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Modification of Adsorptive Properties of Bagasse Fly Ash for Uptaking Cadmium from Aqueous Solution

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Novel low-cost adsorbents were developed from industrial bagasse fly ash (BFA) waste using facile chemical modification. The uptaking of cadmium from wastewater using pretreated BFA adsorbents was investigated. The influence of solution pH, contact time, initial metal concentration, adsorbent dosage, and temperature on the adsorption performance of Cd (II) onto natural and modified BFA adsorbents was examined by a batch method. Surface properties of developed BFA adsorbents were characterized by the pH_{PZC}, C, H, N, and S elemental analysis and FTIR spectrum. Equilibrium data were analyzed using Langmuir and Freundlich isotherm models. Results indicated that the Langmuir isotherm fitted best. Chemical modification to BFA with HCl and HNO_3 resulted in enhancing sorption capacity of BFA for Cd (II) uptake from 19.8 to 47.6 and 25.1 mg/g and then decreasing to 11.9 mg/g upon pretreatment with EDTA, respectively. Kinetic studies showed that the cadmium sorption process followed a pseudo-second-order kinetic model. Thermodynamic calculations point towards feasibility of an adsorption process with spontaneous and endothermic nature. Overall, it can be concluded that the modified BFA can be operated as an alternative material to more costly adsorbents used for cadmium (II) in wastewater treatment processes.

Keywords: Chemical modification, Bagasse fly ash, cadmium removal, batch studies

1. Introduction

The persistence of heavy metals in industrial wastewater represents an important source of environmental pollution. Harmful toxic heavy metals that are discharged by chemical industries include: cadmium, mercury, lead, chromium, copper, nickel, and zinc. Particularly, cadmium is one of the most toxic metal ions as it is a non-essential and non-biodegradable metal ion. Accordingly, it is accumulated in the blood causing a variety of symptoms such as high blood pressure, kidney damage, and destruction of red blood cells. Cadmium is used in a wide variety of industries such as the electroplating industry, nickel-cadmium batteries, pigments, plastics, pesticides, dyes, and textile operation (Yavuz et al. 2007). The permissible limit for cadmium as described by the World Health Organization (WHO) is 0.01 mg/L (Peterlene et al. 1999). Therefore, the removal of cadmium from wastewater is one of the considerable significance from an environmental point of view. Several physico-chemical methods have been developed to remove cadmium from aqueous solutions including: filtration, ion exchange, reverse osmosis, solvent extraction, membrane separation, and adsorption by activated carbon. Among all, the adsorption is a promising process for removal of metal ions from water and wastewater, because it is a simple, economic and suitable operation method, and it is significant to exploit simple, novel and high efficient adsorbents for this approach (Deng et al. 2010; Mall et al. 1996).

In the purification process, low cost adsorbents are preferred. Activated carbon is regarded as the most effective adsorbent for removal of organic and inorganic substances, however, due to its high cost and about 10–15% loss during regeneration, agro-industrial wastes like wood, saw dust, peat, lignite, bagasse fly ash (BFA), sugar cane bagasse, bagasse pith, etc., have attracted the attention of several researchers (Bailey et al. 1996). The utilization of industrial solid wastes for treatment of wastewater from another industry could be helpful not only to the environment in solving the solid waste disposal problem, but also to the economy. Sugar industry is one of the most important agro–based industries in Egypt. Bagasse fly ash, waste generated from sugar industry, causes a disposal problem as it accumulates in huge amounts. Currently this solid is being used as filler in building materials. Earlier studies have analyzed bagasse fly ash as raw material for producing potential materials such as silica gel, ceramic, cement, concrete additives, catalysts, cosmetics, paints, coatings (Patchorin et al. 2009; Vital et al. 2008; Fotovat et al. 2009).

Recently, utilization of BFA as adsorbent has attracted a lot of attention because of their abundance, economic viability, and adsorption capacity (Gupta and Ali 2000 and 2004; Gupta et al. 2003; Shouman et al. 2011; Mall et al. 2005; Srivastava et al. 2006). Gupta and coworkers studied (2003 and 2004) extensively the removal of heavy metals by using BFA treated with hydrogen peroxide. However, the recorded values of maximum adsorption capacities for both metals were low (2.50 and 4.35 mg /g for Pb and Cr, 2.00 and 1.70 mg/g for Cd and Ni, respectively). Adsorption of congo red dye using untreated and treated bagasse fly ash with H_2O_2 has been studied (Mall et al. 2005; Shouman et al. 2011). The chemical composition and porosity of the parent BFA and pretreated BFA with H_2O_2 have been already presented elsewhere (Shouman et al. 2011). They observed that the major constituent in BFA was silica (85.2% SiO_2) with low percentage of other minerals such as 2.85% of MgO, 4.66% of K_2O, 4.25% of CaO, 1.38% of CuO, 1.33% of ZnO, and 0.63% of Fe_2O_3, respectively. The internal porosity of parent BFA such as the BET surface area, total pore volume and average pore diameter were found to be 255 m^2/g, 0.127 cm^3/g, and 20Å, respectively. Throughout the chemical oxidation of parent BFA with H_2O_2, mineral oxides were leached out from BFA, and hence, leading to a decrease in adsorption capacity towards congo red dye from 20.1 to 11.5 mg/g. Thus, wet oxidation with hydrogen peroxide as an oxidizing agent negatively affected chemical composition and surface texture of BFA.

