Activated Carbon from Spent Brewery Barley Husks for Cadmium Ion Adsorption from Aqueous Solution

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ABSTRACT

This study investigated the feasibility of using acid activated carbon prepared from brewery spent barley husks for the adsorption of cadmium ion from aqueous solution. The effects of operation parameters such as pH, contact time, adsorbent dosage, concentration and temperature were verified. The amount of cadmium ion adsorbed increased with increase in solution pH, initial solution concentration and with the amount of adsorbent dosed. A time of 5 min was required for attainment of equilibrium. The equilibrium data obtained were analyzed by using the non-linear forms of both Langmuir and Freundlich isotherm models. The data were better described by Langmuir model because it presented a higher correlation coefficient and lower error values than Freundlich model. Non-linear kinetic modeling of the adsorption process revealed that the adsorption of cadmium ion by the activated carbon followed the pseudo-first order kinetic. The thermodynamic parameters revealed that the removal of cadmium by the activated carbon was exothermic and spontaneous. Thus, activated carbon obtained from brewery spent barley husks can be employed as an economically viable low-cost adsorbent for removing cadmium ion from aqueous solution.

Keywords: *Cadmium; activated carbon; barley husk; adsorbent*

ABSTRAK

Kajian ini meneliti kelayakan penggunaan karbon teraktivasi asam yang dibuat dari sekam jelai untuk mengadsorpsi ion kadmium dari larutan. Pengaruh parameter operasi seperti pH, waktu kontak, dosis adsorben, konsentrasi dan temperatur diverifikasi. Jumlah kadmium yang teradsorpsi meningkat dengan kenaikan pH larutan, konsentrasi awal ion cadmium dan dengan jumlah dosis adsorben. Untuk mencapai ekuilibrium diperlukan waktu 5 menit. Data ekuilibrium yang diperoleh dianalisis dengan menggunakan bentuk non-linear dari model isoterm Langmuir dan Freundlich. Data lebih baik dijelaskan dengan model Langmuir karena menghasilkan nilai koefisien korelasi lebih tinggi dan nilai kesalahan lebih rendah daripada model Freundlich. Pemodelan kinetik non linear menunjukkan bahwa adsorpsi ion cadmium oleh karbon aktif mengikuti kinetika pseudo-orde pertama. Parameter termodinamika menunjukkan bahwa adsorpsi ion kadmium oleh karbon aktif bersifat eksotermik dan spontan. Dengan demikian, karbon aktif yang diperoleh dari sekam jelai dari tempat pembuatan bir dapat digunakan sebagai adsorben murah yang layak secara ekonomis untuk menghilangkan ion cadmium dari larutan.

Kata Kunci: *Kadmium; karbon aktif; sekam jelai; adsorben*

INTRODUCTION

Heavy metals are constantly introduced into the aquatic environment principally through industrial activities. These metals can be absorbed by organisms easily because of their high solubility in water. Once they enter the food chain, large concentrations of heavy metals may accumulate in human body. If the metals are ingested beyond the permitted concentration, they can cause serious health disorders [1]. Therefore, it is necessary to treat metal-contaminated wastewater prior to its discharge to the environment. Heavy metal removal from inorganic effluent can be achieved by conventional treatment processes such as chemical precipitation, ion exchange, adsorption and electrochemical removal. These processes have significant disadvantages, which are, for instance, incomplete metal removal, high-energy requirements, and production of toxic sludge [2-3]. Of these conventional techniques, adsorption and ion exchange are the most efficient [2]. In addition, numerous approaches have been studied for the development of cheaper and more effective technologies, both to decrease the amount of wastewater produced and to improve the quality of the treated effluent.

Adsorption using activated carbon has been proved to be one of the best alternative treatment methods because it is simple, cheap, efficient, and

relatively ecofriendly [4-5]. Activated carbon is known to be very efficient for heavy metal removal due to its high porosity, large surface area, variable characteristic surface chemistry, high degree of surface activity and high affinity for metals [6-7]. Barley grain husk is the most abundant by-product generated from the beer brewing process representing approximately 85% of the total by-products obtained. This material is usually obtained as a solid residue after worth production [8].

