concentration and temperature was performed with solutions of initial pH 4.5 – 5.

3.2 Effect of Cd(II) concentration in initial solutions

The influence of the initial solution concentration on the Cd(II) sorption by pit coal fly ash from Iasi thermal power plant is given in Table 1. From Table 1 it is obvious that the amount of Cd(II) retained on the tested fly ash (q) increased with increasing metal ion concentration. The enhancement of the Cd(II) uptake at higher initial concentration is the result of the high values of the ratio between the initial number of Cd (II) mmoles and the limited number of available binding sites. One the other hand, the Cd(II) sorption percentage(R%) decreased, as a consequence of the occupation of the total active sites on fly ash which hinders the access of Cd (II). In this context it can be concluded that the fly ash resulted by burning energy pit coal might be an efficient sorbent for the removal of Cd(II) from wastewaters with low content in the tested cation.

Table 1. Influence of Cd(II) initial solution concentration on Cd(II) retention by fly ash under study

C_0, mg/L q,	q, mg/g	R, %
20	3.94	89.2
40	5.3	80.5
60	6.55	75
80	7.5	65.3
100	9.75	59
120	11.27	50.25
140	12.55	49

3.3 Effect of contact time and kinetic parameters

The effect of contact time on Cd(II) sorption by the pit coal fly ash under study at different initial concentrations of Cd(II) is given in Figure 2. The kinetic data in Figure 2 indicate that the extent of Cd(II) sorption increased sharply with increasing contact time, attaining values that stay almost constant. At all the tested ranges of concentration, the sorption equilibrium is reached in 120 minutes. This fact emphasizes that the equilibrium time is independent of the initial Cd(II) concentration. . This observation may be ascribed to the reduction in immediate metal ions sorption, owing to lack of available active sites required for high initial concentration of metal ions.[16]
According to the literature data, the sorption process involves three common steps: the mass transfer across the external boundary layer film of liquid surrounding the outside of the particle→ the sorption process at individual site on the internal or external surface → the diffusion of the sorbate species to an sorption site either by a pore diffusion process through the liquid filled pores or by a solid surface diffusion mechanism [18]. One or any combination of this adsorption process could be the rate-controlling mechanism[19].

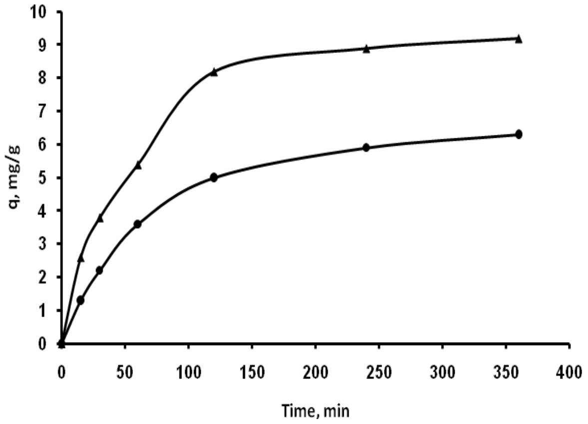

Fig. 2. Effect of contact time and on retention of Cd(II) ions by pit coal fly ash: (●) 60mg/L; (▲)100mg/L ; ash dose = 10g/L, initial pH = 4.5- 5

In order to study the controlling mechanism of the Cd(II) sorption process on the tested fly ash, the obtained kinetic data were fitted to the linear form of pseudo-first-order and pseudo-second-order kinetic models. The pseudo-first-order model is used to describe the reversibility of the equilibrium between liquid and solid phases and is based on Lagergren equation [20]:

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} \cdot t$$

where q_e and q_t are the amounts of Cd(II) (mg/g) sorbed at equilibrium and at time t, respectively and k_l is the pseudo-first order sorption rate constant(min^{-1}). The kinetic parameters obtained from the linear Lagergren plots are given in Table 2, together with the corresponding correlation coefficients (R^2).

Table 2. Pseudo–first and pseudo–second kinetic parameters for Cd(II) sorption on pit coal fly ash at pH = 5 and t = 20^{0}C.