Accordingly, to our knowledge, the improvement in adsorption capacity of BFA using HCl, HNO_3, and EDTA has been not reported in literature yet. The present study shows that the performance of BFA to remove cadmium has significantly increased after pre-treating it with HCl and HNO_3, as compared to BFA modified with H_2O_2 (Gupta et al. 2003) which is expressed in a sequence order: BFA- H_2O_2 < BFA-ED < BFA-HN < BFA-HC. This research is devoted to enhance the proportion of active surfaces, to eliminate soluble components of mineral oxides, and hence, to increase the binding sites in bagasse fly ash for attracting metal ions. Thus, the present study is focused on the evaluation potentiality of pretreated BFA using HCl, HNO_3, and EDTA as sorbent materials for removing cadmium from the aqueous solution. Batch sorption studies have been conducted to examine the efficiency of the modified BFA on Cd (II) ions binding and the equilibrium data have been analyzed using Langmuir and Freundlich isotherm models.

2. Materials and Methods

2.1. Reagents

Chemicals such as HCl, HNO_3, ethylenediaminetetraacetic acid (EDTA), and NaOH were supplied by Merck as analytical-grade reagents, and de-ionized water was used. The standard solutions of Cd (II) ions were prepared by dissolving reagent grade Cd $(NO_3)_2\cdot4H_2O$ with distilled water to the desired concentrations. In batch experiments, the optimum pH of the solution was adjusted to 5.0 by addition of 0.1 M NaOH or 0.1 M HCl solution.

2.2. Preparation and characterization of natural and modified BFA samples

Bagasse fly ash (BFA) was collected from a local sugar factory at Kom-Umbo, Aswan City, Egypt (Shouman et al. 2011). Natural BFA was chemically modified by the following route. A portion of 10 g of BFA and 100 ml of HCl and HNO_3 solutions were mixed into flasks separately, at a volume ratio (1:1 v/v), and then heated at 100°C for 1 h and left overnight. For modification with EDTA, a 10 g of BFA was added to 100 ml of 0.1M EDTA, stirring thoroughly for 1 h and also left at 60°C overnight. Subsequently, the solution containing BFA was allowed to separate, and the resulting samples were washed several times with distilled water and dried in an air oven at 100°C overnight, keeping in tightly closed containers. The pretreated BFA samples using HCl, HNO_3 and EDTA were labelled as BFA-HC, BFA-HN and BFA-ED, respectively.

Physico-chemical characteristics, such as pH of both slurry and point of zero charge (pH_{PZC}), and elemental analysis for the investigated samples were measured. The pH measurements were determined by HANNA (Model pH1110). The pH of point of zero charge (pH_{PZC}) for the samples was carried out by the previous procedure described elsewhere (Leon and Radovic 1994). Elemental analysis provides a means for rapid determination of carbon, hydrogen, nitrogen and sulfur (CHNS) in organic matrices and other types of materials. For this purpose, the samples were ground to fine powder (40 mesh size) and used for CHNS analysis (Perkin-Elmer 2400 Series). Additional FTIR analysis was performed with a Fourier transform infrared spectrometer (FTIR–6100 JASCO) in the range 4000–400 cm^{-1} to identify the surface functional groups present in the hereby samples. The results of these analyses are presented in Table 1.

2.3. Adsorption experiments

Some experimental conditions such as solution pH, contact time, adsorbent dose, and adsorption temperature as it relates to adsorption of metal ions were studied. For each experiment run, 0.04 g of adsorbent with 25 ml of metal ions solution of a desired concentration in a 100 ml stoppered conical flask using a shaking thermostat machine at the speed of 120 rpm for 2 h was performed. The effect of solution pH on the equilibrium adsorption of Cd (II) ions was investigated under similar experimental conditions between pH 2.0 and 8.0. The influence of contact time on batch experiments was examined by varying the contact time of suspensions from 5 to 120 min. The adsorbent doses used were varied between 0.01–0.1g/25ml with an initial cadmium concentration of 50mg/L. In the isotherm experiments, 0.04 g of adsorbent was added to 25 ml of metal ions solution at various concentrations (10–100 mg/L). The adsorption temperature effect was carried out on BFA-HC adsorbent at 25, 40 and 60°C. Once the preset contact time was reached (2 h), the residual concentrations of Cd (II) ions were determined using an atomic absorption spectrophotometer (*AAS, Varian model 210*). The amount of adsorbed metal ions was calculated from the mass balance expression given by:

$$q_e = \frac{(C_0 - C_e)}{\mathrm{m}} V \qquad (1)$$

The adsorption percentage of metal ions was calculated as follows:

$$\%\,\mathrm{Removal} = \left(\mathrm{C_0 - C_e} \big/ \mathrm{C_0}\right) \times 100 \qquad (2)$$

where

q_e - amount of metal ions adsorbed by BFA adsorbents, mg/g;
C_0 - initial ion concentration of Cadmium, mg/L;
C_e - equilibrium concentration of metal ions after the adsorption procedure, mg/L;
m - mass of adsorbent in, mg;
V - volume of metal solution in contact with the adsorbent, ml.

