Carbon Science Vol. 7, No. 4 December 2006 pp. 249-258

Removal of Cu (II) and Cd (II) Ions Onto Water Hyacinth Based Carbonaceous Materials

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(Received September 20, 2006; Accepted December 18, 2006)

Abstract

Treatment of water hyacinth with sulphuric acid produces carbonaceous materials that have been used to remove Cu(II) and Cd (II) ions from aqueous solutions. Untreated water hyacinth was also used for the subject of comparison. The textural properties of the carbonaceous materials were determined from nitrogen adsorption at 77 K. The optimum pH for the sorption of Cu (II) and Cd (II) ions on the investigated sorbents was determined. Dynamic adsorption measurements have been taken at 298 K whereas equilibrium measurements were carried out at 298, 313 and 323 K. The adsorption of nitrogen at 77 K on the untreated sample was too low and the surface areas of the treated samples 2, 3 and 4 were found between 70-208 m^2/g. The total pore volumes of these samples which were determined for the carbonaceous materials investigated were found to be 0.076-0.140 ml/g. The kinetic adsorption data of Cu (II) and Cd(II) were applicable to both pseudo – first and pseudo-second order but fit more the latter order. The equilibrium adsorption data were found to fit Freundlich and Langmiur equations. The values of DG, DH and DS are all negative indicating the feasibility and the spontaneous nature of the sorption of Cu (II) and Cd (II) ions by the sorbents investigated.

Keywords : *water hyacinth, adsorption, Cu and Cd kinetics*

1. Introduction

Environmental contamination due to heavy metals is caused by several industries such as metal plating, mining's, painting and car radiator manufacturing, and also by agricultural sources such as fertilizers and fungicidal sprays [1]. Copper, nickel, zinc, cadmium and chromium etc., are harmful waste materials, produced by galvanization industry [2]. The concentrations of heavy metals in waste materials are normally much higher than the standards set by environmental agencies and must therefore be decreased to lower limits before discharge. Unlike most organic pollutants, heavy metals are generally refractory and cannot be degraded or readily detoxified biologically and therefore cause adverse health in that they are important class of human carcinogens [3-6].

Several processes have been developed for the removal of heavy metals from waste discharges. These unit operations include chemical precipitation [7-9], coagulation/flocculation [10, 11], ion exchange [12], solvent extraction [13], cementation [13], complexation [14, 15] electrochemical operation [16], biological operations [17, 18], adsorption [18-22], evaporation [23], filtration [24] and membrane processes [25]. Each of these processes has advantages and suffers from some disadvantages. The advantages and disadvantages are based on simplicity, flexibility and effectiveness of the operation, cost, technical problems and maintenance.

Adsorption of heavy metals from waste discharges is a current trend. Many adsorbents such as silica, clays, cellulose, and its derivatives and metal oxides are reported to show high capacity for the removal of heavy metals [26-30]. However, activated carbons are by far more effective in this application because of their high efficiency and removal capacity. On the other hand, the capital and regeneration costs of these types of sorbents are high. Hence researchers have been encouraged to look for other types of low – cost sorbents. Different types of agricultural materials and solid wastes have been used for this purpose [31-35]. Carbonization of agricultural materials can be performed by dehydration with sulphuric acid and resulting in a colloidal porous active charcoal at considerably lower cost compared with conventionally activated carbons [36, 37].

Water hyacinths is an aquatic plant growing densely in irrigation canals and channels retarding thus the flow of water for irrigation processing, hindering fishing and generally affect aquatic life. Although efforts are usually made to take this plant away, large amounts are always left behind. Besides the negative impact of the plant left uncollected plant does not yet find any economic use. This encouraged us to get use of water hyacinth as an adsorbent for the removal of pollutants from water [38]. As a continuation the present investigation is devoted to use as- received dried water hyacinth (sample 1) for the removal of copper and cadmium from water. Three colloidal carbons have been also prepared by dehydrating water hyacinth with concentrated sulphuric acid. Sample 2 was obtained by hydration at 25°C whereas samples 3 and 4 were obtained by dehydration at 160°C. Sample 3 was dried before using in sorption experiments whereas sample 4 was kept wet and added in this form to the aqueous solution of copper or cadmium ions. Samples 1-3 were characterized by nitrogen adsorption and FTIR. The adsorption isotherms of cadmium and copper at 25, 40 and 50°C were followed and the kinetics of adsorption was determined at 25°C.

Table 1. Analysis of the inorganics in Water hyacinth.

Element	Spectral type	Atomic %	Compound %	
Mg	ED	5.04	Mg O	6.73
Si	ED	6.55	SiO_2	13.05
Cl	ED	16.86	–	–
K	ED	16.10	K_2O	25.12
Ca	ED	4.56	CaO	8.48
Cu	ED	5.08	CuO	13.38
Zn	ED	4.98	ZnO	13.43
O	ED	40.82		

2. Experimental

2.1. Materials

Water hyacinth was collected from an irrigation canal at Giza Governorate (Giza, Egypt). The plant was taken off with all its parts, washed several times with running tap water and then with distilled water constantly added along five days 12 h every day. The thoroughly washed plant was dried at 353 K. The dried plant was chopped into very small pieces, crushed and then sieved to 0.46-2.0 mm particle size, this gives sample 1. Sample 2 "colloidal carbon" was obtained by reacting sample 1 (10 g) with 100 ml (12 mol/dm^3) sulphuric acid at 298 K for 24 h. The resulting black mixture was allowed to cool and then filtered using a buchner funnel. The carbonized product was washed several times with distilled water until the pH was between 3.5 and 4.5 and did not give a precipitate with barium chloride solution. The carbonized product was dried and stored in dry clean and well closed bottle. Sample 3 was similarly prepared except that reaction with sulphuric acid was carried out at 433 K for 2 h. Sample 4 was prepared following the same procedure for preparation of sample 3 but, sample 4 was stored undried in a clean well closed bottle with the minimum amounts of water and acetone which change periodically to prevent the formation of bacteria and meanwhile to keep the sample wet.

