

Removal of Pb(II) and Cd(II) From Aqueous solution Using Oxidized Activated Carbons Developed From Pecan Shells.

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Abstract

Oxidized activated carbons were prepared by reacting steam-activated carbon developed from pecan shells with nitric acid of varying strength (15, 30, 45 and 60%). The textural properties and the chemistry of the surface of the non-oxidized and of the oxidized carbons were determined from nitrogen adsorption and base neutralization capacities. The uptake of Pb(II) and Cd(II) from aqueous solution by these carbons was determined by kinetic and equilibrium experiments as well as by the column method.

Treatment with nitric acid brought about drastic decrease in surface area and remarkable increase in the pore size of the carbon with these changes depending on the strength of nitric acid. Nitric acid increased the surface acidity by developing new surface oxygen functional groups of acidic nature. HNO₃-oxidized carbons exhibited high adsorption capacities for Pb(II) and Cd(II). The adsorption of these ions increased with the decrease of the surface pH of the carbon and with the increase of the solution pH from 2.5 to 6 and 7. The amount adsorbed from lead and cadmium was also related to the amount of surface acidity, the pH of the point of zero charge and on some metal ion parameters. Cadmium and lead uptake by the investigated carbons followed pseudo-second order model and the equilibrium sorption data fitted Langmuir adsorption model.

Keywords : Pecan shells, Active carbons, Oxidation, Adsorption, Pb(II), Cd(II)

1. Introduction

Contamination of heavy metals in our water supplies has steadily increased over the last years as a result of over-population and expansion of industrial activities. Elements such as mercury and cadmium exhibit human toxicity at extremely low concentration. The elements such as lead and copper also exhibit toxic properties to humans and animals although the concentrations are order of magnitude higher than that required for Hg or Cd toxicity.

Several processes have been developed for the removal of metals from waste discharges. These unit operations include: chemical precipitation [1,2], coagulation/flocculation [3], ion exchange/solvent extraction [4], cementation, complexation [5,6], electrochemical operations, biological operations [7,8], adsorption [8-11], evaporation, filtration [12] and membrane processes [13]. Each of these processes has advantages and suffers from some disadvantages. These 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 removal of heavy metals [14-17]. However, activated carbons (ACs) are by far more effective

due to some specific characteristics that enhance their use for the removal of contaminations including heavy metals from water supplies [18].

ACs are extremely versatile adsorbents used in major industrial applications and in a wide range of processes concerned principally with the removal of undesired species from the gaseous or liquid phases in order to effect purification or the recovery of chemicals. ACs can be produced from virtually many carbonaceous solid precursors, both naturally occurring and synthetic, provided that these precursors are readily available at low cost.

A current trend in the preparation of ACs is the use of various kinds of waste materials [19] and agricultural byproducts [20-23]. It is well known that ACs may be prepared both by physical activation and chemical activation [24]. Physical activation involves the gasification of a carbonization product with an oxidizing gas such as steam or carbon dioxide at temperatures between 800 and 1100°C [25] to a certain percentage of burn-off. Chemical activation, on the other hand involves impregnation of the carbonaceous precursor in a concentrated aqueous solution of an activating agent followed by carbonization at temperatures between 400 and 800°C in absence of air or in inert atmosphere. Several chemicals have been reported as being useful as activating agents for this purpose. The most widely used are phosphoric

acid [26], zinc chloride [27] and alkali metal compound [28].

The texture of ACs may be adapted to suit the situation by adequate choice of the activation procedure. It is possible to prepare ACs with different proportions of micro, meso and macro pores [27]. The nature and the concentration of the surface functional groups may be modified by suitable thermal and chemical post treatments [28]. Oxidation of carbon increases the concentration of the surface oxygen groups whereas heating under inert atmosphere may be used to selectively remove some of these functions. Carboxylic, phenol, quinone, carbonyl and lactone groups have been identified on carbon surfaces [29]. Oxidation of ACs is usually carried out at room temperature or at the boiling point of the oxidizing solution. Oxidized ACs are characterized by their enhanced cation exchange capacity, sorptive selectivity, hydrophilic surface and acidic character [18]. Modification with concentrated nitric acid caused the most pronounced surface changes [30].

The objective of the present research was to gain more understanding on the change in the textural properties and in the surface chemical properties of a steam-activated carbon due to surface oxidation with different concentrations of nitric acid. These changes were followed using nitrogen adsorption, surface pH of ACs and acid-base titration methods. Steam-activated carbon and its HNO₃-oxidized products were used for the adsorption of Pb(II) and Cd(II) from aqueous solution at different pH values. The kinetic and equilibrium adsorption of these ions were also investigated. Breakthrough experiments were also carried out in the form of column tests. These studies were performed to elucidate the relationship between sorptive performance and the surface properties of these materials.