C_0, mg/L	Pseudo-first order			Pseudo-second order			
	k_1(.min^{-1})	q_0 mg/g	R^2	k_2 (g/mg.min)	h (mg/g.min)	q_0 (mg/g)	R^2
60	8.75x10^{-3}	5.28	0.9964	1.83x10^{-3}	0.105	7.58	0.9871
120	9.36x10^{-3}	7.25	0.9902	1.96x10^{-3}	0.212	10.39	0.9884

On the basis of pseudo–second–order kinetic model is following equation [21]:

$$\frac{1}{q_t} = \frac{1}{h} + \frac{1}{q_e} \cdot t$$

where h = $k_2 \cdot q_e^2$(mg/g ·min) can be regarded as initial sorption rate constant of the pseudo–second–order sorption (g.mg^{-1}·min^{-1}). The kinetic parameters derived from the plots of the liniarized form of the pseudo–second–order equation are recorded in Table 2*,* along with the corresponding correlation coefficients.

As can be seen from Table 2, the plots for the pseudo–first order model yield better values of the correlation coefficients as compared with the plots of pseudo–second order. This result suggests that the Cd(II) ions sorption on the tested fly ash follows better the pseudo–first order kinetic model. This finding is in good agreement with data of previous studies. Thus, the reported data point out that the kinetics of Cu(II), Zn(II) and Pb(II) sorption on the thermal power plant ash is very well described by the

Lagergren pseudo-first order equation[14]. In addition, it can be seen that Cd(II) concentrations have a significant influence on the rate of sorption. Thus, for an increase in Cd(II) initial concentration from 60 mg/L to 120 mg/L, the values of the pseudo – first rate constant increased from 8.75x10^{-3} min^{-1} to 9.36x10^{-3}min^{-1}, respectively.

3.4 Cd(II) sorption isotherms

In order to obtain information about the homogenity and heterogenity of the fly ash surface and to design the Cd(II) sorption process effectively, the equilibrium data at three different temperatures were analyzed by employing two widely used isotherms,Langmuir and Freundlich.

The Langmuir isotherms for Cd(II) sorption on the investigated energy pit coal at three different temperatures are presented in Figure 3.The retention of Cd(II) on the fly ash under study is characterized in Table 3 by means of the Langmuir constants obtained from the corresponding linear Langmuir plots.

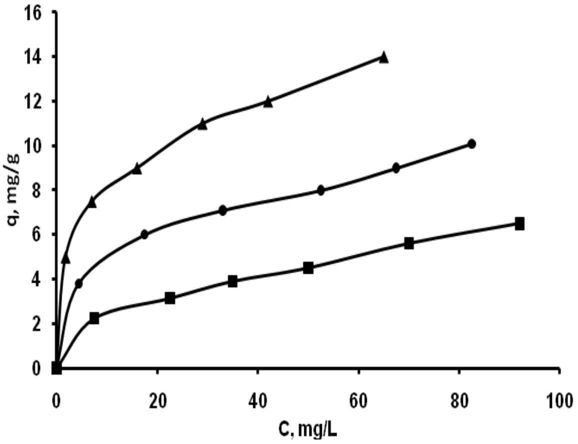

Fig. 3. Langmuir isotherms of Cd(II) sorption on the tested fly ash at : (■) 4^{0}C; (•)25^{0}C; (▲) 50^{0}C; (•) (pH= 4.5-5; fly ash dose= 10g/L)

Table 3. Characterization of Cd (II) sorption on the pit coal fly ash under investigation by means of Langmuir isotherm model

Equation[22]	Isotherm parameters, significance	Assumptions	Temperature, K	q$_0$, mg/g	K$_L$, L/mol	R^2
$q = \frac{K_L \cdot C \cdot q_0}{1 + K_L \cdot C}$	K_L – binding energy (relative sorption affinity) q_0– maximum capacity of sorption	Formation of a monolayer coverage of metallic ion at the sorbent surface containing a finite number of homogeneous sites of sorption	277 298 323	6.45 10.15 13.75	6754 10131 19235	0.9931 0.9904 0.9904

It is obvious from the Table 3 that the conversion of the fly ash waste under study to a value–added sorbent for Cd(II) ions is viable .The high values of K$_L$ constants recorded in Table 3 involve strong bonds between the Cd(II) ions and the thermal power plant fly ash. As can be seen from Table 4, the low value for Cd(II) maximum sorption capacity is comparable with those reported in the literature for the sorption of Cd(II) on other types of ashes.