2.2. Methods

Nitrogen adsorption isotherms at 77 K were constructed using a conventional volumetric apparatus. Before carrying out adsorption measurements, the carbon sample was degassed at 100°C under a reduced pressure of 10^{-5} Torr.

The carbon content and the inorganic content of dry clean and crushed water hyacinth (0.46-2.0 mm particle size) were determined using ICP-AES.

The elemental analysis of the inorganic matters is given in Table 1.

The functional groups on the surface of samples 1, 2 and 3 were identified by using Mattson – FTIR Spectrometer using the KBr disc technique. The pH of the aqueous suspension or slurries of the sorbents as well as the pH of the aqueous solution of Cu (II) and Cd (II) were measured using digital pH meter (Pope Model No. 1501).

The adsorption of copper (II) and cadmium (II) was carried out as follows. Defined amount of the sample was shaken for different periods of time (kinetic experiments) at 298 K or for 6 h (equilibrium experiments) at 298, 313 and 323 K. Before the concentrations of Cu (II) and Cd (II) ions present in the solution were measured, the adsorbent sample was filtered from the mixture. The concentration of Cu (II) and Cd(II) ions were measured using a Perkin – Elmer model 2380 atomic spectrophotometer, with hollow cathode lamps and a 10 cm – slit burner for an air / acetylene flame wavelengths of 324.8 and 283.3 nm were employed for the determination of copper and cadmium respectively. In all kinetic and equilibrium experiments of the concentrations of Cu(II) or Cd (II) ions were lower than or equal to 5 mmol / dm^3.

The Batch adsorption technique was use for the determination of the distribution coefficient K_D and the equilibrium constant K_C. Other conditions, i.e. the amounts of adsorbent and adsorbate and the shaking time were kept constant.

3. Results and Discussion

The carbon content was reported to be ≥ 90% and the inorganic content in dry water hyacinth was determined by igniting in air at 873K (5 g), in a crucible tills the disappearance of all the carbon, as indicated by the absence of the black color and attainment of a constant weight. The loss ignition was determined to be 91.2% and the inorganic content (left as ash) was 8.8%. The quantitative analysis of the inorganic matters in water hyacinth was determined by ICP-AES.

3.1. Surface Functionality of the sorbents

FTIR spectra of samples 1-3 (not illustrated) indicated some differences in the intensity, area and shape of their absorption peaks. However, these differences don't represent clear evidences to allow strong conclusions. With some reservation and based on the data reported in literature and summarized in Table 2, one can give general explanations as follows. All the samples investigated exhibited surface phenolic, carboxylic, carbonylic, cyclic ether groups, phenolic and C-H aromatic structure. Sulphuric acid – untreated (sample 1) exhibited the most developed free OH and C-H aliphatic structure and the less developed acidic groups (phenolic, carboxylic and carbonylic). Sample 3, on the other hand exhibited the less developed OH and C-H aliphatic structure and mean while the well developed absorption peaks assigned from surface acidic carbon- oxygen groups. Sample 2 showed spectra intermediate between those exhibited by samples 1 and 3. This may be taken as an evidence that oxidation with sulphuric acid of cellulosic materials concentrates the acid functionality on the surface of the resulted carbonization product.

The results obtained from FTIR qualitative coincide with the surface pH values of the aqueous suspensions of the samples which were 6.5, 5.3, 4.2 and 3.5 for samples 1, 2, 3, and 4, respectively. Evidently, the pH values decreased upon treatment with sulphuric acid with the decrease depending on the severity of the treatment.

3.2. Textural properties

The adsorption capacity of an adsorbent is determined by its texture (surface area and porosity). Chemically – activated carbons and physically – activated carbons are characterized by high surface area and wide range of pore size distribution. Colloidal carbons prepared by dehydrating cellulosic materials with concentrated sulphuric acid possess considerably lower surface areas and less developed pore structure. Equally important to the texture of an adsorbent in determining its adsorption capacity particularly from solution is the chemistry of its surface.

The textural properties are determined from the adsorption of nitrogen at 77 K. Prior to nitrogen adsorption, the sorbent sample was degassed at 100°C under a reduced atmosphere of 10^{-5} Torr. The adsorption was continued until near saturation, i.e. at a relative pressure approaching 1.0. The nitrogen adsorption isotherms of sorbents 2-4 are shown in Fig. 1. The adsorption of nitrogen at 77 K on sorbent 1 (untreated) was too low to allow reproducible or trustful values for the textural parameters.