This study was undertaken to prepare activated carbon from brewery spent barley husks and determine the feasibility and efficiency of the activated carbon as an adsorbent for treating cadmium laden wastewater. The effects of operating parameters such as pH, contact time, concentration, adsorbent dosage and temperature on the adsorption of cadmium from aqueous solution were also investigated. Both Langmuir and Freundlich isotherm models were employed to describe the isotherm parameters of the process.

EXPERIMENTAL SECTION

Collection and Preparation of Activated Carbon from Brewery Spent Barley Husk

Spent barley husks were obtained from Nigeria Breweries Plc, Ibadan, Oyo State, Nigeria. The husks were thoroughly washed with distilled water and sun-dried for 6 h and later oven dried at 105 °C to remove the remaining moisture content. The dried husks were stored in desiccators to avoid exposure to atmospheric moisture and transferred into a well-sealed and air- tight container in readiness for carbonization and activation.

Carbonization

The carbonization of the husks was carried out in the Chemistry laboratory of Afe Babalola University, Ado-Ekiti, Ekiti State, Nigeria using a muffle furnace (Vecstar Ltd England) which allows little supply of air. Carbonization was done at 350 °C for 30 min. The carbonized material was then collected into a desiccator and allowed to cool at room temperature [9].

Chemical Activation with Phosphoric Acid (H₃PO₄)

The chemical activation of the carbonized husks was carried out according to the method of [9] with slight modifications. Portions of the carbonized sample were sieved with a 425 µm mesh in Biology Laboratory of Afe Babalola University, Ado-Ekiti and a carefully weighed amount (25.0 ± 0.01 g) was placed in a beaker containing 500 cm^3 of 0.3 M Ortho-phosphoric acid (H₃PO₄). The contents of the beaker were thoroughly mixed and heated on a magnetic stirrer with a hot plate

until it formed a paste. The paste was transferred to an evaporating dish which was placed in a furnace and heated at 500 °C for 30 min. This was allowed to cool to room temperature overnight. It was then neutralized with KOH and washed with distilled water till the pH was constant. This was further oven dried at 105 °C to a constant weight and was kept in an air tight 1000 mL reagent bottle.

Fourier Transform Infrared Spectroscopy

To give qualitative and preliminary analysis of the main functional groups that might be involved in heavy metal removal, FT-IR analysis in solid phase was performed on the adsorbents before and after heavy metal removal using Fourier Transform Infrared Spectrometer (Shimadzu 100 series spectrometer, USA). This was conducted at the central research laboratory of Ladoke Akintola University of Technology, Ogbomoso, Oyo State. Five milligrams (5 mg) of the adsorbent was homogenously mixed with dry potassium bromide and made pellets in a disc by applying pressure. The spectra of the adsorbents were measured within the range of 4000–400 cm^{-1} wave number. The spectra were plotted using the same scale on the transmittance axis for the adsorbents before and after adsorption.

Preparation of Stock Solution

A stock solution containing 1000 mgL^{-1} of the metal was prepared by dissolving 1.85 g of analytical grade Cd(NO₃)₂.4H₂O with distilled water in a 1 L standard flask. This was made to mark with distilled water. Standard solutions of different concentrations, as might be required, were later prepared from this stock.