2. Experimental

2.1. Materials

The activated carbon S was obtained by carbonization of clean crushed pecan shells at 600°C in nitrogen atmosphere followed by gasification with steam at 950°C to a burn-off =21%. Details of steam activation are reported elsewhere [25]. The steam-activated carbon was crushed and sieved and the fraction of 0.5-1.5 mm was used for adsorption experiments and also for the preparation of HNO₃-oxidized carbons. 15, 30, 45 and 60% HNO₃ solutions were obtained by the appropriate dilution with doubly distilled water of 70% HNO₃ from Sigma-Aldrich. During oxidation of carbon S, distilled water was added to this carbon and the mixture was heated to 90°C. Nitric acid was added to the reaction mixture and the reaction was continued for 24 h before the solution was decanted and the remaining carbon was thoroughly rinsed with distilled water. The acid-oxidized carbon samples were then washed with 0.1 M NaOH to remove

humic type substances formed as byproduct. The heat treatment was conducted at 200°C for 24 h. The samples were washed with 0.1 M HNO₃ and finally rinsed with doubly distilled water and then the carbons samples were dried for 2 h at 110°C prior to being used. HNO₃-oxidized carbons were designated as SN15, SN30, SN45 and SN60, where N refers to nitric acid and the arabic number stands for % HNO₃ used.

2.2. Techniques

The textural properties (surface areas in m²/g, total pore volumes in ml/g and the mean pore radii in nm) were determined from the nitrogen adsorption isotherms obtained at 77 K, using conventional volumetric apparatus. Prior to any adsorption measurement, the carbon sample was degassed at 200°C for 6h under a reduced pressure of 10⁻⁵ Torr.

The nature of the oxygen groups on the surface of samples S and SN60 were recorded between 4000 and 400 cm⁻¹, using Mattson 5000 spectrometer. Discs were prepared by first mixing 1 mg of dried carbon sample with 500 mg of KBr (Merck, for spectroscopy) in an agate mortar and then pressing the mixture successively at 5 tons per cm² for 5 min and at 10 tons per cm² for 5 min under vacuum.

The surface pH values were measured in a suspension of 1 g of carbon in 20 cm³ of CO₂-free distilled water. After a contact time of 48 h at 298 K. The pH-meter used was of digital type (Pope model No. 1501). The same pH-meter was also used to measure the pH values of the external solutions. The pH values at the point zero charge pH_{pzc}, were determined as suggested by Noh and Schwarz [31] by adding various amounts of solid to 0.1 M NaCl solution (prepared in pre-boiled water). The sealed bottles were placed in a constant temperature shaker overnight and the equilibrium pH values of the mixtures then measured. The limiting pH was taken as the pH_{pzc} value. Zeta potential values were recorded using a Malvern instruments zetazizer.

The relative concentrations of the different surface functional groups in ACs investigated were determined by Boehm's method [32]. Amounts of 0.2 g of dry carbon were weighed into 50 ml conical flasks prior to addition of 20 ml of bases of varying strength, e.g., 0.1 N solution of sodium hydrogen carbonate, sodium carbonate, sodium hydroxide and sodium ethoxide. The mixtures were agitated for 24 h at 298 K. The supernatant solutions were separated using 0.45 μm PTFE syringe top filters. 5 milliliters aliquots were then titrated with 0.1 M HCl using methyl red as indicator. Doubly distilled water was used in all titration experiments. The effect of the pH of the external solution on the extent of adsorption was investigated at 303 K in the pH range 2.5-7.0. Preliminary experiments have indicated that very small or un-measurable adsorption was observed at pH values lower than 2.5.

The kinetics of lead and cadmium sorption were carried out at 303 K and pH 6, using samples SN30 and SN60. 2

Table 1. Textural properties of the investigated carbons

Carbon	S_{BET} m ² /g	S_{a} m ² /g	V_{T} ml/g	r_{m} nm	V_{m} ml/g	V_{n} ml/g
S	872	883	0.482	1.12	0.305	0.177
SN15	740	746	0.465	1.26	0.270	0.195
SN30	544	549	0.581	2.14	0.168	0.313
SN45	248	252	0.397	3.20	0.091	0.306
SN60	144	143	0.372	5.18	0.062	0.310

mM solution of Pb(II) and Cd(II) were prepared and the ratio of carbon to solution was 0.5 g/dm³. The stirrer speed was maintained at 1000 rpm. All kinetic experiments were conducted for 3 h and repeated twice. Equilibrium adsorption studies of Pb(II) and Cd(II) were undertaken at 303 K and pH 6 for all carbons. An equilibrium time of 120 h was allowed to ensure the attainment of equilibrium conditions.

Micro-column experiments were undertaken to determine the sorption performance of SN30, SN45 and SN60 for the removal of lead and cadmium at 303 K and pH 6. The carbon samples were packed in mini-columns of nominal capacity of 5 cm³. The carbon was supported on polyethylene frits. The solution concentration was 2 mM and was passed through the column to generate the breakthrough curves at a flow of 20 bed volume per hour (20 b.v.).