The nitrogen adsorption isotherms of sorbents 2-3 are type II according to the BDDT classification [45], indicating the

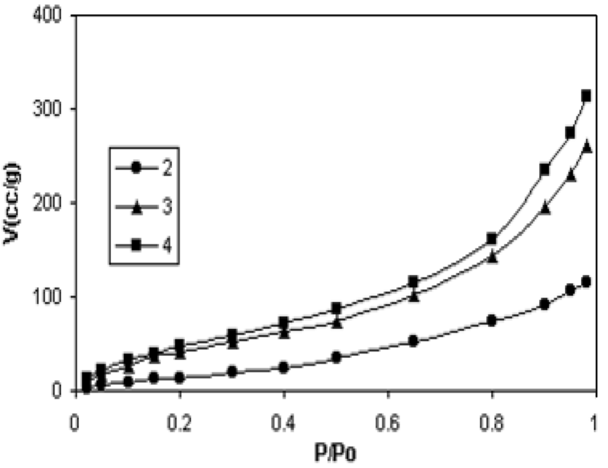

Fig. 1. Nitrogen adsorption isotherms at 77 K onto the water hyacinth investigated.

Table 2. Assignment of FTIR Bands.

Wave number cm^{-1}	Assignment	Groups	References
900-740	C-H (out of plane bending)	Aliphatic Structure	39,41
220-1000	C-OH (stretching)	Phenolic group	39,40,42
1591;1440 1382;1285 1073;1019	Composed	Carbonate and/or Carboxylic structure oxygen surface group	39
1119;1073 1154;1283	Composed	Highly stable cyclic ether containing CoCoC groups	39,40,42
1640	Carbonyl adjacent hydroxyl	Enol Structure	44
1705	Free carboxyl		44
1730;1750 1760	Carbonyl of carboxyl	Ester and/or Lactone	44
2966;2918;2854	C-H (Stretching)	Aliphatic Structure	39,40,42
3030	C-H (Stretching)	Aromatic structure	40
3280;3388	O-H (Stretching-vibration)	Aromatic	43
3444	O-H (Stretching with possible H-bending between O-H) groups	Phenolic	39,41
>3500	O-H (Stretching)	Free OH	43

Table 3. Textural properties of sorbents 1-3 as determined from nitrogen adsorption at 77 K.

Sample	S_{BET} (m^2/g)	V_T (ml/g)	r' (nm)	V_{mic} (ml/g)	V_{mic}/V_T (dimensionless)
2	70	0.184	5.3	0.014	0.076
3	192	0.408	4.3	0.042	0.103
4	208	0.480	4.6	0.050	0.104

domination of mesopores. The BET equation [46] was applied to determine the surface area S_{BET} (m^2/g) for each sample. The total pore volume V_T (ml/g) for each sorbent samples was also determined from the volume of nitrogen adsorbed near saturation.

The mean pore radius, r' (nm) was calculated from the relation ship.

$$r' = \frac{2V_T}{S_{BET}} \times 10^3$$

The volume of nitrogen adsorbed at relative pressure = 0.1 may be taken as a measure of the micropore volume V_{mic}, this allowed the determination of the ratio V_{mic}/V_T.

Inspection of Table 3 reveals that (i) sorbent 2 measured the lowest surface area and the largest mean pore diameter (ii) the surface area of sorbent 4 (stored wet) is about 8% higher than the surface area of sorbent 3 (store dry). The mean pore radius of sample 4 is also about 7% larger than that of sorbent 3. (iii) the microporosity in sorbents 2-4 represents a small fraction of the total pore volume, i.e 8-10% of the total porosity. The predominating pores are of mesoporous type, i.e. $\geq 90\%$ of the total porosity. Concentrated sulphuric acid acts as a dehydrating agent and as oxidant for cellulosic materials resulting therefore in colloidal and porous active carbons. Colloidal charcoal has a small particle size and therefore one can expect that most of the surface area of these carbons is considered as external surface area and the other part is located in mesopores. Colloidal carbons are there completely different than chemically- or physically – activated carbons. The surface areas of the latter are considerably higher. Also most of their surface areas are located in micropores. It seems that dehydration and oxidation of cellulosic materials and formation of colloidal carbons requires heating to temperatures approaching 473 K. This explains the low surface area and porosity of sample 2 which was treated with sulphuric acid at 298 K, i.e treatment at such low temperature brought about incomplete dehydration and /or oxidation product [37].

3.3. Adsorption of Cu (II) and Cd (II) ions

3.3.1. Effect of pH

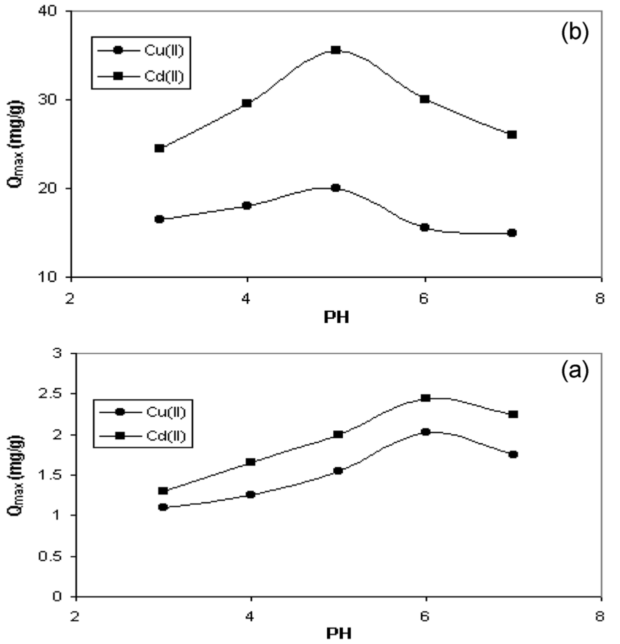

Fig. 2. Effect of PH on sorption of Cu(II) and Cd(II) ions at 298 K onto a-Untreated water hyacinth (b) Sulphuric treated water hyacinth.