General Procedure for Batch Studies

Adsorption experiments were carried out through batch process in 100 mL conical flasks containing 25 mL cadmium solution. A water bath shaker (Search Tech Instrument SHZ-82 Thermostatic, India) operated at a constant speed was used. Unless otherwise stated, all experiments were carried out by agitating 0.1 g of activated carbon with 20 mgL^{-1} of cadmium solution at room temperature for 90 min. The mixture of the adsorbent and the cadmium solution was filtered under vacuum after agitation and the absorbance of the residual cadmium present in the filtrate was determined by AAS (Atomic Absorption Spectrometer) model 752 (Gallenkomp, UK). The amount of cadmium adsorbed per unit mass of adsorbent was determined according to Eq. (1) while the percentage cadmium removal (%R), was calculated according to Eq. (2).

$$q = \frac{(C_i - C_f)V}{m} \qquad (1)$$

$$\%R = \frac{(C_i - C_f) \times 100}{C_i} \qquad (2)$$

where, m is the mass of the activated carbon (g), V is the volume of the solution (L), C_i is the initial concentration of Cd (mgL^{-1}) and C_f is the concentration of the metal left in the liquid phase (mgL^{-1}).

Determination of Optimum pH

The pH of different standard solutions (each containing 20 mgL^{-1} Cd) was adjusted differently to pH 1.5, 2, 3, 4, 5, 6, 7 and 8. The pH range was not increased beyond 8 to avoid precipitation of cadmium ions. Twenty five milliliters (25 mL) of each solution of known pH was measured into different conical flasks. Then 0.1g of the prepared activated carbon was measured into each conical flask. The mixture was agitated for 90 min. The mixture was filtered and 1 mL of the filtrate was diluted to 5 mL with distilled water. The concentration of Cd(II) was determined using Atomic Absorption Spectrometer.

Determination of the Effects of Agitation Time, Initial Cd Concentration and Temperature

The effect of agitation time was determined by varying the agitation time from 2 to 90 min while all other parameters were kept constant as described under general procedure. The effect of initial metal concentration was investigated by keeping other parameters constant but changing the initial concentration of the cadmium solution as follows: 15, 20, 25, 30, 35, 40, 45, and 50 mgL^{-1}. In investigating the effect of temperature, the temperature range of 25–45 °C was used while other parameters were kept constant. All the experiments under this section were conducted at the optimum pH earlier determined.

Statistical Evaluation of the Kinetic and Isotherm Parameters

The kinetic and equilibrium models used in this study were fitted by employing the non-linear fitting method to determine the kinetic and isotherm parameters. This was carried out by minimizing the respective coefficient of determination, R^2 between the experimental and the model predicted or calculated adsorption capacity using the *solver* add-in software on Microsoft's Excel spreadsheet, Microsoft's Corporation. In addition, the Chi Square (X^2) error function was also used to minimize the error distribution between the

experimental q data and the model predicted data. The Chi Square error function is presented in Eq. (3).

$$X^2 = \sum_{i=1}^{n} \frac{(q_{e\,cal} - q_{e\,exp})}{q_{e\,exp}} \qquad (3)$$

where $q_{e\,cal}$ is each value of q predicted by the fitted model and $q_{e\,exp}$ is each value of q measured experimentally and n is the number of experiments performed.

RESULT AND DISCUSSION

FTIR Analysis of the Adsorbent before and after Cadmium Adsorption

The interaction between Cd and the active functional groups on the surface of the activated carbon was studied using FTIR spectroscopic analysis. The IR spectrum of the activated carbon before Cd adsorption is shown in Fig. 1a while its spectrum after adsorption of Cd is shown in Fig. 1b. A list of the major functional groups on the adsorbent surface before and after Cd adsorption is shown in Table 1. It is obvious that the adsorbent was carbonaceous because all the absorption bands shown in Fig. 1 and Table 1 revealed only the presence of carbon based functional groups. The increase in the intensity of the peaks at 2921.46 and 1576 cm^{-1} after adsorption of Cd(II) can be attributed to stretching vibration of C-H out of plane and C=C stretching vibration, respectively. Additional peaks between 800 and 466 cm^{-1} can be due to C–H out of plane bending vibration [10].

