

Evaluation of Modified Bagasse Fly Ash Nanoparticles on Cadmium (II) Removal from Contaminated Waters

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Abstract – The present essay deals with adsorption of cadmium (Cd(II)) ion on to nano and micro scales of bagasse fly ash (BFA) from single component system. Bagasse fly ash is an industrial waste of sugar industry that used for removal of Cadmium ion under batch test conditions. Raw bagasse was pretreated with 0.1 N NaOH followed by 0.1 N CH₃COOH before its application. Effect of various operating variables such as, solution pH, equilibrium time, adsorbent dose, adsorbate concentration on the removal of Cadmium has been studied. Maximum adsorption of cadmium occurred at a pH value of 6 using both adsorbent. A dose of 4 g.L⁻¹ and 10 g.L⁻¹ nano and micro adsorbent was sufficient for the optimum removal of Cadmium ion respectively. Adsorption process by using nano and micro particles was attained equilibrium within 15 min and 80 min respectively. The sorption data has been correlated with Freundlich and Langmuir adsorption models. The materials exhibit good adsorption capacity and the adsorption data followed the Freundlich model better than Langmuir model.

Keywords – Adsorption, Aqueous Solution, Bagasse Nanoparticles, Cadmium.

I. INTRODUCTION

The presence of trace metals in the aquatic environment has been of a great concern because of their toxicity and non-biodegradable nature (Maccarthy et al, 1995). This metal exist in various industries, such as electroplating, plastics, pigments, mining and find their way to the aquatic environment through wastewater discharges which jeopardize the environment and human lives severely. Therefore, a systematic study on the removal of Cadmium from wastewater is of considerable significance from environmental point of view. Activated Carbon adsorption is a well-known method for the removal of heavy metals. But the high cost of it restricts large-scale use for the abatement of heavy metals pollution. Due to its high cost and about 10- 15% loss during regeneration, unconventional adsorbents like bagasse fly ash, peal, wood, saw dust, etc have attracted the attention of several investigators. Nano technology is being explored for its potential to provide new solutions to managing and cleaning up pollution in our water and land, and improving the performance of unconventional technologies used in cleanup efforts. researchs is needed to develop pollution control technologies and determine the application of nanotechnology to enhance manufacturing efficiencies so that pollution is prevented. For instance, nano materials from natural bio products may replace some pollution is prevented. For instance, nano materials from natural bio products may replace some petroleum-based materials,

thus reducing the pollution that occurs in the production and disposal of these products. Examining the potential of some organic particles to remediate industrial waste contaminated generated as a result of manufacturing and power-generation operation. The aim of the present study is to (i) study the feasibility of using BFA as an adsorbent for removal of Cd(II) metal ion from aqueous solutions.(ii) investigation the novel methods which are being generated by the nano technology for produce organic nano scale materials to remove Cd(II) from wastewater. (iii) determine the effect of initial (pH₀), contact time, adsorbent dose and initial concentration of adsorbate (iv) comparing the capability of nano particles and micro particles adsorbent.

II. THEORY

A. Adsorption Isotherm

To optimize the design of an adsorption system for the adsorption of adsorbates, it is important to establish the most appropriate correlation for the equilibrium curves. Various isotherm equations like those of Freundlich, Langmuir have been used to describe the equilibrium characteristics.

B. 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 on to the surface. This isotherm suggest that uptake occur on homogeneous surface by monolayer adsorption without interaction between the adsorbed materials.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (1)$$

where K_L is the Langmuir adsorption (L/mg) related to the energy of adsorption and q_m signifies the adsorption capacity of the adsorbent (mg/g), C_e is the equilibrium liquid – phase concentration of the adsorbate (mg/L) and q_e is the equilibrium adsorbate loading on to the adsorbent (mg/g).

RMSE value and higher R² value are regard to show goodness of agreement between measured and estimated Cd²⁺ adsorbed data.