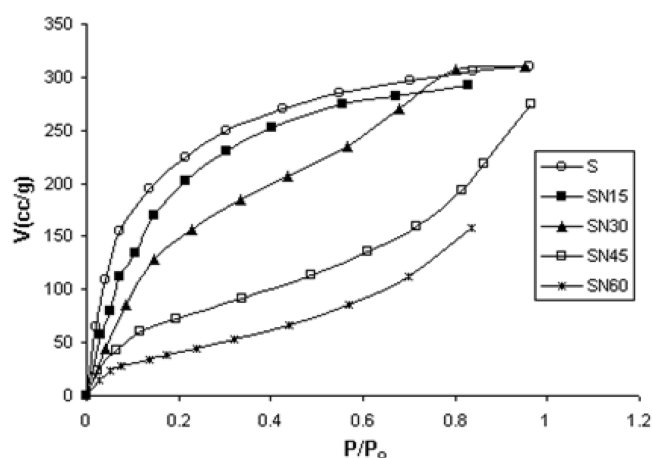
2.3. Analysis

The analyses of metal solution in kinetic, equilibrium or column experiments were made using Varian Spectra AA-200 atomic absorption spectrophotometer (AAS) in flame mode with an air-acetylene flame.

3. Results and Discussions

3.1. Textural Properties

The adsorption of nitrogen at 77 K proved to be rapid with

**Fig. 1.** Nitrogen adsorption isotherm at 77 K.

the equilibrium attained within one hour in case of carbons S and SN15 and within 30 min in case of the other investigated carbons. The nitrogen isotherms of carbons S and SN15 are of type I, that of SN3 shows the characteristics of type I and II. Typical type II isotherms are exhibited by SN45 and SN60. Fig.1 depicts the nitrogen adsorption isotherms of the investigated carbons. The monolayer capacities of the ACs were determined and the corresponding surface areas S_{BET} were calculated. The total pore volumes V_{T} (ml/g) were read from the amount adsorbed near saturation, i.e., at a relative pressure of 0.95. The mean pore radius r_{m} (nm) was calculated from equation (1).

$$r_{\text{m}} \text{ (nm)} = 2V_{\text{T}} \times 10^3 / S_{\text{BET}} \quad (1)$$

Another set of surface areas S_{α} were calculated using the α method of Sing [33], the nitrogen adsorption data on a non-porous carbon was taken as a standard [34]. This method allowed also the determination of the micropore volume V_{m} (ml/g) and the non-micropore volume V_{n} (ml/g).

Table 1 lists the textural properties of the ACs and reveals that (i) the values of S_{BET} and S_{a} are comparable (ii) the surface area decreased and the mean pore volume increased upon oxidation of the steam-activated carbon S with nitric acid. The extent of the change depends on the concentration of nitric acid used. Treatment with 15% nitric acid decreased the surface area by approximately 38%. This decrease in the area was associated with about 10% increase in the mean pore radius. A drastic decrease in surface area associated with a tremendous increase in r_{m} were obtained upon oxidation of carbon S with 60% HNO₃, (SN60). (iii) concentrated nitric acid may cause destruction of the texture of the carbon. (iv) The change of the type of nitrogen adsorption isotherm from type I characteristic of microporous sorbents to type II indicating multilayer adsorption in mesoporous solids is another evidence for the dramatic change in the texture. (v) the micropore volume V_{m} of sample S represents 63.3% of its total pore volume V_{T} , whereas V_{m} of the sample SN60 amounts only to 16.6% of the total pore volume V_{T} of the sample.

3.2. Chemistry of the Carbon Surface

The chemistry of the surface of a carbon is more important than its textural properties in determining its adsorption from aqueous solution particularly when the adsorption involves interaction with the surface functional groups via ion ex-