Table 1 revealed the presence of no other functional groups than carbon related functional groups. No absorption bands for amine, amide, nitro group or sulphide were noticed. Of course, the presence of these functional groups should not be expected because of carbonization. It is also revealing that there were very slight shifts in the FTIR absorption bands after cadmium removal by the activated carbon. This shows that no bonds were formed between the surface of the activated carbon and the adsorbed cadmium ion. Therefore, adsorption of Cd onto the surface of the activated carbon was purely physical in nature

Effect of pH

Of all the parameters affecting adsorption from aqueous medium, solution pH usually plays a major role in adsorption and seems to affect the solution chemistry of metals (particularly metal speciation) and the activity of the functional groups of the adsorbent [11]. Furthermore, high solution pH tends to decrease
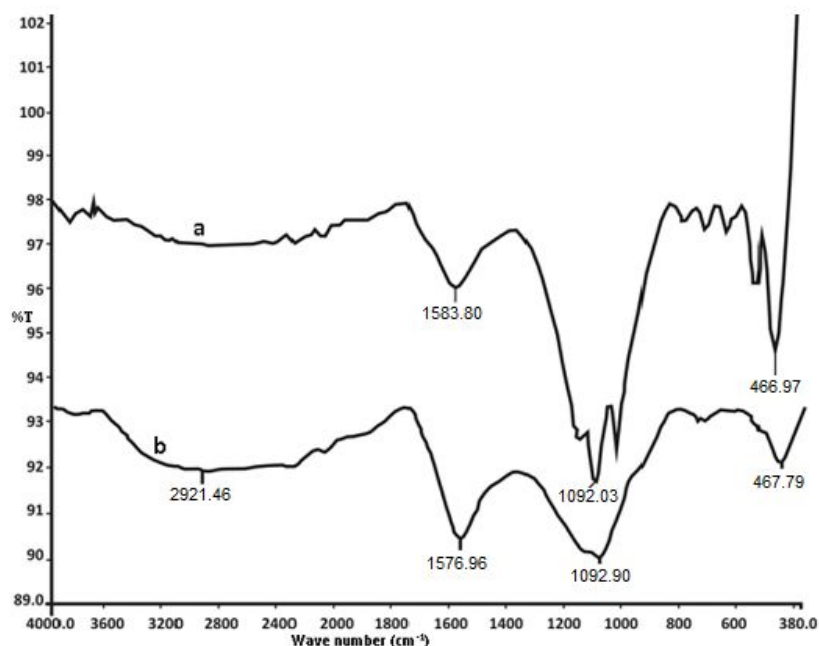
Fig1. FTIR spectrum of acid activated carbon from spent barley husk (a) before adsorption and (b) after adsorption

Table 1. FTIR spectral characteristics before and after cadmium removal

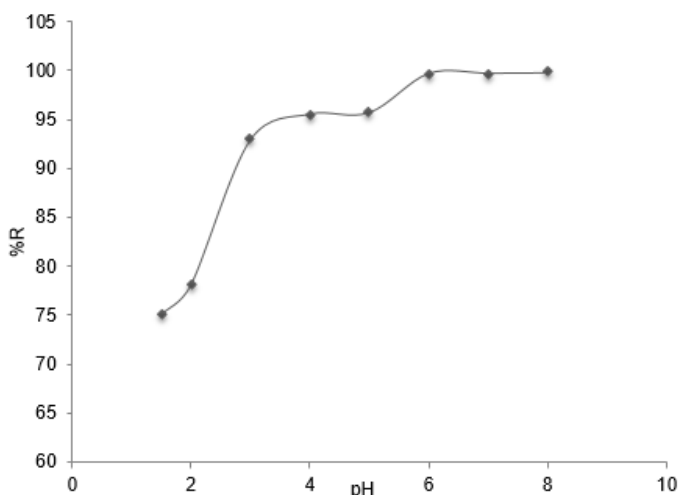| IR Peak (cm^{-1}) Before Adsorption	IR Peak(cm^{-1}) After Adsorption	Bond Type	Remarks
466.97	467.79		Increase in vibrational band
1092.03	1092.90	C-O stretching	Increase in vibrational band
1583.80	1576.96	C=C ring stretch of aromatic rings	Decrease in vibrational band
-	2921.46	C-H stretching	Appearance of bands 2921.46cm^{-1}.