C. Freundlich isotherm

The Freundlich isotherm represent the most widely nonlinear adsorption models. This model proposes monolayer sorption with a heterogeneous energy distribution of actives sites, accompanied by interaction between adsorbed molecules. The Freundlich equation can be represented as follow.

$$q_e = K_f C_e^{1/n} \quad (2)$$

D. Goodness of model fit

In this research, the goodness of fit between experimental and model estimated data was assessed by the linear coefficient of determination (R^2) and Root mean square error (RMSE) as follows:

$$RMSE = \sqrt{\frac{\sum_{i=1}^n (q_e - q_c)^2}{n}} \quad (3)$$

where q_e and q_c are the measured and model estimated amount of Cd^{2+} adsorbed, respectively, estimated Cd^{2+} adsorbed data.

III. EXPERIMENTAL METHODOLOGY

All chemicals used in this study were of analytical purity. The experiments were performed at room temperature ($20 \pm 2^\circ C$) using 250 mL Erlen Mayer containing 50 mL Cadmium solution. Stock solution of single heavy metal was prepared by dissolving $Cd(NO_3)_2 \cdot 4H_2O$ in double distilled water and diluted to desired concentrations when being used. HCl and NaOH were used to adjust the pH value of experimental solutions. A pH meter (ino lab 1 model) was used for pH measurements. X-ray diffraction analysis of BFA was carried out using (XRD wp Philip 1840 model). The specific surface of the adsorbents was measured. By Brunauer-Emmett-Teller (BET) method. IR spectra of the samples were recorded on an infrared spectrophotometer (NEMOB BM 102 model). The moisture and density of the adsorbent were determined by ASTM (D2867-99) standard and specific gravity bottles, respectively. Particle-size Analysis of nano and micro particles were carried out using Laser Particle-sizer "Analystte 22" Nano Tec model and standard sieves respectively. SEM pictures were taken for determination of particles surface morphology and particles size.

A. Adsorbent development

Bagasse, a solid waste material of the sugar industry, was collected from a sugar factory. Bagasse was first washed thoroughly with the distilled water to remove the dust particles and dried under the sun rays. Dried bagasse was then soaked 5 hours in the 0.1 N NaOH solution to remove the lignin content (Chhatre et al., 1996) and again washed well with double distilled water. The bagasse was then soaked in 0.1 N CH_3COOH for a period of 1-2 hours to remove the traces of NaOH (Rao et al., 2002). Thereafter bagasse was thoroughly washed again with double water till the wash water become colorless and the combusted in the oven at $100^\circ C$ for a period of 24 h. The prepared substance sieved for 4 hours at rate of 340 rpm to produce nano particle size. Also for providing micro particle size (150- 200), it sieved for 20 min at rate of 60 rpm. Nano particles adsorbent was then soaked 2 hours in 2% Triton X- 100 in order to disperse particles. After separation, solid nano particles vacuum-dried for 3 h and stored in desiccator.

B. Adsorption isotherm experiment

For single metal- BFA system, initial metal ion concentration was varied from 2 to 20 $mg \cdot L^{-1}$. In all cases, The pH of the solution was maintained at 6.0. This pH was found to be the optimum on the basis of batch tests carried out to determine the effect of pH on adsorption capacity of BFA for metal ion. The removal of efficiency (R) of Cadmium was calculated as: (Bahrami et al; 2012, malekian et al; 2011).

$$R = \frac{C_i - C_f}{C_i} \times 100 \quad (4)$$

The amount of cadmium adsorbed on the sorbent phase ($mg \cdot g^{-1}$) was calculated as:

$$q = \frac{C_i - C_f}{C_i} \times V \quad (5)$$

where q is the amount of Cadmium adsorbed per unit weight of adsorbent, V is the volume of the liquid phase (L), m is the weight of adsorbent (g) and C_i and C_f are the initial and final concentration of Cadmium ($mg \cdot L^{-1}$) in water.