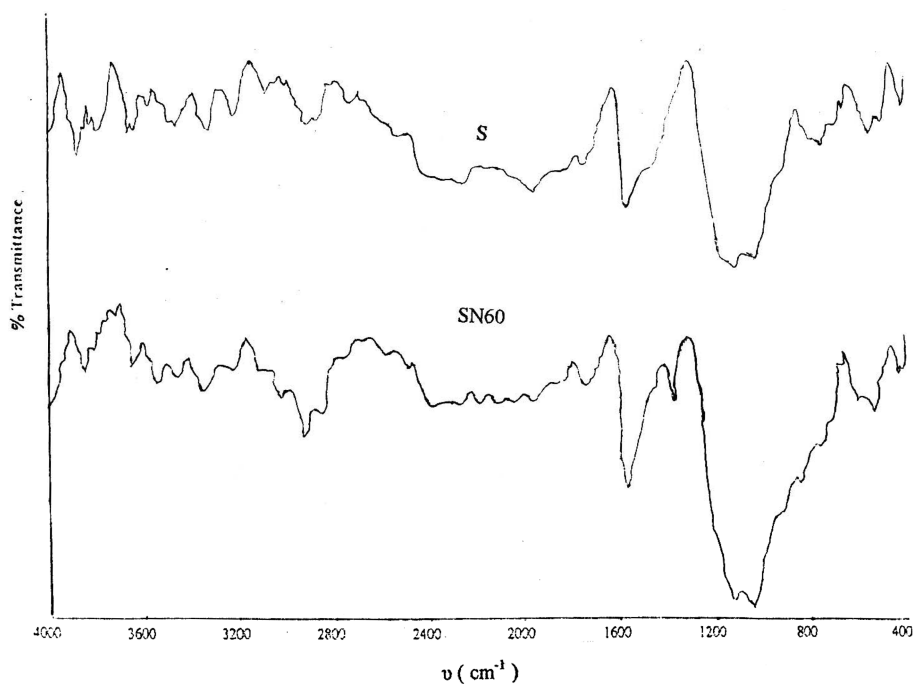


Fig. 2. FTIR Spectra of carbons S and SN60.

change and/or complex formation which is most probably the case in adsorption of metal ions on ACs. The chemistry of the carbon surface is attributed to the existence on the surface of carbon-oxygen functional groups of acid or basic character. The FTIR spectra of samples S and SN60 are depicted in Fig. 2. The modifications produced on the chemical surface groups due to oxidation with nitric acid can be seen in the FTIR spectra in Fig. 2. In sample S there is a doublet at 1750 and 1710 cm^{-1} which can be assigned to a C=O stretching vibration [35] of lactonic group. The band near 1600 cm^{-1} was ascribed to C=C stretching mode of aromatic ring or to C=O group conjugated with aromatic rings [36].

In general, the bands observed in the range 1460-900 cm^{-1} are produced by oxygen chemical groups in several forms. Stable carboxyl carbonates, phenols-OH, CO-COC groups, or other bridges between rings [37]. Shoulder between 1500 and 1400 cm^{-1} together with those between 1200 and 1000 cm^{-1} can be assigned to thermally stable carboxyl carbonates structures [37].

Although this analysis can not be considered quantitative, it can be concluded that oxidation with nitric acid produces an increase in C=O lactonic groups. Also an increase in the thermally stable carboxyl carbonate structures [38].

The pH of the aqueous slurry of the carbon material provides a convenient indicator of the type and concentration of the surface functional groups. Table 2. lists the surface chemical parameters of the ACs investigated. Table 2 reveals that: (i) the surface pH of carbon S (8.3) indicates its surface basicity, i.e. the basic function groups on the surface of non-

oxidized carbon are more dominating compared with those of acid type. The same is also true for SN15 of surface pH=7.4. Steam activation involves gasification with steam at 950°C of the carbonaceous product leading to the formation of carbon-oxygen groups of basic character [39]. Oxidation of a carbon with nitric acid creates surface acid groups decreasing thus the surface pH. Treatment with 15% nitric acid although decreased the surface pH from 8.3 to 7.4, yet the strength of the acid was not high enough to turn over the surface pH in the acid range. Successive decrease in surface pH was exhibited with the increase of nitric acid strength used in the surface oxidation of carbon S. Thus, for example, the surface pH of carbon SN60 was 4.3. (ii) The pH of the zero point of charge, pH_{pzc} is also a very important parameter in determining the sorption properties of the solid. The values of pH_{pzc} of the investigated carbons are given in column 3 of Table 2. They are lower than the corresponding surface pH values, but follow the same trend. (iii) the base neutralization capacities expressed in (meq./g) give quantitative measure of the type and amount of the surface functional groups. The surface acidic groups could be detected by the selective neutralization with series of bases of varying strength. NaHCO_3 , Na_2CO_3 , NaOH and NaOEt, NaHCO_3 neutralizes carboxylic groups whereas those neutralized by Na_2CO_3 but not by NaHCO_3 were believed to be lactones. The weakly acidic groups neutralized by NaOH but not by Na_2CO_3 were postulated as phenols. The reaction of NaOEt was not considered as a true neutralization reaction since it did not involve change by H^+ or Na^+ ions. The groups reacting with NaOEt but not with NaOH was

Table 2. Surface chemical parameters of the investigated carbons

Carbon	Surface pH	pH _{zpc}	Carboxyl (meq./g)	Lactonic (meq./g)	Phenolic (meq./g)	Carbonyl (meq./g)	Total (meq./g)
S	8.3	5.4	0.19	0.18	0.16	0.22	0.75
SN15	7.4	5.1	0.48	0.40	0.46	0.38	1.72
SN30	6.6	4.6	0.68	0.62	0.64	0.74	2.68
SN45	5.4	4.4	1.00	0.88	1.02	1.50	4.40
SN60	4.3	3.9	1.38	1.16	1.44	1.86	5.84

suggested to be carbonyl groups [40]. Table 2 indicates that the concentration of the different groups increased with the increase of the nitric acid used in carbon oxidation.