In order to ensure reproducibility of the obtained results, all the adsorption experiments were performed in triplicate and the average values were used in data analysis. Relative standard deviations were found to be ± 3 %. Correlation coefficient analysis (R^2) was applied to determine the best fitted isotherm model with the experimental data obtained in this study.

3. Results and Discussion

3.1. Feature surface characteristics of BFA adsorbents

Adsorption properties of BFA, BFA-HC, BFA-HN, and BFA-ED adsorbents may be related to the chemical nature of the surface rather than to the surface area and porosity. Therefore, the pH of both slurry and point of zero charge of the prepared adsorbents may give a good indication about the surface oxygen complexes and the electronic surface charges present on adsorbents. This surface charge arises from the interaction between the adsorbent surface and the aqueous solution. The complexes on the adsorbent surface are generally classified as acidic, basic, or of neutral character (Noh and Schwarz 1989). Results of determination of slurry pH and point of zero charge for natural and modified BFA sorbents are given in Table 1. Slurry pH values show that BFA, BFA-HC, and BFA-HN have neutral pH ~7.20 (i.e., acidic sites ≈ basic sites), while BFA-ED sample exhibited acidic surface with pH 3.50. Furthermore, when the investigated adsorbents conducted into cadmium solution, the solution pH of Cd (II)–BFA adsorbents decreased from 7.20 to 6.73, 6.44, 5.83 and 3.53 for the following samples BFA, BFA-HC, BFA-HN and BFA-ED, respectively. That behavior indicated that H^+ ions were released from these samples and meanwhile Cd (II) ions were adsorbed onto all of them.

In addition, the value of pH_{PZC} for BFA decreased from 7.40 to 5.33, 4.67 and 2.74 for the samples BFA-HN, BFA-ED and BFA-HC, respectively. Hence, the modified BFA samples have predominant acidic sites. The BFA-HC and BFA-HN samples possess $pH \geq pH_{PZC}$, and thus the surface becomes more negative. On the other hand, the BFA-ED sorbent has pH value lower than that of pH_{PZC}, and therefore, its surface forms a portion of positive charges, thus, it does not favor the removal of Cd (II). Generally speaking, when solution pH is higher than pH_{PZC}, the adsorbent surface favors the adsorption of cation species, while for a solution pH is lower than the pH_{PZC}; accordingly the surface preferred the adsorption of anion species. Chemical modification of raw BFA with acids led to an increase in the formation of acidic oxygen functional groups that have been examined by FTIR analysis (*cf.* Table 1).

Results of elemental analysis of BFA and modified BFA with HCl, HNO_3, and EDTA acids are also recorded in Table 1. As shown in this Table, the samples are basically composed of carbon, hydrogen, and oxygen. Relatively high content of oxygen to carbon is probably due to the presence of metal oxides in samples. Also, the weight fraction of oxygen increased when BFA treated with oxidizing agents as oxygenated groups were introduced on the surface of BFA during the oxidation process.

In order to confirm the surface functional groups on the prepared adsorbents, an FTIR study was carried out. The chemical groups assigned by FTIR spectra are also listed in the same Table. According to FTIR spectra, a broad band between 3200 and 3700 cm^{-1} in BFA sorbents indicated the presence of both free and hydrogen bonded to OH and NH stretching on the adsorbent surface (Abou-Mesalam 2003). This stretching is due to both the silanol groups (Si–OH) and adsorbed water (peak at 3400 cm^{-1}) on the surface (Abou-Mesalam 2003). The stretching of the O–H groups bound to methyl radicals presented a very light signal ~2920 cm^{-1} for BFA. The spectra of modified BFA sorbents indicated sharp peaks in the region of 1600–1800 cm^{-1}, corresponding to the C=O group stretching from carboxyl, aldehydes, and ketones. The FTIR spectra of BFA showed transmittance in the 1050–1290 cm^{-1} region due to the vibration of the C=O group in lactones (Davila-Jimenez et al. 2005). The 1360–1380 cm^{-1} band may be attributed to the aromatic C–H and carboxyl–carbonate structures (Ricordel et al. 2001). The FTIR spectrum of BFA-HN clearly shows the presence of the characteristic band of N=O stretching at the region 1733–1633 cm^{-1} (Silverstien et al. 2005). The peak at 1100 cm^{-1} is due to C–O–H stretching and OH deformation (Silverstien et al. 2005). Also, the shoulder absorption bands emerging between 870 and 480 cm^{-1} are ascribed to C–H, Si–H, and O–H bending in an aromatic ring, respectively. Accordingly, the presence of polar groups on the surface is likely to give considerable cadmium exchange capacity to the modified BFA adsorbents.