IV. RESULT AND DISCUSSION

A. Physical and chemical properties of adsorbents.

Curve of particles size analysis of nano adsorbent is shown in fig 1. The particle size of micro BFA were < 125 (40.20%), 180 (35.00%) and 250 (25%) μm . moisture content, Bulk density of BFA were 4.48%, 168 kg/m^3 respectively for nano adsorbent and 6.61%, 258 kg/m^3 for micro adsorbent. X-ray spectrum of nano BFA reflects the presence of SiO_2 (Quartz), C (Cliftonite), SiC (Moissanite), Fe (Hematite), Ti_6O (Titanium. Oxid) and Cao (Calsite). X-ray spectrum of micro BFA reflects the presence of Si_2O , SiC and Cao (Vimal Chandra et al; 2005). The specific surface area was measured by N_2 adsorption isotherm. Nitrogen was used as cold bath (77.15K). The BET surface area were 210.80 and 154.40 m^2/g for nano and micro particles respectively. FTIR spectrometer was employed to determine the presence of functional groups in nano and micro BFA at room temperature. Pellet (pressed - disk) technique by using the same ratio of each adsorbent in KBr was used for this purpose.

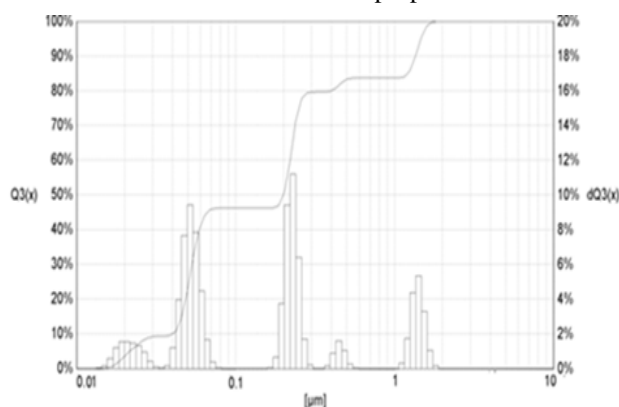


Fig.1. Result of Laser particle size Analysis (LPSA) of nano particles of bagasse fly ash

According to FTIR spectra, a broad band between 3100 and 3700 cm^{-1} in BFA indicated the presence of both free and hydrogen bonded OH groups on the adsorbents surface (Kamath et al, 1998). The FTIR spectra of BFA adsorbents indicated peaks in region of 1600 – 1800 cm^{-1} corresponding to C=O the surface is likely to give considerable cation exchange capacity to the adsorbents (Ho et al, 2001).