3.3. Adsorption of Pb(II) and Cd(II)

3.3.1. Effect of solution pH

The first step in studying adsorption from solution is to determine the effect of surface pH on the adsorption capacity of the adsorbents under investigation. This step is however, more important when adsorption of metal ions is concerned because these ions most probably compete with the hydrogen ions in solution for the sorption sites on the surface. In the present investigations the carbon samples S, SN30 and SN60 were selected to determine the role of solution pH. The sorption was followed at 303 K and an equilibrium time of 30 h was allowed for both Pb(II) and Cd(II). Preliminary experiments have shown that the adsorption of both ions at solution pH lower than 2.5 was either negligible or non-measurable. Based on this, the adsorption of the metal ions was followed in the pH range 2.5 - 7.0. Figs (3a,b) depict the equilibrium adsorption capacities, expressed as (mmol/g) as a function of pH.

It is shown that in between pH 2.5 and 3.5 or 4.0, the amount of metal ion adsorbed remarkably increased with the increase of pH. Beyond pH 3.5 or 4.0 until pH 5.0, the increase of metal uptake was sharp and tends to exhibit a plateau at pH of 5.5. The role of solution pH may be ascribed as follows: (i) at low pH values lower than 2.0, the hydrogen ion concentration is too high to retard the ionization of surface acidic groups such as carboxylics and phenolics. Also at such low pH values the repulsion between cations and the positively charged surface of carbons will take place. (ii) with the increase of solution pH ionization of surface groups may start to take place, the carbon surface becomes less positive allowing thus the possible competition of the cations for the adsorption sites. (iii) the sharp increase in the metal ion uptake in the pH range 3.5 - 5.0 is probably related to the zero point of charge, the pH of this point is known as pH_{pzc}. Evidently, pH_{pzc} values of the zero point of SN30, SN45 and SN60 lie between 3.9 and 4.6. pH_{pzc} of S and SN15 are 5.4 and 5.1, respectively. This may be ascribed to the effect of their surface pH, being > 7.0.

Figs. (3a,b) show also that for all carbons and at all surface pH values the uptake of Pb(II) is by far higher than

Cd(II) uptake. The amount of metal ion adsorbed is determined by many factors, the most important of which are the ionic radius, ionic potential, chemical properties and hydrolysis. The hydrated radius of Pb(II) equals 0.401 nm whereas that of Cd(II) equals 0.426 nm [41]. This may allow lead ions to have greater access to the surface. Lead also has a higher ionic potential (3.3) compared with cadmium (1.9). The pH of the hydroxide of lead ion (3.7) is much lower than that of cadmium (8.0) [42]. The pH of the hydroxide is a measure of its tendency to hydrolyze. This probably contributes to the high adsorption of Pb(II) onto the carbons investigated.

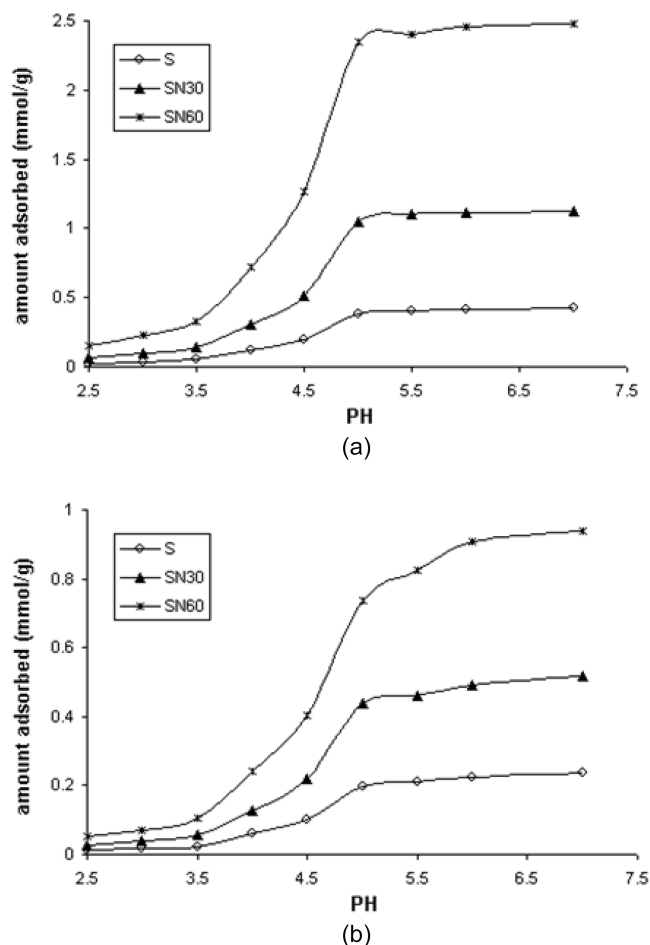


Fig. 3. Effect of solution pH on Cd(II) sorption on carbons S, SN30 and SN60.