Table 1. Physico-chemical measurements of BFA adsorbents

Properties	***BFA-ED***	***BFA-HN***	***BFA-HC***	***BFA***
pH measurements				
Slurry pH	3.50	7.40	7.20	7.20
pH_PZC	4.67	5.33	2.74	7.40
Elemental analysis				
C, %	48.8	40.1	42.9	31.3
H, %	6.31	5.47	7.98	25.4
N, %	3.37	2.33	1.21	3.50
O, %	39.6	49.8	46.4	36.7
S, %	1.92	2.30	1.51	3.10
FTIR, Assignments	**Wavenumber (cm^{-1})**	**Wavenumber (cm^{-1})**	**Wavenumber (cm^{-1})**	**Wavenumber (cm^{-1})**
O–H, N–H and Si–OH	**3770 – 3431**	**3770 – 3425**	**3770 – 3425**	**3774 – 3434**
C–H stretching of alkenes	**2922 – 2854**	**2926 – 2857**	**2926 – 2857**	**2925 – 2855**
O–H stretching in COOH group, C≡C in alkynes	**–**	**–**	**2433**	**2200**
C=O stretching of aromatic groups, C=C, N=O stretching of alkenes and aromatic	**1623 – 1437**	**1733 – 1633**	**1713 – 1594**	**1713– 1618**
C–O, C–OH stretching in carboxylic, lactones, alcohols, Si–O–Si	**1437 – 1380 – 1094**	**1344 – 1193 – 1100**	**1344 – 1193 – 1100**	**1385 – 1103**
C=C bending, C–OH, Si–H	**– 480**	**796 – 478**	**796 – 478**	**870 – 470**

3.2. Distribution coefficients as a function of initial concentration

A distribution coefficient of an adsorbent is defined as the ratio of a metal ion adsorbed to the amount in the liquid phase ($K_\text{d} = q_e/C_e$, L/g). The values of the distribution coefficient lower than 1.0 shows low adsorption efficiency. Figure 1 (a and b) illustrates K_d as a function of initial cadmium concentrations. It can be observed that the K_d values increase with a decrease in the concentration of metal ions. In other words, the K_d values increase as dilution of metal ions proceeds in the solution. In this study, the distribution coefficients of the metal ion between the BFA adsorbents and the aqueous phase are higher than 1.0 and dependent on the initial metal ion concentrations as represented in Figure 1. Moreover, the estimated values of the distribution coefficient (K_d, L/g) indicated that BFA-HC exhibited high efficiency of removal of Cd (II) ions. In the case of BFA-ED sample, the distribution coefficient of cadmium seems steady over an increase in initial concentrations.

3.3. Effect of solution pH

The extent of heavy metals adsorption is strongly governed by pH of the solution. The effect of pH solution on the removal percentage of Cd (II) ions using BFA and its modified samples was examined over the pH range of 2.0–8.0 as shown in Figure 2. As seen in this Figure, removal of cadmium increased by increasing the solution pH. The maximum Cd (II) removal occurred in the pH range of 5.0–8.0 and cadmium was very slightly adsorbed at pH 2.0. At pH 8.0, cadmium was completely removed onto BFA-HC. Similar results have been reported for the adsorption of Cd (II) on natural and oxidized corncobs as well as adsorption of cadmium onto activated carbons (Leyva-Ramos et al. 1997; Leyva-Ramos et al. 2005).

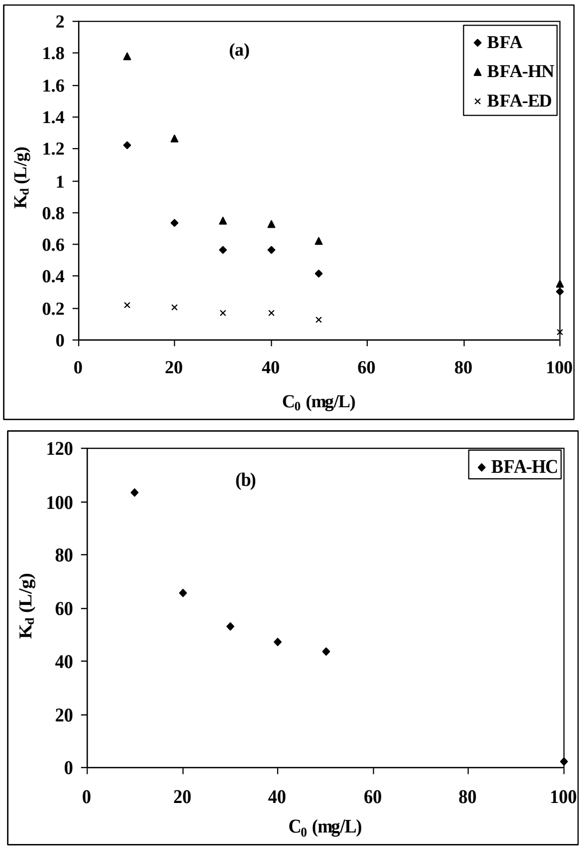

Fig 1. Variation of distribution coefficients for Cd (II) ions on natural and modified BFA as a function of initial concentrations, m = 0.04 g, V = 25 ml, time 2 h and T =25^{o}C

According to the Cd (II) speciation diagram (Leyva-Ramos et al. 1997; Leyva-Ramos et al. 2005), Cd^{2+} is a predominant ionic species at pH less than 7.0 and at pH values just below 9.0, Cd (II) precipitates as Cd $(OH)_2$. At pH 8.0, the species distribution is approximately 90% of Cd^{2+} and 10% of $Cd(OH)^+$. Thus, Cd (II) was principally adsorbed on the BFA as Cd^{2+} since all experiments were carried out at a pH less than 8.0. Thus, pH was kept constant at 5.0 to constitute a suitable value for metal adsorption by the studied adsorbents. It is well-known at slightly acidic pH values; divalent transition metal (M^{2+}) concentrations are the highest and suitable for metal sorption (Leyva-Ramos et al. 1997).