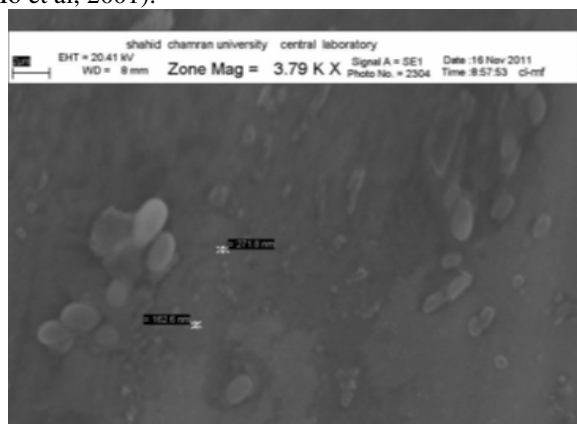


Fig.2. SEM picture for nano particles of bagasse

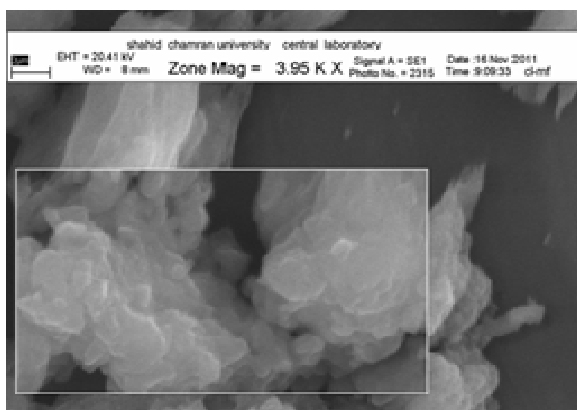


Fig.3. SEM picture for micro particles of BFA

B. Effect of operating variables

a) effect of initial pH

The pH of the adsorbate solution has significant effect on the sorption of adsorbates on different adsorbent. This is due to the fact that at pH 3 and 4, the hydrogen ion itself is a strong competing adsorbate, thus explain the weak adsorption in acid medium. partly due to the chemical speciation of metal ions under the influence of the solution pH. It is known that cadmium species are present in deionized water in the forms of Cd^{2+} , $\text{Cd}(\text{OH})^+$, $\text{Cd}(\text{OH})_2(\text{s})$. The concentration of The hydrolyzed cadmium species depends on the solution pH and cadmium concentration. It is evident that Cd^{2+} ions are the only ionic species present in the solution for $\text{pH} < 6$ and alkaline range precipitation plays main role in removing the cadmium ion attributed to the formation of precipitation of $\text{Cd}(\text{OH})_2(\text{s})$. The effect of pH_0 on the removal of individual Cd(II) ion by nano and micro particles of BFA are shown in fig (4). The removal of metal ion is found to increase with an increase in the pH_0 from 3 to 6. Themaximum uptake of metal ion was obtained at $\text{pH}_0=6$. The removal of metal ion decrease at pH between 6 to 8. Decrease of

cadmium adsorption at $\text{pH} > 6$ was due to formation of dissolved hydroxyl groups (Rahmani et al., 2010; Shih and Dong, 2009; Krishnan and Anirudhan, 2003).

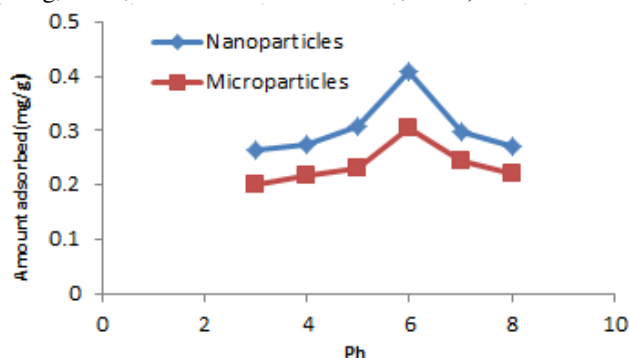


Fig.4. Effect of pH on adsorption of Cd(II)

b) Effect of contact time

The adsorption data for the uptake of cadmium versus contact time for a fixed adsorbents dose of 10 g.L^{-1} are shown in fig (5). The initial concentration of 20 mg.L^{-1} for cadmium was taken for experiment. These plot indicate that there is no appreciable change in the removal of cadmium in the case of nano particles adsorbent after 15 min and 80 min in the case of micro particles adsorbent. During the initial stage of sorption, a large number of vacant surface sites are available for adsorption. After a lapse of some time, the remaining vacant surface sites are difficult to occupied due to repulsive forces between the adsorbate molecules on the solid surface and in the bulk phase(VimalChandhra et al, 2005).

c) Effect of adsorbent dose

The effect of the adsorbent dose on the removal of cadmium using nano particles and micro particles of BFA are shown in fig (6). The efficiency of adsorption of cadmium increased from 2 to 4 g.L^{-1} in case of nanoparticles adsorbent and then with increasing adsorbent dose the removal of cadmium decreased. This was because of the availability of more binding site it in the solution is made the particles to be stuck, therefore they can't uptake the metal ions, although amount of adsorption has been lost by increasing adsorbent but the efficiency is most at the (4 g.L^{-1}) nanoparticles, hence this amount is the optimum dose. The result indicate that a dose of 10 g.L^{-1} of micro particles adsorbent is sufficient for the optimum removal of Cadmium ion.