The adsorption from solution in general and of metal ions in particular depends to a great extent on the pH of the adsorption medium. The influence of pH value of the metal ion solution on the adsorption of the latter from single component metal ion systems Cu(II) or Cd(II) was studied using a dosage of 100 mg sorbent and initial metal ion concentrations of 20 mg/dm^3. The initial metal ion solutions, i.e. before the addition of the sorbent were adjusted to different pH values (ranging from 3 to 7) via the addition of dilute NaOH or HNO_3 solutions. After agitating for a period adequate for reaching equilibrium adsorption on the basis of kinetic adsorption measurements, the final pH was recorded and the equilibrium concentration of the metal ions was determined. Fig. 2 shows the variation of the maximum adsorption capacity of Cu(II) and Cd (II) ions onto sorbents 1 and 4. It is shown that for Cu (II) and Cd (II) ions adsorption on untreated sample (sorbent 1), the amount adsorbed increased with the increase of pH from 3 to show maximum at pH 6 and then slightly decreased with the further increase of the solution pH to 7, i.e. the adsorption of both metal ions on the untreated sorbent exhibited its maximum around neutral conditions. For sulphuric acid – treated sorbent 3, the maximum adsorption of Cd (II) is exhibited at pH value = 4.5, with the adsorption of this metal ion considerably lower at pH values lower or higher than 5. The adsorption of Cu (II) by sorbent 3 seems to be less sensitive to variation in the solution pH between 3 and 7. However, slightly higher adsorption values of Cu (II) has been found at pH = 5.0. The high adsorption of Cu (II) and Cd (II) on sulphuric acid treated water hyacinth (sorbent 3) at pH value = 5 may be attributed to a change in the charge on the carbon surface

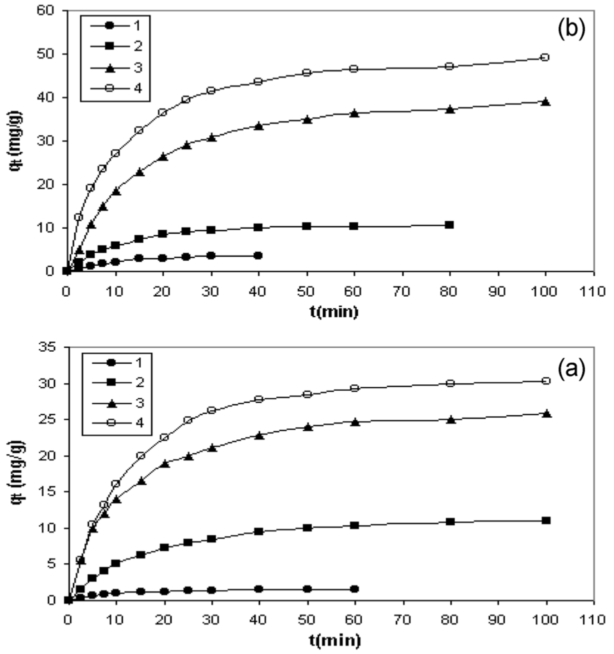

Fig. 3. Kinetics of a)-Cu(II) and, b)-Cd(II) ions sorption onto untreated sulphuric acid treated-water hyacinth.

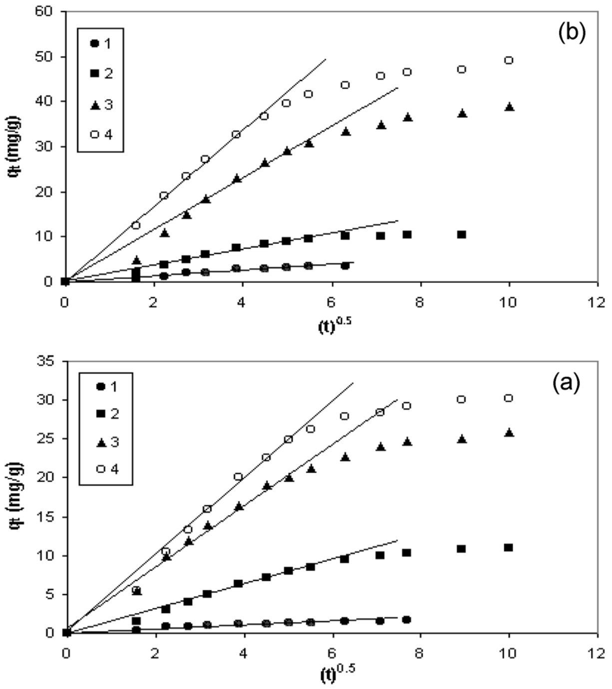

Fig. 4. A plot for the rate of pore diffusion of a)-Cu(II) and, b)-Cd(II) on untreated and sulphuric acid treated-water hyacinth.

with the change in the pH values. Electrostatic repulsion between cations and positively charged surface of the carbon occurred at low pH values, while metal ions replaced hydrogen ions on the carbon surface at higher pH values leading to an increase in the extent of adsorption.