3.4. Effect of adsorbent dose

The effect of an adsorbent dose on the removal of Cd (II) ions is shown in Fig.3. The Figure shows. that the removal of cadmium increases up to a certain limit and then it remains almost constant over 0.04 g. Hence, the optimum dose from BFA, BFA-HC, BFA-HN, and BFA-ED samples was found to be 0.04 g/25 ml (i.e., 1.6 g per liter of cadmium solution). The increase in cadmium removal with an adsorbent dose can be attributed to availability of more adsorption sites. The rate of uptake increases with an increase in the adsorbent dosage, because it leads to the greater surface area for adsorption. Since there is no significance change in the adsorption rate above 0.04 g/25 ml at initial concentration of 50mg/L, this amount was fixed and assumed for all the adsorption studies.

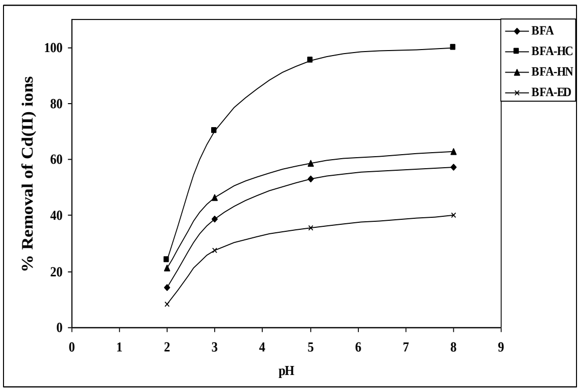

Fig 2. Effect of pH upon the % removal of Cd (II) ions onto BFA and its modified samples as a function of initial concentration = 50 mg/L, m = 0.04 g, V = 25 ml, time 2 h and T =25^{o}C

3.5. Effect of initial metal concentration and contact time

The effect of initial cadmium concentration (C_0) on the removal efficiency by BFA adsorbents at an optimum dose (0.04 g/25ml) is shown in Figure 4 (a). It can be concluded that the BFA-HC adsorbent performs the best removal of cadmium from the solution. Also, it is evident that the Cd (II) removal decreased with an increase in C_0 from 10 to 100 mg/L. This behavior may be due to an increase in the driving force. The effect of contact time on removal of Cd (II) by BFA adsorbents at 0.04 g/25ml and C_0 = 50 mg/L is shown in Figure 4 (b). As seen in this Figure, there is a rapid adsorption rate of metal ions in the first 5 min, and thereafter the adsorption rate gradually decreases, and adsorption reaches equilibrium within 30 min for all the samples.

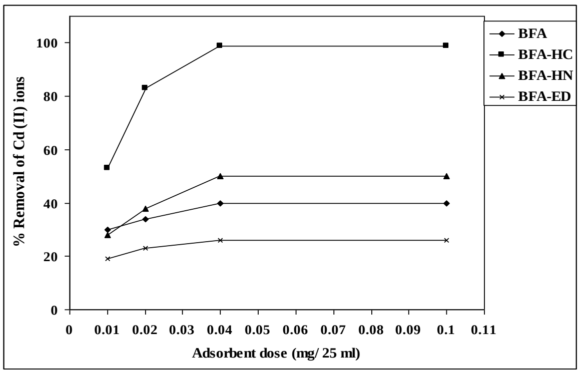

Fig 3. Effect of adsorbent dose upon the removal of Cd (II) onto BFA and its modified samples as a function of initial concentration = 50 mg/L, m = 0.04 g, V = 25 ml, time = 2 h, and, T =25^{o}C

The maximum amount of cadmium is attained within the first 30 min (25.8–97.5%) followed by a slower adsorption rate, until the equilibrium is reached. This behavior indicates that the developed adsorbents are more effective for removing cadmium from wastewater.

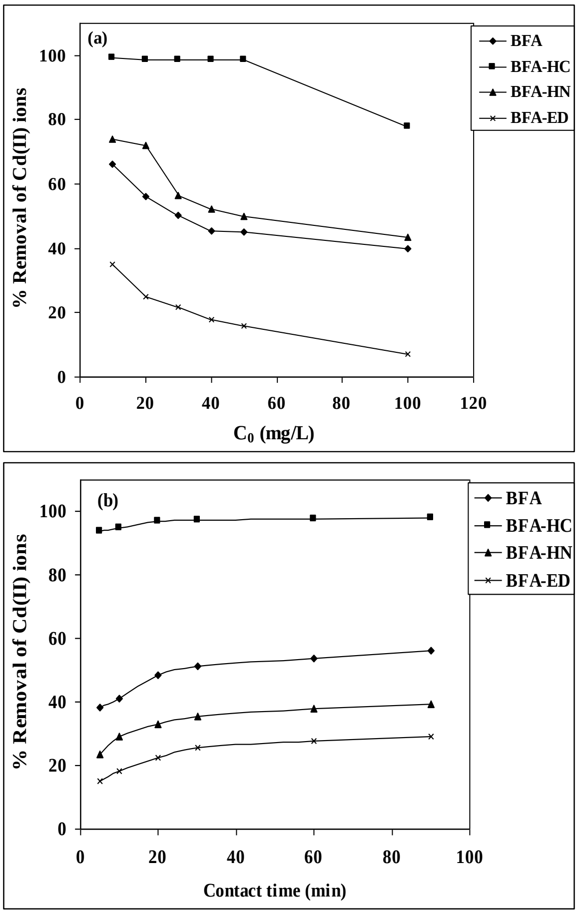

Fig 4. Effects of (a) initial Cd(II) concentration and (b) contact time upon the % removal of Cd (II) ions onto BFA and its modified samples as a function of initial concentration = 50 mg/L, m = 0.04 g, V = 25 ml, time 2 h and T =25°C