The sorption of Cd(II) by the investigated fly ash is described in Table 5 by means of Freudlich isotherm model.

The n in Table 5 values are above unity, indicating favorable sorption of the tested cation by the fly ash under study at all working temperatures. The K$_F$ values determined in this study are smaller than those reported in previous studies using nettle ash as low–cost sorbent for Cd(II) ions [27].

To compare the Langmuir and Freundlich isotherm models, the experimental data were statistically processed by linear regression. High values of the linear regression correlation coefficients (R^2) for both Langmuir and Freundlich plots (Table 3 and Table 5) suggest that monolayer sorption as well as heterogeneous surface conditions may co–exist under applied experimental conditions

Table 4. Comparison of the sorption capacity of various kinds of ash for Cd(II)

Ash	Cd(II) sorption capacity, mg/g	Reference
Treated fly ash from Thailand	14.33	[16]
Bagasse fly ash	1.267(30^{0}C) 1.67(40^{0}C) 2.00(50^{0}C)	[25]
Pellets made from fired coal fly ash	18.98	[24]
Wood ash	2.128 - 5.6	[25]
Bottom fly ash from a thermal power plant in India	0.969	[26]
Nettle ash	142.8	[27]
Alkali – treated oil shale ash	12.05	[28]
Pit coal fly ash	**10.15**	**This study**

3.5 Effect of temperature and thermodynamic parameters

It is obvious from Table 3 and Table 5 that the temperature has a favorable influence on the process of Cd(II) sorption by the fly ash under study.

The characteristic thermodynamic parameters calculated on the basis of the values of the Langmuir sorption constant K_L at different temperatures are given in Table 6.

Table 5. Freundlich description of Cd(II) sorption on energy pit coal fly ash

Equation[29]	Isotherm parameters, significance	Assumptions	Temperature, K	n	K_F,	R^2
$\log q = \log K_F + (1/n)\log C$ (linearised form)	K_F - sorption capacity n–energy of sorption	Logarithmic decrease in the enthalpy of sorption with the increase in the fraction of occupied sites	277 297 323	2.04 3.15 4.35	1.75 2.32 3.88	0.9887 0.9971 0.9903

Table 6. Thermodynamic description of the Cd(II) sorption on the pit coal fly ash

Thermodynamic parameter	Equations [13]	T, K	Obtained values
Free energy change (ΔG)	$\Delta G = - RT \ln K_L$ R is the gas constant; T is the absolute temperature	277 298 323	- 20.29 kJ/mol - 22.75 kJ/mol - 26.46 kJ/mol
Enthalpy change (ΔH)	$\ln K_L = \text{constant} = -\Delta G / RT$ R is the gas constant; T is the absolute temperature	277 298 323	26.73 kJ/mol
Entropy change (ΔS)	$\Delta S = (\Delta H- \Delta G)/T$	277 298 323	166.5 J/mol.K 166 J/mol.K 166 J/mol.K

The negative values of the free energy change in Table 6 indicate the spontaneous nature of the Cd(II) sorption process on fly ash. The endothermic nature of the process of Cd(II) retention is revealed by the positive value of enthalpy change from Table 6. The positive value of entropy change suggests the increase in randomness at the solid – liquid interface during the sorption of Cd(II) on the energy pit coal from a thermal power plant in Iasi, Romania.

4. Conclusions

The energy pit coal fly ash has been found to be a suitable sorbent for the Cd(II) ions. Within the initial pH range of 1 to 5 under study, the fly ash sorption ability increased with increasing pH until 3.5. At the initial pH values higher than 3.5, the amount of sorbed Cd(II) did not increase further. The sorption kinetic data were satisfactorily described by pseudo – first order equation.

The Cd(II) maximum sorption capacity of the fly ash under investigation is 10.15 mg/g at 25^0C.The sorption isotherms could be well fitted by both Langmuir and Freundlich equations. Thermodynamic studies indicate that the process was spontaneous and endothermic. The data thus obtained may be helpful for designing a treatment plant for the removal of Cd(II) from wastewaters.

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[*] Corresponding author: RodicaWe@clalit.org.il