3.3.2. Sorption kinetics

After determining the optimum pH at which Cu (II) and Cd (II) sorption should be followed, the kinetics of sorption of Cu (II) and Cd (II) must be determined. Mean while, the change of the sorption capacity, with time allowed the determination of the time required to attain equilibrium which is essential to construct the adsorption isotherm. The kinetic of Cu (II) ions sorption and of Cd(II) ions sorption at 293 K are shown in Fig. 4(a) and (b), respectively. It is evident that the adsorption capacity of sorbent 4 for Cu (II) and Cd (II) is the highest among all investigated sorbents. Generally, the sorption capacities for Cu (II) and Cd (II) follow the order sorbent 4 > sorbent 3 > sorbent 2 > sorbent 1.

It is evident also that Cd (II) is more adsorbed than Cu (II), this is true for all investigated sorbents. It is also predicted from Fig. 3(a) and (b) that the initial adsorption is rapid and that after 40-60- min. insignificant increase of adsorption with time was observed. The uptake of Cu (II) and Cd (II) was found to vary linearly with the half power of time ($t^{0.5}$), in the initial stages of sorption Fig. 4(a) and (b). Similar results were previously reported) by applying the equation.

$$q_t = K_d\, t^{0.5}$$

where q_t is the amount adsorbed (mg/g) and K_d is the rate constant of pore diffusion.

This behavior is predicted when a large initial fraction of the reaction is controlled by intraparticle diffusion [18] K_d values of 0.35, 1.60, 4.20 and 4.90 mg·g^{-1} min$^{0.5}$ were calculated for the adsorption of Cu (II) onto sorbets 1,2,3 and 4, respectively, the K_d values for Cd (II) sorption onto these sorbents were calculated to be 0.6, 1.5, 5.8 and 8.9.

It was found also that Cu (II) and Cd (II) uptake also followed first order rate equation expressed as

$$\mathrm{Log}_{10}\,(q_e - q_t) = \log_{10} q_e - \frac{K_1 t}{2.303}$$

where q_t and q_e are the amount adsorbed at time t and at equilibrium in (mg/g), respectively K_1, is the first order rate constant (min^{-1}) of Cu (II) or Cd (II) up take at 25°C. Fig. 5 (a) and (b) shows satisfactory straight lines when $\log_{10}(q_e - q_t)$ values were plotted versus time. The K_1 values for Cu (II) and Cd (II) uptake are listed in Table 4.

A trial has been also made to apply the pseudo- second order rate equation to the uptake of Cu (II) and Cd (II) on the investigated sorbent at 298 K, with time.

$$t/q_t = 1/(K_2\, q_e^2) + (1/q_e)\, t$$

q_t and q_e have been previously defined and K_2 is the pseudo-second order rate constant (q/mg min), of Cu (II) and Cd (II) sorption. Evidently, typical straight lines with the least – Scatter of points were obtained, Fig. 6(a) and (b). The K_2

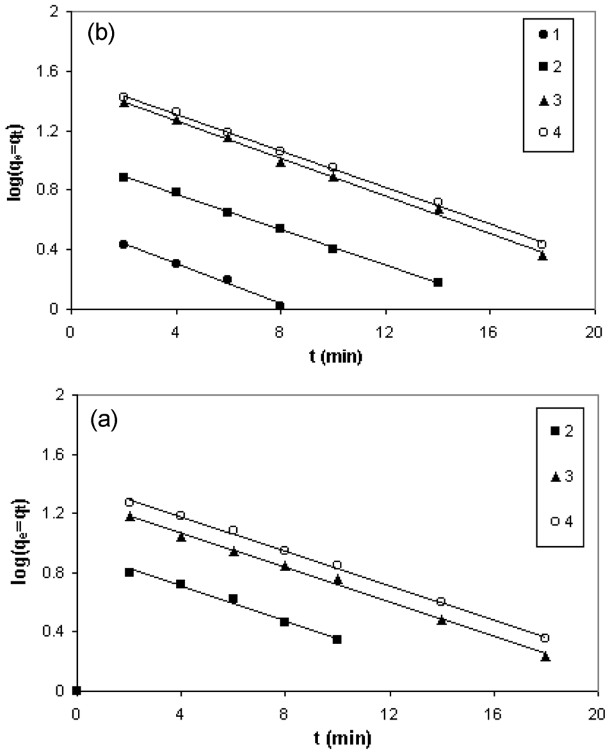

Fig. 5. A plot for the first-order reaction for a)-Cu(II) and, b)-Cd(II) on untreated and sulphuric acid treated water hyacinth.

Table 4. Kinetic parameters for the sorption of Cu (II) and Cd (II) onto the investigated sorbents.