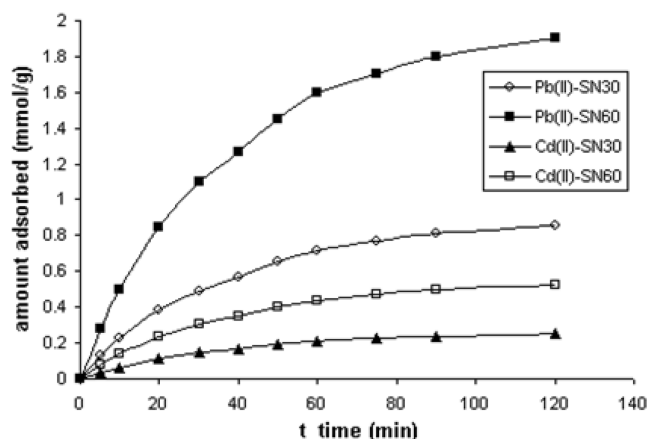


Fig. 4. Kinetic curves of Pb(II) and Cd(II) sorption at 303 K onto SN30 and SN60.

3.3.2. Sorption kinetics

After the determination of the appropriate pH for Pb(II) and Cd(II) adsorption, the sorption kinetics must also be studied to determine the order of the reaction and its rate constant. Following the kinetics of the adsorption allowed also the determination of the equilibrium time that should be considered in constructing the equilibrium adsorption isotherm.

The kinetic adsorption isotherms of Pb(II) and Cd(II) at 303 K and pH 6 are shown in Fig. 4. It is shown that the adsorption capacity of SN60 is considerably higher than that of SN30. It seems also that in all cases there were two step reaction mechanism, a rapid initial stage followed by a much slower reaction to attain equilibrium. The most accessible sites appear to be loaded in the first stage, followed by a second stage, that may be attributed to slower reaction rates of sites on the internal surface area of the samples.

Data of (Pb) and Cd(II) sorption were found to fit well the pseudo-second order model described by equation 2.

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (2)$$

Where q_e and q_t are the amounts of metal adsorbed at equilibrium and at time t per unit weight of the sorbent (mmol/g) and k_2 is the rate constant of the pseudo-second order reaction ($\text{g mmol}^{-1}\text{min}^{-1}$). Here, the initial sorption rate constant $h = k_2 q_e^2$ ($\text{mmol g}^{-1}\text{min}^{-1}$). Fig. 5 presents t/q_t versus t for both Pb and Cd ions adsorption onto SN30 and SN60. q_e and k_2 values as determined for Pb(II) and Cd(II) sorption on SN30 and SN60 at 303 K and pH 7.0 are listed in Table 3. Included also in this table are the values of the

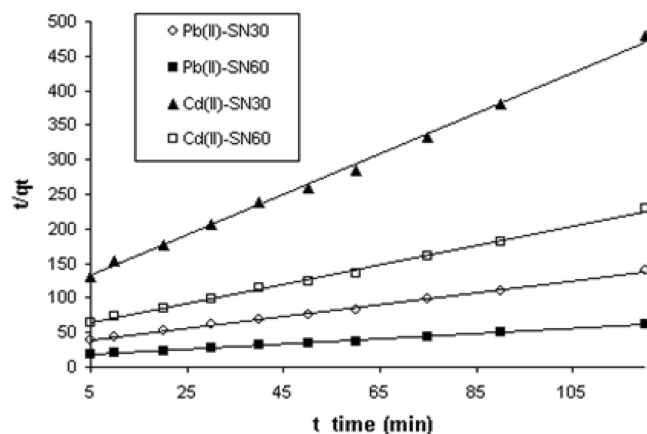


Fig. 5. Linear plot of t versus t/q_t of Pb(II) and Cd(II) sorption at 303 K onto SN30 and SN60.

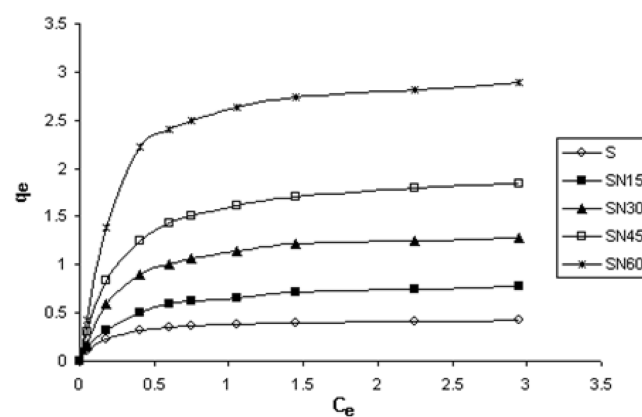


Fig. 6. Equilibrium adsorption isotherms of Pb(II) at 303 K and pH 6 onto ACs investigated.

regression coefficient of each adsorption system. Table 3 reveals that sorption of lead and cadmium complies very well with pseudo-second order reaction and an activated sorption mechanism as indicated by the high values of R^2 . This may be taken as an evidence that the rate of the reaction depends on both the sorbent and sorbate concentrations [41]. The values of K_2 decreased with the increase of the amount of metal sorbed at equilibrium q_e .