3.6. Effect of temperature

Temperature dependence of cadmium adsorption onto BFA-HC was carried out at 25, 40, and 60°C as shown in Figure 5 (a). This study was carried out on the BFA-HC sample due to its high adsorption capacity. It was found that the adsorption capacity increased from 30.8 to 31.8 mg/g with an increase in the temperature from 25 to 60°C for an initial concentration of 50 mg/L and adsorbent dosage of 0.04g/25ml. This confirms that the adsorption process of Cd (II) onto BFA-HC is an endothermic process.

Thermodynamic parameters such as standard Gibbs free energy (ΔG^0), enthalpy (ΔH^0), and entropy changes (ΔS^0) for the sorption process can be determined using the following equations:

$$\Delta G^0 = -RT \ln K_d \qquad (3)$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta \mathrm{H}^0}{\mathrm{RT}} \qquad (4)$$

where

K_d - distribution coefficient;

$K_\mathrm{d} = q_e / C_e$ (L/g).

From Van't Hoff equation (4), the values of ΔH^0 and ΔS^0 were obtained from the slope and intercept of the linear plot of $\ln K_d$ vs $1/T$ as presented in Fig. 5(b). Values of these parameters are listed in Table 2. Values of ΔG^0 are negative, confirming that adsorption of cadmium onto BFA-HC is spontaneous and thermodynamically favorable. The more negative values of ΔG^0 imply a greater driving force to the adsorption process. The value of ΔH^0 is positive indicating that the adsorption process is endothermic in nature. The positive value of ΔS^0 may be attributed to an increase in randomness during adsorption of cadmium on the BFA-HC surface.

3.7. Sorption isotherm

The results of the study on Cd (II) metal ions concentration dependence were subjected to the analysis by means of both Langmuir and Freundlich adsorption isotherms. The linear form of Langmuir isotherm is represented by the equation:

$$1/q_e = 1/Q_0 + 1/bQ_0\, C_e \qquad (5)$$

where,

q_e - amount adsorbed, mg/g;

C_e - equilibrium concentration of the adsorbate, mg/L;

Q_0, b - Langmuir constants related to maximum adsorption capacity and energy of adsorption, respectively.

When $1/q_e$ is plotted against $1/C_e$, a straight line with slope $1/bQ_0$ is obtained (not shown), which indicates that the adsorption of cadmium follows the Langmuir isotherm. Langmuir constants b and Q_0 are given in Table 3.

Table 3. Langmuir and Freundlich constants for the uptake of cadmium

Adsorbents	*Freundlich constants*			*Langmuir constants*			
	R^2	1/n	K_F	R^2	R_L	b, L/g	Q_0, mg/g
BFA	0.8557	0.352	2.07	0.9756	0.135	0.064	19.8
BFA-HC	0.6916	3.08	1.31	0.9996	0.345	0.019	47.6
BFA-HN	0.8215	1.83	1.32	0.9822	0.128	0.068	25.1
BFA-ED	0.8833	1.77	2.88	0.9745	0.039	0.245	11.9

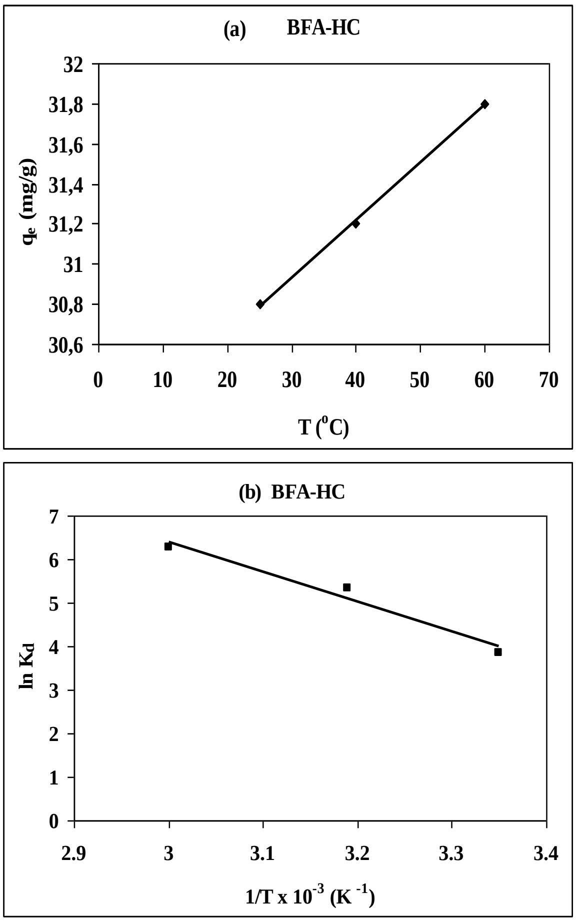

Fig 5. (a) Effect of the temperature on the cadmium adsorbed amount onto BFA-HC and (b) Van't Hoff plot for adsorption of Cd (II) by adsorbent dosage 0.04g/25ml, pH 5.0, C_0= 50 mg/L

Adsorption data of cadmium were also analyzed by the linear form of the Freundlich equation model as given:

$$\ln q_e = \ln K_F + 1/n \ln C_e \qquad (6)$$

where

K_F and $1/n$ - Freundlich constants related to adsorption capacity and adsorption intensity, respectively (Weber 1972).