Sorbent	First order kinetics			Pseudo – second order kinetics	
	K_1 (min^{-1})	q_e (mg/g)	R^2	K_2 (g/mg min)	R^2
			Cu (II) sorption		
1	0.065	1.3	0.9600	0.076	0.9947
2	0.055	7.2	0.9800	0.0056	0.9925
3	0.050	19.2	.0.9602	0.0025	0.9987
4	0.048	23.0	0.9550	0.0026	0.9970
			Cd (II) Sorption		
1	0.056	3.0	0.9720	0.0310	0.9888
2	0.052	8.5	0.9600	0.0080	0.9976
3	0.50	26.8	0.9700	0.0014	0.9981
4	0.49	36.5	0.7012	0.0013	0.9976

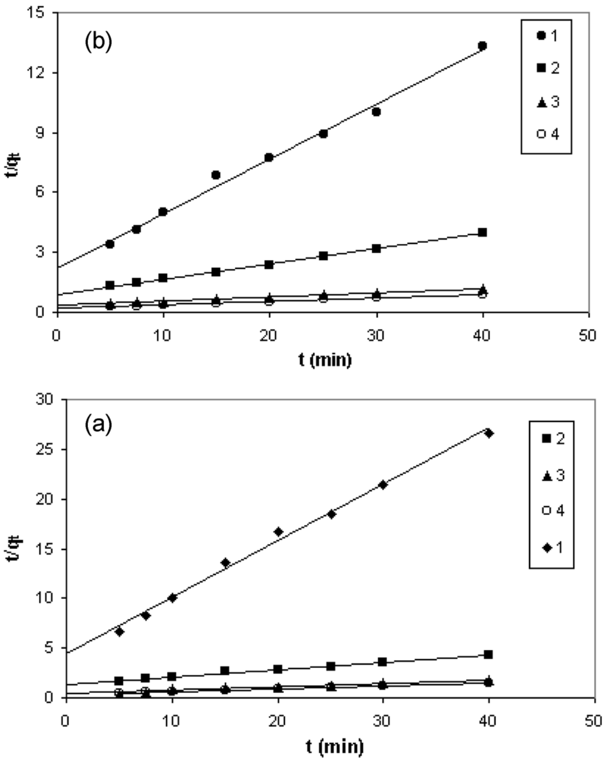

Fig. 6. A plot for the second-order reaction for a)-Cu(II) and, b)- Cd(II) On untreated and sulphuric acid treated water hyacinth.

values are listed in Table 4.

Table 4 indicates that the amounts of Cd (II) adsorbed at equilibrium (q_e) are always higher than those adsorbed from Cu (II). It is also shown that both K_1 and K_2 for sorbent 1 are considerably higher than those determined for sorbent 2. This is true for both Cu (II) and Cd (II) uptake. This may be attributed to the difference in nature of these sorbents. Sorbent 1 is a cellulosic matter on which adsorption takes place on the external surface since no pores are existing. On treatment of sample 1 with concentrated sulphuric acid to have sorbent 2, one would expect partial carbonization and development of some porosity in which the rate of adsorption decreased. This explains the relatively low values of K_1 and K_2 of Cu (II) sorption onto sorbent 2 relative to those for sorbent 1. K_1 and K_2 for Cu (II) and Cd (II) ions sorption by sorbent 3 and 4 are more or less equal and are very low compared with those calculated for sorbents 1 and 2. This may be taken as an additional evidence for the same explanation. Sample 3 and 4 were treated with sulphuric acid at 433 K where carbonization is expected to be very high and the fraction of microporosity is predominating. The rate of adsorption in micropores is probably low compared with the rate in mesopores on the external surface. It remains now to point out that the uptake of Cu (II) and Cd (II) ions by the investigated adsorbents follows pseudo–second order kinetics since the correlation coefficient R^2 were higher for this kinetic model relative to R^2 for first order kinetics.

3.3.3. Adsorption isotherms

We have already determined the appropriate pH values for the sorption of Cu (II) and Cd (II) ions by investigated sorbents (pH = 6) for sorbent 1 and (pH = 5) for sorbents 2-4. It is shown also from the kinetic curves, Figs. 3(a) and (b)

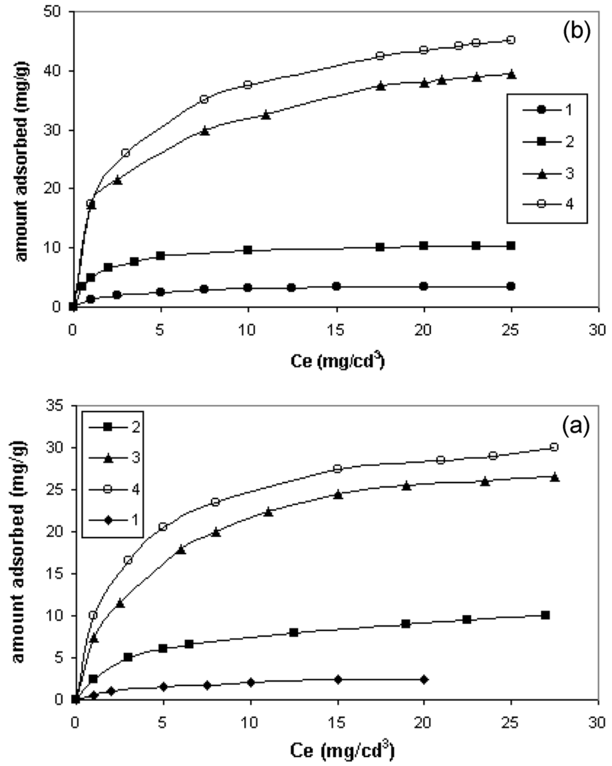

Fig. 7. Adsorption isotherms of a)-Cu(II) and, b)-Cd(II) onto untreated and sulphuric acid treated water hyacinth at 298 K.

that beyond 100-120 min contact, no significant increase in the sorption capacity with time was observed. However, the sorbents were soaked for 6 h to ensure the attainment of equlibrium conditions. This equilibrium time is much shorter than that reported for adsorption of heavy metals by activated carbons since the latter contain a large fraction of the surface located in micropores [18].