3.3.3. Equilibrium sorption of Pb(II) and Cd(II)

The adsorption isotherms of Pb(II) and Cd(II) on ACs investigated are shown in Figs (6 and 7). The isotherms are of Langmuirian type, i.e. Type L with steep initial portion

Table 3. Application of pseudo-second order model to Pb(II) and Cd(II) on SN30 And SN60

Sample	Pb(II) Sorption			Cd(II) Sorption		
	q_e (mmol/g)	k_2 (mmol/g.min)	R^2	q_e (mmol/g)	k_2 (mmol/g.min)	R^2
SN30	0.875	0.0378	0.9978	0.352	0.067	0.9971
SN60	2.690	0.0077	0.9979	0.730	0.034	0.9977

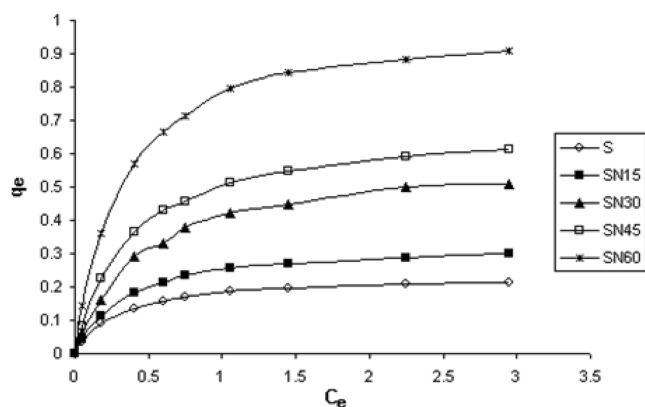


Fig 7. Equilibrium adsorption isotherms of Cd(II) at 303 K and pH 6 onto ACs investigated.

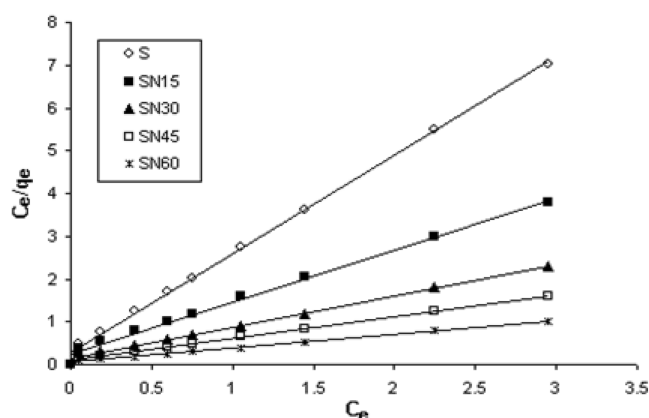


Fig. 8. Linear Langmuir plots for equilibrium adsorption isotherms of Pb(II) at 303 K and pH 6 onto ACs investigated.

and with a plateau starting at relatively low concentration and covers a wide range of equilibrium concentrations. The adsorption isotherms were analyzed using the linear form of the Langmuir equation, i.e., equation 3.

$$C_e/q_e = C_e/q_m + 1/b q_m \quad (3)$$

Where q_e (mmol/g) is the amount adsorbed at equilibrium concentration C_e (mmol/dm³). q_m (mmol/g) is the maximum sorption capacity, conventionally considered as the monolayer capacity and b is the Langmuir adsorption constant (dm³/mmol). The linear Langmuir plots of Pb(II) and Cd(II)

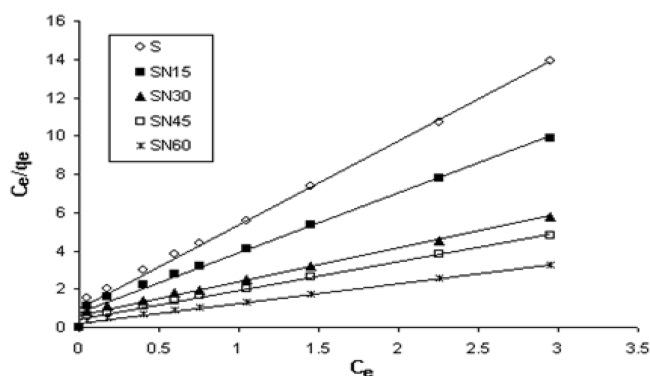


Fig. 9. Linear Langmuir plots for equilibrium adsorption isotherms of Cd(II) at 303 K and pH 6 onto ACs investigated.

adsorption on all the investigated carbons are shown in Figs. (8 and 9). Values of q_m and b are listed in Table 4 together with the values of regression coefficients R^2 of each system. The high values of R^2 refers to the excellent fit of the results obtained to the Langmuir model.