Fig 2. Effect of pH on the removal of cadmium by activated carbon from brewery spent barley husks

solubility of metal complexes thereby bringing about precipitation, which may complicate the sorption process [11]. The result of the experiment conducted on the effect of pH on the adsorption of Cd(II) by the activated carbon produced from brewery spent barley husks is presented in Fig. 2. It is observed that increase in

solution pH brought about increase in the percentage of cadmium removed. The percentage removal of Cd increased from 75 to 99.75% when the pH was raised from pH 1.5 to 6. This happens because at low pH values, the surface of the activated carbon is saturated with hydrogen ions. This discourages the removal of Cd^{2+} ions because of the mutual repulsion that exists between cadmium and hydrogen ions [12-14]. However, at high pH values, the concentration of hydrogen ions decreases and this in turn increases the amount of Cd(II) adsorbed. The pH of optimum adsorption was found to be 6. pH increase from 6 to 8 seemed to have little or no effect on percentage removal of Cd(II). The interaction between the adsorbent and Cd(II) was electrostatic. At low pH values, the repulsive forces between the proton laden adsorbent surface and Cd^{2+} hindered much metal removal while at high pH values the surface of adsorbent was loaded with high hydroxide ions. This obviously caused increased metal removal.

Effect of Agitation Time

The result of agitation time on the removal of Cd(II) by activated carbon prepared from brewery spent

barley husks is presented in Fig. 3. The result shows that the rate of metal removal occurred rapidly within the first 5 min of the adsorption and thereafter proceeded to equilibrium with maximum percentage removal of 99.24%.

This indicates that most of the adsorption occurs on the surface rather than the pores of the activated carbon [15]. This further confirms that the adsorption of Cd(II) by activated carbon was physical in nature.

The data obtained for the effect of agitation time were evaluated using nonlinear forms of pseudo-first order, pseudo-second order and Elovich kinetic equations as expressed in Eq. (4-6).

$$q_t = q_e \left[1 - Exp^{(-k_1 t)} \right] \tag{4}$$

The pseudo-second order kinetic equation is presented as

$$q_t = q_e \left[1 - \frac{1}{1 + q_e k_2 t} \right] \tag{5}$$

where q_e is the amount of Cd(II) adsorbed at equilibrium (mgg^{-1}), q_t is the amount of Cd(II) adsorbed at time t (mgg^{-1}); k_1 is the pseudo-first order rate constant (min^{-1}) and k_2 is the pseudo-second order rate constant (g mg^{-1}min^{-1}).

The Elovich equation is expressed as:

$$q_t = \frac{1}{\beta} \ln(\alpha.\beta.t + 1) \tag{6}$$

where α and β are constants. The parameter α represents the rate of chemisorption at zero coverage, the parameter β is related to the extent of surface coverage and to the activation energy for the adsorption.

The results of the kinetic evaluation are presented in Table 2. It is obvious, judging from the coefficient of determination and chi square values, that the kinetic modelling followed the pseudo-first order equation. In addition, the q_e value evaluated from the first-order (5.0 mgg^{-1}) is closer to the experimentally determined value of 4.972 mgg^{-1} than the value (5.25 mgg^{-1}) evaluated from the pseudo-second order equation.

In most literature reports involving adsorption, the pseudo-first order equation has been found not to fit well over the entire contact time range and is generally applicable over the initial periods of the sorption process. This is mainly due to use of linearized form of Eq. (4), which requires previous knowledge of the equilibrium sorption capacity (q_e) [11]. Conversely, there is no prior need to know q_e for solving the linear form of a pseudo-second order equation. Due to above merits, the

pseudo-second order equation is able to describe almost all kinetic data originating from metal adsorbents.