Representative sorption isotherms of Cu (II) and Cd (II) ions on the investigated sorbents at 298 K are shown in Fig. 7 (a) and (b). The isotherms are typical type L according to the classification reported by [47] for the adsorption isotherms from dilute solutions. The equilibrium sorption data allowed the determination of two important parameters, namely the distribution coefficient K_D and the equilibrium constant K_C.

$$K_D = \frac{C_o - C_e}{C_e}\ \frac{v}{m}$$

Where C_o and C_e are the initial and equilibrium concentration of Cu (II) and Cd (II) (mg/dm^3), respectively. V and m are the volume of the equilibrated solution and the mass of the sorbent, respectively

$$K_c = q_e/C_e$$

q_e is the equilibrium concentration of Cu (II) or Cd (II) on the sorbent surface (mg/g) and C_e has been previously identified.

Table 5. K_D and K_C for Cu (II) and Cd (II) adsorption at 298 K.

Sorbent	Cu II		Cd II	
	K_D	K_C	K_D	K_C
1	1028	0.074	984	0.179
2	981	0.374	963	0.490
3	820	0.904	861	2.00
4	814	0.885	850	1.74

Table 5 lists the value of K_D and K_C for Cu (II) and Cd(II) ions sorption at 298 K on the investigated sorbents.

Table 5 reveals that (i) for Cu (II) and Cd (II) sorption, K_D for the sorbents investigated follows the order $1 > 2 > 3 > 4$. This evidently the same order of increasing the sorption capacity adsorption parameter (ii) K_C of the sorbents follows the order $3 > 2 > 1$ which is the same trend as the sorption capacity. Sorbent 4 is an exception since its value for K_C is lower than that for sorbent 3 although the latter exhibited lower sorption capacity. This is true for Cu (II) and Cd (II). Among the investigated sorbents, sorbent 4 was stored wet as previously described in the experimental part. Diffusion of the sorbed ions at the interface may affect the equilibrium constant of sorption on the particular sample.

The adsorption isotherms of Cu (II) and Cd (II) at 298, 313, and 323 K onto the investigated sorbent were analyzed using Langmuir and Freundlich equations. The linear form of Langmuir equation is written as

$$1/q_e = 1/K_L + (1/K_L\, b) \cdot (1/C_e)$$

k_L is a parameter related to the maximum adsorption capacity, b is the equilibrium adsorption constant and can be used to determine the Gibbs free energy (ΔG), enthalpy of adsorption (ΔH) and entropy of sorption (Δs) using the following relation ships.

$$\ln b = \ln b - \Delta H/RT$$
$$\ln 1/b = \ln b'\ \Delta H/RT$$
$$\text{and } \Delta S = (\Delta H - \Delta G)/T$$

where b is the adsorption energy constant, R is the universal gas constant and T is the absolute temperature °K. The plot of ln (1/b) versus (1/T) gives ΔH.

The linear form of the Freundlich equation can be written as

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

K_F and (1/n) are constants related to the sorption capacity and sorption intensity, respectively.

Representative linear Langmuir plots are shown in Fig. 8 (a) and (b). Also, representative linear Freundlich plots are shown in Fig. 9(a) and (b).

The Langmuir and Freundlich constants derived from these plots are listed in Table 6 from which it is obvious that the

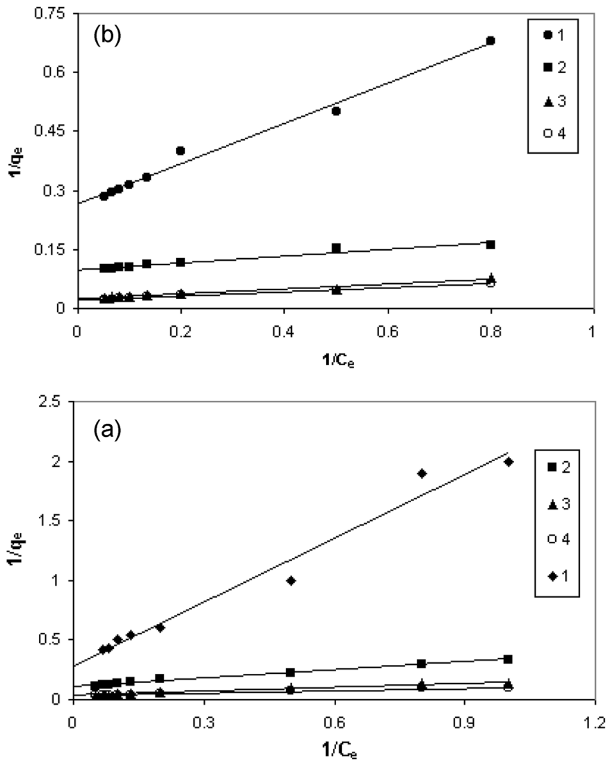

Fig. 8. Linear Langmuir plots of a)-Cu(II) and, b)-Cd(II) ions sorption at 298 K onto untreated and sulphuric acid treated water hyacinth.