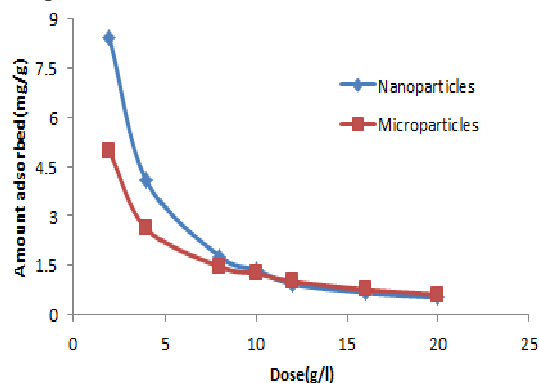


Fig.6. Effect of adsorbent dose on amount of adsorption Cd(II)

d) Effect of initial concentration

The effect of initial concentration on the adsorption of Cadmium by using two adsorbents is showed in fig (7). These plot showed that the total metal ion adsorbed increased sharply in the beginning and then slowly towards the end of the run. At low initial solution concentration, the surface area and the availability of adsorption sites were relatively high, and the Cd(II) ions were easily adsorbed. At higher initial solution concentration, the total available adsorption sites are limited, thus resulting in a decrease in percentage removal of Cd(II) ions.

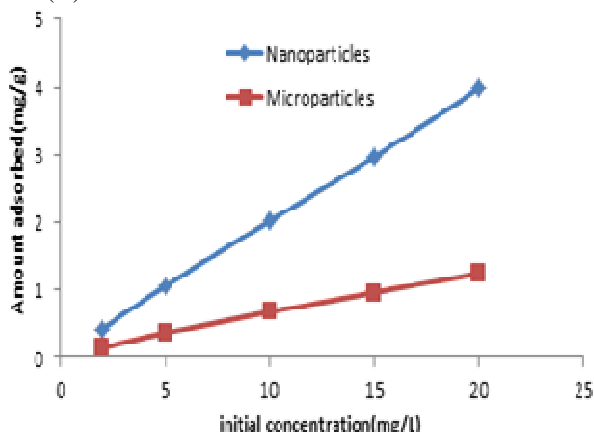


Fig.7. Effect of initial concentration on adsorption of cadmium

e) Adsorption Isotherm

To optimize the design of an adsorption system for the adsorption of adsorbates, it is important to establish the most appropriate isotherm model. Various isotherm equations like those of Freundlich, Langmuir have been used to describe the equilibrium characteristics of adsorption of Cd(II) ion on to BFA. The experimental equilibrium adsorption data were obtained by varying the concentrations of Cd(II) ion with a fixed dosage of BFA (4 g.l⁻¹) for nanoparticles and (10 g.l⁻¹) for micro particles adsorbent. The adsorption parameters for metal ion obtained from the fitting of different isotherm models with the experimental data are listed in table (1). The R² values are closer to unity and RMSE values are less for Freundlich models than that for the Langmuir model. It is expected that the Freundlich isotherm equation can better represent the equilibrium sorption data. Therefore, BFA has a heterogeneous surface for the adsorption of metal ion. Moreover, in the case of nanoparticles of BFA the maximum adsorption capacity (q_m) was 5.69 mg.g⁻¹ which is more than values of cadmium adsorption on activated carbon (3.37mg.g⁻¹) (An et al., 2001) and hematite (4.96mg.g⁻¹) (Singh et al., 1998). Isotherm models of Cd(II) adsorption by both adsorbents have been shown in fig 8 and 9.

Table 1: Isotherm parameters values for the removal of Cadmium (II) by nano and micro particles of bagasse fly ash

RMSE	R ²	q _m (mg/g)	K _L (L/mg)	Langmuir
0.4067	0.9393	5.694	0.3559	Nano particles adsorbent
0.02445	0.9977	3.266	0.08055	Micro particles adsorbent
RMSE	R ²	n	K _F	Freundlich
0.1664	0.9934	1.18	1.187	Nano particles adsorbent
0.01751	0.9988	1.31	0.268	Micro particles adsorbent