When lnq_e is plotted against lnC_e, a straight line with slope $1/n$ is not obtained (not shown), which indicates that the adsorption of cadmium does not follow a Freundlich isotherm. Freundlich constants K_F and $1/n$ are calculated from the intercept and slope of the plot lnq_e *vs* lnC_e and given in Table 3. A value of 1/n below one indicates a normal Langmuir isotherm, while 1/n above one is indicative for cooperative adsorption (McKay et al. 1982) as seen in Table 3.

Also, dimensionless separation factor (R_L) (McKay et al. 1982) was calculated from Langmuir isotherm using the following equation: $R_L = 1/(1+ bC_e)$. The values of R_L were found to be 0.039–0.345 for cadmium, which indicates favorable adsorption ($R_L < 1$). In addition, correlation coefficients for a straight line drawn by Langmuir isotherm are higher than that drawn by Freundlich isotherm as seen in Table 3 (R^2 = 0.9745–0.9996 > 0.6916–0.8833). According to the above findings, it became clear that the Langmuir equation fitted the data better than the Freundlich equation by describing the data over the entire concentration range. The cadmium adsorption capacity (Q_0, mg/g) by BFA adsorbents was found to be in a decreasing order as follows: BFA-HC>BFA-HN>BFA>BFA-ED (*cf.* Table 3). BFA-HC showed the highest cadmium uptake (Q_0= 47.6 mg/g) in comparison with other samples. Finally, the chemical modification on BFA *viz.* HCl and HNO_3 resulted in enhancing the sorption capacity of BFA for Cd (II) uptake from 19.8 to 47.6 and 25.1 mg/g, and decreasing to 11.9 mg/g upon pretreatment with EDTA, respectively. Out of these adsorbents BFA-HC is an efficient one.

3.8. Kinetic studies

Kinetics of adsorption data was analyzed using different kinetic models, such as pseudo-first order, pseudo-second order, and intraparticle diffusion (Lagergren 1898; McKay and Ho1999; Ho 2004) which expressed in the following equations:

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (7)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\,2}} + \frac{t}{q_e} \qquad (8)$$

$$q_t = k_{id}\, t^{1/2} + C \qquad (9)$$

where

q_e and q_t - amounts of cadmium adsorbed (mg/g) at equilibrium and at time (t) (min), respectively.

k_1 and k_2 – constants, pseudo-first adsorption rate (min^{-1}) and pseudo-second adsorption rate (g/mg. min), which can be obtained from the linear slope of $\log (q_e–q_t)$ *vs* t *and* t/q_t *vs* t plots (not shown), respectively.

k_{id} , $t^{1/2}$ and C - intraparticle diffusion rate constant (mg/ g.min$^{1/2}$), square root of the time (min)$^{1/2}$, and intercept, respectively.

In a batch reactor with rapid stirring, there is also a possibility that the transport of cadmium (II) from the solution into the pores of the adsorbent is a rate-controlling step. This possibility was tested in terms of a graphical relationship between the amount of cadmium (II) adsorbed (mg/g) and the square root of time (min). Values of k_{id} and C are calculated from the slope and intercept of linear portion of $q_t – t^{1/2}$ plot as shown in Fig.6**.** The value of C is related to the thickness of a boundary layer. The extrapolation of linear straight lines to the time axis gives intercepts C. If C is equal to zero, the only controlling step is intraparticle diffusion. However, if $C \neq 0$, it indicates that the adsorption process is rather complex and involves more than one diffusive resistance. The values of these constants and correlation coefficients (R^2) for the three models are given in Table 4.

By applying a pseudo-first order model, it was observed that this model fits well for the first 20 min and thereafter the data deviate from Lagergren theory (1898), and then cannot be applied to the entire adsorption process. A similar trend was previously observed by Kalavathy et al. (2005) for copper adsorption onto activated rubber wood sawdust. This confirms that it is not applicable to predict the adsorption kinetics for Cd (II) onto BFA adsorbents for the entire sorption process. The correlation coefficient values (R^2) were found to be in the range of 0.5431–0.9252, as well as the q_e values were generally lower than the experimental ones which show that this model can not be applied (*cf.* Table 4).

From Table 3, it was assessed that the calculated pseudo-second order constants ranged from 3.51×10^{-3} to 0.119 g/mg. min, and the initial sorption rates ($h= k_2q_e^2$) were found to be in the range of 1.33 – 197 mg/g. min, which is high for the sorption of cadmium onto BFA-HC sorbent. Moreover, the calculated q_e values are reasonably closer to the experimental values than those from the pseudo-first order model, and yielded R^2 higher than 0.99 for all the adsorbents studied. This suggests that a pseudo-second order model can be considered for the entire adsorption process and confirms the chemisorption of cadmium onto adsorbents by rate-limiting mechanism through sharing or exchange of electron between sorbent and sorbate (McKay and Ho1999).