Effect of Sorbent Mass

Fig. 4 presents the result of the influence of adsorbent mass on the adsorption capacity and percentage removal of Cd(II). The figure reveals that adsorption efficiency increased with increase in the mass of the activated carbon dose up to a maximum
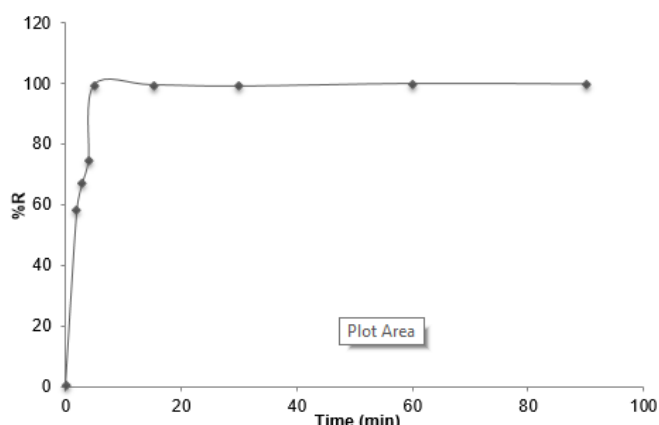
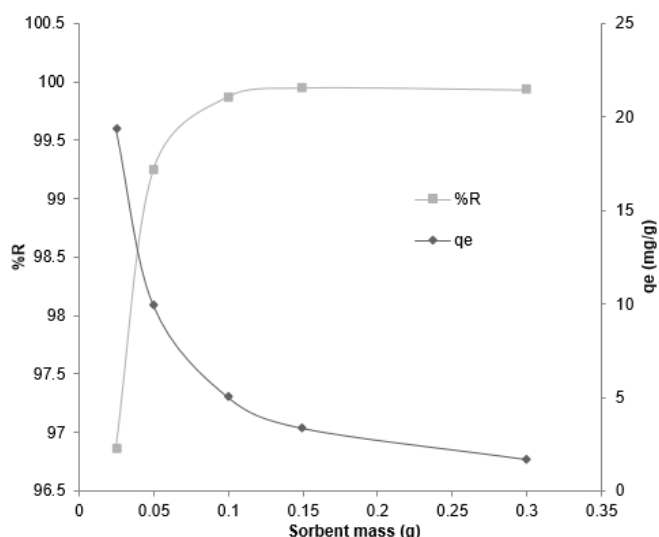**Fig 3.** Effect of contact time on the removal of cadmium by activated carbon from brewery spent barley husks

Fig 4. Effect of sorbent mass on the removal of cadmium by activated carbon from brewery spent barley husks

Table 2. Kinetic parameters for the adsorption of Cd by activated carbon prepared from brewery spent barley husks

Pseudo-1st order				Pseudo-2nd order				Elovich			
q_e	K_1	R^2	X^2	q_e	K_2	R^2	X^2	α (x10^3)	β	R^2	X^2
5.00	0.41	0.9510	0.12	5.25	0.13	0.9070	0.20	1.37	2.53	0.7798	0.57

Table 3. Thermodynamic parameters for the adsorption of cadmium by activated carbon prepared from brewery spent barley husks

T (K)	$\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (kJ K^{-1}mol^{-1})
298	-87.61	-87.612	-0.294
308	-14.90		
318	-11.95		

Table 4. Isotherm parameters for the adsorption of cadmium by activated carbon prepared from brewery spent barley husks

Langmuir		Freundlich	
q_m (mgg^{-1})	6.64	n	2.28
K_L (in L$^{1/n}$ g^{-1} mg$^{-1/n}$)	1.08	K_f (Lmg^{-1})	0.87
R^2	0.7752	R^2	0.6213
X^2	0.83	X^2	13.98

(almost 100% adsorption) when the mass of the activated carbon dosed was 0.1 g. The increase in the percentage of metal removal with adsorbent dose could be attributed to increase in the number of adsorption sites associated with increase in the mass of the adsorbent and this directly increase the surface area, as already reported in the literature [16]. Conversely, the adsorption capacity of the activated carbon decreased gradually from 19.38 to 1.67 mgg^{-1} when the mass of activated carbon dosed was increased from 0.025 to 0.3 g. this observation can be linked to concentration gradient.