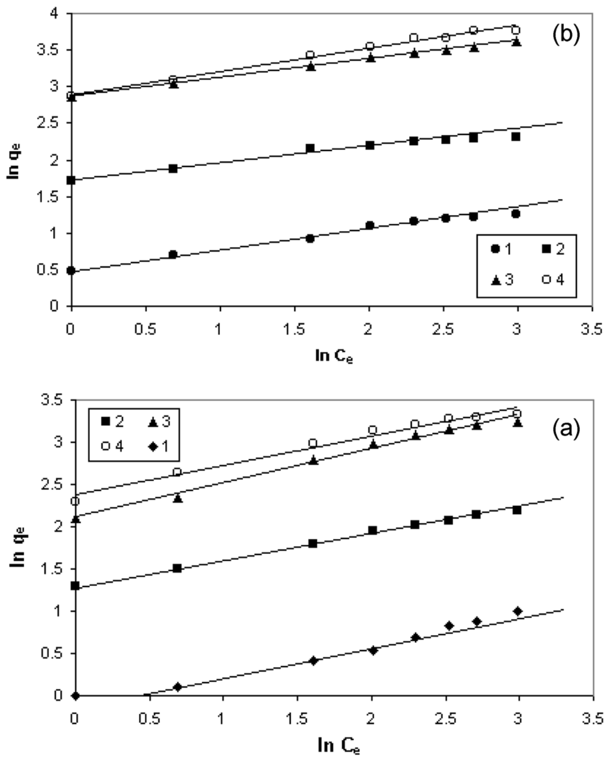

Fig. 9. Linear Freundlich plots of a)-Cu(II) and, b)-Cd(II) ions onto untreated and sulphuric acid treated water hyacinth.

values of K_L and K_F although are different but they follow the same trend because both are function of the adsorption capacity. It is also evident from Table 5 that b decrease with the increase of k_L, i.e., with the increase of the adsorption capacity.

3.3.4. Thermodynamic parameter of Cu (II) and Cd (II) adsorption

The determination of the sorption of Cu (II) and Cd (II) ions the investigated sorbents at 293, 313 and 323 K allowed the evaluation of the thermodynamic parameters considering the Langmuir model. Table 6 summarizes the values of ΔG, ΔH and ΔS for every sorbent adsorbate system.

It is predicted from Table 6 that all the values of the standard free energy change (ΔG°) are negative suggesting thus the spontaneous nature of the sorption of Cu (II) and Cd (II)ions on the investigated sorbent and meanwhile refers to

Table 6. Thermodynamics parameters of Cu (II) and Cd (II) sorption.

Sorbent	289 K		313 K		323 K		
	-ΔG° KJmol^{-1}	-ΔS° Jmol^{-1}K^{-1}	-ΔG° KJmol^{-1}	-ΔS° JmolK^{-1}	-ΔG° KJmol^{-1}	-ΔS° JmolK^{-1}	-ΔH°
				Cu (II) Sorption at			
1	0.40	29	5.13	35	5.77	27	8.1
2	2.25	50	4.25	54	4.30	56	6.7
3	2.92	61	4.06	62	5.75	65	15.2
4	4.77	50	6.57	54	7.50	56	10.5
				Cd (II) sorption at			
1	2.38	221	3.93	214	5.61	212	63
2	1.95	350	5.76	337	8.46	335	99.8
3	3.14	125	5.72	126	6.82	126	33.9
4	4.49	85	6.27	84	6.31	81	20.7

the feasibility of the sorption process. The negative values of the standard enthalpy change (ΔH°) indicates that the interaction of Cu(II) and Cd (II) with the investigated sorbent is exothermic in nature, thereby demonstrated that the process is stable energetically. All the values of (ΔH°) are negatively low compared with heats evolved in chemisorptions process. The values of (ΔH°) may ascribe specific interaction between the adsorbed ion and the adsorbent surface. Negative values of (ΔS°) indicated that the adsorption complexes are stable. Such negative values may be attributed to association, fixation or immobilization of Cu (II) and Cd (II) ions on the sorbent surface due to adsorption, there by decreasing the degree of freedom of these ions.

4. Conclusion

Treatment of water hyacinth with sulphuric acid at 298-433 K is a simple low cost technique to produce carbonaceous materials of developed porosities and relatively high surface areas.

The carbonaceous materials produced by treating water hyacinth with sulphuric acid exhibited high adsorption capacities for Cu (II) and Cd (II) from their aqueous solution, where it is found to be 23 mg/g for Cu and 36.5 mg/g for Cd.

The adsorption of Cu (II) and Cd(II) ions at 298 K proved to be rapid and the dynamic adsorption data were applicable to first order and pseudo- second order kinetic with the latter well fitted.

The equilibrium adsorption data obeyed Freundlich and Langmuir equations. The thermodynamics parameters of the adsorption of Cu (II) and Cd (II) on the sorbents investigated have been evaluated. The negative values of the standard free energy change (ΔG°) indicate the spontaneous nature and the feasibility of the sorption process. The negative values of the standard enthalpy change demonstrates that the process of sorption is stable energetically and the values of (ΔH°) refer to some sort of specific interaction. The negative values of (ΔS°) may be attributed to association, fixation or immobilization due to adsorption, there by decreasing the degree of freedom of the sorbed ions.

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