Figure 6 shows the intraparticle diffusion plots which represent two stages for adsorption of Cd (II) onto the pretreated BFA adsorbents. The initial curved portion relates to the boundary layer diffusion (film diffusion) and the latter linear portion refers to the intraparticle diffusion. Additionally, it should be emphasized that linear plots obtained for an intraparticle diffusion model do not pass through the origin. From these results it can be stated that the intraparticle diffusion is not solely responsible for the rate controlling.

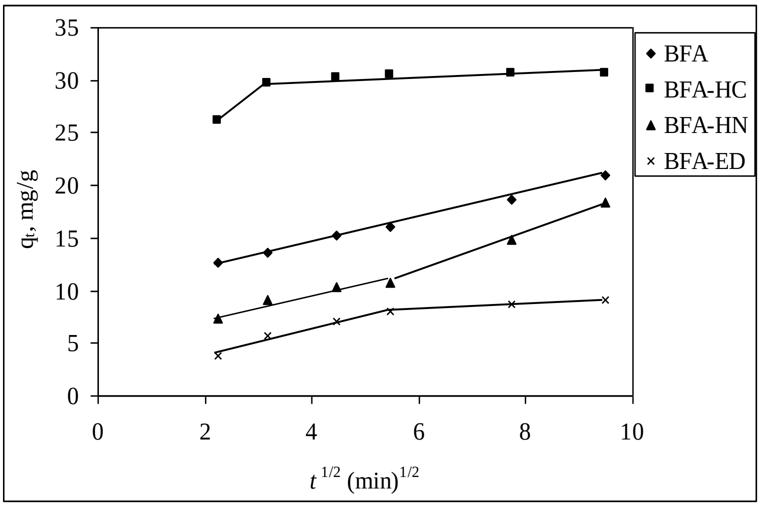

Fig 6. *Intraparticle diffusion plots for adsorption of cadmium onto BFA adsorbent*

Table 4. *Calculated kinetic model parameters and correlation coefficients for adsorption of Cd (II) using BFA adsorbents at* C_0 *= 50 mg/L, m = 0.04 g/25ml, time =2 h and T= 25°C*

Adsorbents	*Intraparticle diffusion*			*Pseudo-second order*				*Pseudo-first order*			
	R^2	C	k_{id}	R^2	h	$q_{e, cal}$, mg/g	k_2	R^2	$q_{e, cal}$ (mg/g)	k_1	$q_{e, exp}$ (mg/g)
BFA	0.9504	10.4	0.952	0.9971	3.29	16.8	0.010	0.9251	18.6	5.29×10^{-3}	15.5
BFA-HC	0.7611	29.3	0.162	1	197.1	30.8	0.119	0.7294	1.52	0.012	30.8
BFA-HN	0.8792	4.23	1.30	0.9962	1.33	19.5	3.50×10^{-3}	0.9225	24.7	6.45×10^{-3}	19.6
BFA-ED	0.9046	4.02	0.589	0.9992	1.50	9.69	1.70×10^{-3}	0.5427	42.5	9.44×10^{-3}	8.1

4. Conclusions

In the present study the cadmium sorption characteristics of bagasse fly ash modified by HCl, HNO_3, and EDTA acids were examined. Cadmium adsorption was found to be dependent on pH solution, contact time, initial metal concentration, adsorbent dosage, and temperature. The Langmuir model correlates well with experimental data. Kinetic studies show that the cadmium sorption process follows the pseudo-second-order kinetic model. Adsorption of cadmium was carried out by chemisorption and controlled by film and intraparticle diffusions at lower and higher contact time. The temperature dependence and thermodynamic results indicate an endothermic and spontaneous process. Accordingly, this study showed that the modified BFA sorbents with HCl and HNO_3 acids are more effective than with EDTA because they yielded high cadmium removal capacity, and hence they can be used in removing heavy metals from wastewater.

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Išspaudų pelenų absorbcinių savybių kaita šalinant kadmį iš vandeninių tirpalų

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Straipsnyje aprašomas tyrimas, kaip naudojant apdorotus išspaudų pelenų absorbentus (IPA) galima iš nuotekų šalinti kadmį. IPA yra naujas ir pigus preparatas, išgautas panaudojus paviršinio cheminio modifikavimo metodą. Atliekant tyrimą analizuota šių veiksnių įtaka natūralaus ir modifikuoto IPA aktyvumui šalinant Cd (II): tirpalo pH, sąlyčio laikas, pirminė metalų koncentracija, absorbente dozė ir temperatūra. IPA absorbento paviršiaus savybės analizuotos pagal pHpzc, C, H, N ir S elementų analizę ir FTIR spektroskopiją. Pusiausvyros duomenys analizuoti pagal *Langmuir* ir *Freundlich* izoterminius modelius. Chemiškai apdorojus IPA HCl ir HNO_3 buvo padidintos IPA absorbcinės savybės atitinkamai nuo 19,8 iki 47,6 ir 25,1 mg/g, o apdirbus EDTA sumažėjo absorbcija iki 11,9 mg/g. Kinetinė analizė parodė, kad kadmio absorbcijos procesas atitiko pseudoantrosios eilės kinetinį modelį. Apibendrinus tyrimo rezultatus galima teigti, kad apdorotas IPA gali būti naudojamas kaip alternatyvi medžiaga brangesniems absorbentams, šalinant kadmį (II) iš nuotekų.