Adsorption Thermodynamics

The equilibrium constant K_e was calculated from the concentration of Cd(II) adsorbed at equilibrium (C_i-C_f) and equilibrium concentration (C_f) of the metal in the liquid phase using the following equation [17].

$$K_e = \frac{(C_i - C_f)}{C_f} \tag{7}$$

Vant Hoff's equation Eq. (8) was employed to compute the values $\Delta H°$ and $\Delta S°$ from the equilibrium constant as shown below.

$$\ln K_e = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{8}$$

where T is Temperature in Kelvin and R is the gas constant (kJmol^{-1}K^{-1}).

The values of $\Delta H°$ and $\Delta S°$ were obtained from the slope and intercept of the plot of ln K_e against 1/T while values of $\Delta G°$ at different temperatures were obtained using Eq. (9).

$$\Delta G° = \Delta H° - T \Delta S° \tag{9}$$

The results obtained for the thermodynamic parameters are presented in Table 3. The negative value of $\Delta H°$ for cadmium adsorbed on the acid activated carbon is an indication of the exothermic nature of the adsorption of cadmium. This is a very important value in the sense that no additional energy is needed for this adsorption process thereby making the process very

economical. Evidently, this adsorption process can be conducted at ambient conditions. The negative values of the Gibb's free energy ($\Delta G°$) at different temperatures for acid activated carbon indicate that the adsorption of cadmium in this study was spontaneous at the temperatures considered.

The entropy value for the sorption of cadmium on acid activated carbon indicates that the particles of cadmium on the surface of acid activated carbon were in low state of disorder.

Adsorption Isotherm

The equilibrium data obtained when different initial concentrations of cadmium solution were agitated with 0.1 g of the activated carbon for 90 min at 298 K and pH of 6 were analyzed using Langmuir and Freundlich isotherm models. The non-linear form of Langmuir model is expressed as:

$$q = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{10}$$

The Freundlich isotherm model is expressed in its non-linear form as:

$$q = K_f C_e^{1/n} \tag{11}$$

where q is the uptake (mgg^{-1}), C_e is equilibrium Cd(II) concentration, q_m, is the Langmuir constant which denotes the maximum achievable uptake by a system, K_L is the Langmuir constant which defines the affinity between the sorbate and the activated carbon, and K_f and 1/n are the Freundlich constants related to sorption capacity and sorption intensity, respectively.

The respective values of the Langmuir and Freundlich constants as evaluated from the non-linear equations are presented in Table 4.

The maximum adsorption capacity (q_m) obtained from Langmuir model is 6.64 mgg^{-1}. A look at Table 4 reveals that adsorption of Cd(II) by activated carbon prepared from brewery spent barley husks is better described by Langmuir model because it presented a higher R^2 value and a lower X^2 than the Freundlich

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model. The Freundlich constant n from this study shows that there is a great affinity between the activated carbon and Cd(II) since n<10.

Different experimental conditions employed during adsorption studies might make direct comparison among different adsorbents difficult. However, an attempt was made in this paper to compare the Langmuir maximum adsorption capacity of activated carbon from brewery spent barley husks (this study) with those obtained for activated carbons prepared from other sources. This comparison is presented in Table 5. The table shows that the adsorption capacity of the activated carbon from brewery spent husks for Cd(II) is comparable with some literature reports.

CONCLUSION

The process of removing cadmium from aqueous solution by the activated carbon used in this study was found to be pH, time, temperature and mass of adsorbent dependent. The short period of time (5 min) required for attainment of equilibrium by this process coupled with the negative ΔH value obtained indicated that little or no energy would be required to bring about the removal of Cd(II) from aqueous solution by the activated carbon. This makes activated carbon from brewery barley husk a promising low-cost adsorbent for Cd ion removal.

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