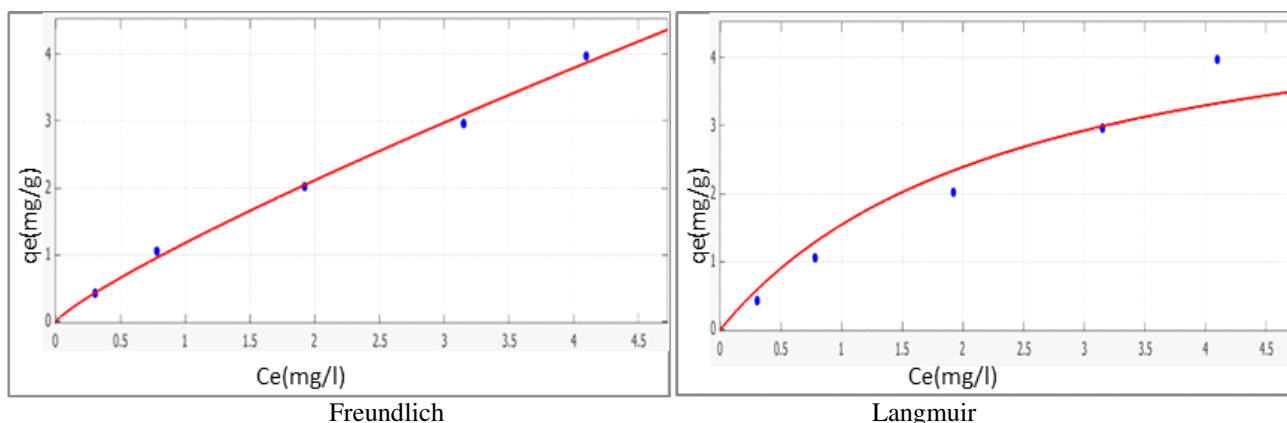


Fig.8. Isotherm models of Cd(II) adsorption using nanoparticles BFA

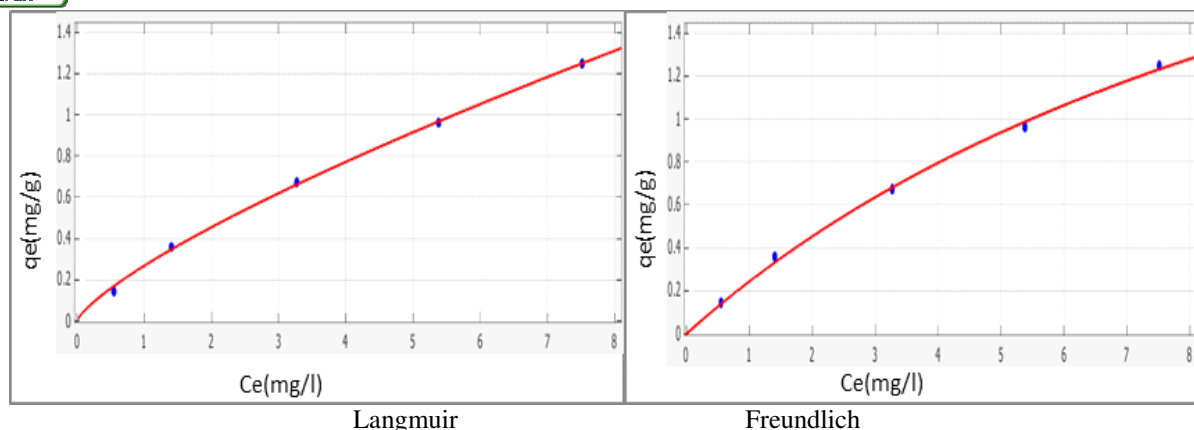


Fig.9. Isotherm models of Cd(II) adsorption using microparticles BFA

V. CONCLUSION

The present study shows that the bagasse fly ash is an effective adsorbent for the removal of Cd(II) metal ion from aqueous solution. The results indicate that the size of particles play a main role in the removal of Cd(II) and nano particles are more effective for abatement of Cd(II) ion from contaminated water. The optimum pH of system was determined 6 value for two adsorbents. The adsorptive uptake of metal ion was very fast during the initial sorption period about 10 min. Freundlich isotherm shows very well fit with the experimental adsorption equilibrium data.

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