Figs (6 and 8) and Table 4 depict that the Pb(II) uptake capacity is enhanced by a factor of 7.8 for SN60 compared with Pb(II) uptake by the non-oxidized carbon S. For Cd(II) sorption the uptake of SN60 is 3.9 times larger than the uptake of S. Modification of the carbon surface via oxidation with concentrated nitric acid introduces a variety of carbon-oxygen functional groups of acidic nature. These groups dissociate in aqueous solutions and participate in the metal binding process. It is likely that other surface oxygen atoms (some of them may not be a component of protonogenic functional groups) may participate in metal complex formation. Thus, one would expect an ion exchange between Pb(II) and Cd(II) with the H⁺ released from the carboxylic and phenolic surface groups and therefore these groups contribute significantly to the enhancement of metal ion uptake. Carbonyl and/or lactonic groups, on the other hand are more likely involved in a complex formation with metal ions like Pb(II) and Cd(II) [5,6].

It has been already mentioned in this paper that oxidation of ACs brought about significant changes in surface areas and pore dimensions of these carbons. Pore widening may enhance adsorption from solution by increasing the accessibility of the adsorption sites on the internal surface area of the sorbent. However, it seems that the changes in the

Table 4. Data obtained from Langmuir plots of Pb(II) and Cd(II) sorption onto the investigated carbons

Sample	Pb(II) Sorption			Cd(II) Sorption		
	q_m (mmol/g)	B (dm ³ /mmol)	R^2	q_m (mmol/g)	b (dm ³ /mmol)	R^2
S	0.431	4.83	0.9976	0.240	3.20	0.9926
SN15	0.840	3.40	0.9931	0.330	2.89	0.9912
SN30	1.370	2.92	0.9927	0.597	2.57	0.9832
SN45	2.220	2.80	0.9943	0.690	2.42	0.9886
SN60	3.360	2.70	0.9949	1.000	2.22	0.9931

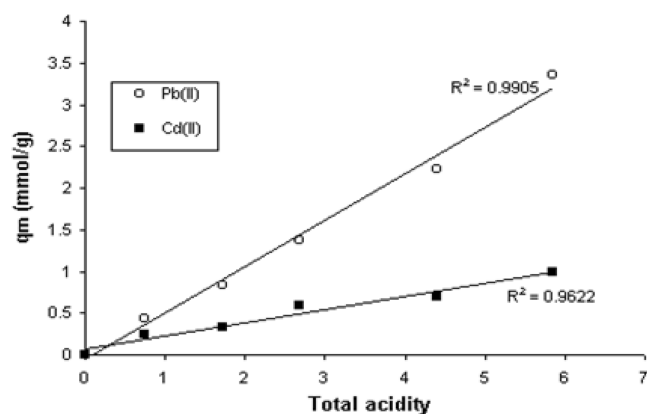


Fig. 10. q_m versus total surface acidity.

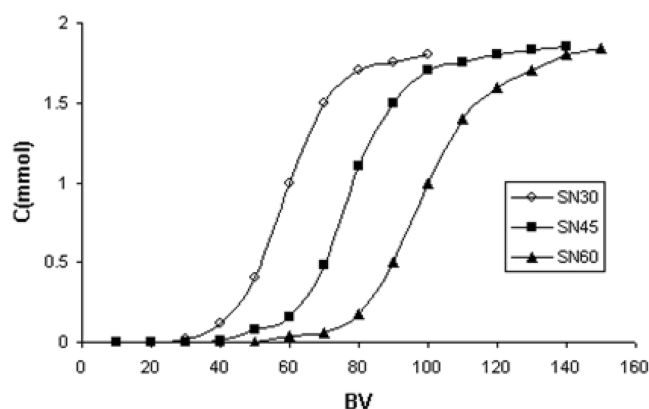


Fig. 11. Breakthrough curves of Pb(II) NS30, SN45 and SN60.

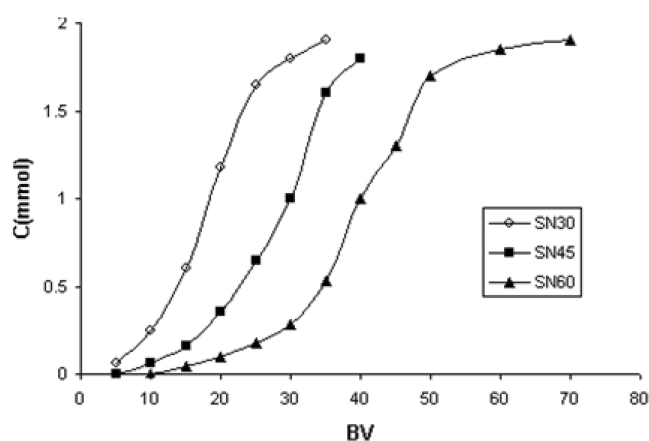


Fig. 12. Breakthrough curves of Cd(II) NS30, SN45 and SN60.

textural properties do not adversely affect metal adsorption. The dramatic increase in the metal uptake by the oxidized carbons may be ascribed to the introduction of new acid functional groups on the surface. A trial has been made to relate the metal ion uptake as expressed by q_m (mmol/g) to the total surface acidity (meq./g). Fig. (10) shows such relation. Two straight lines passing through the origin are

obtained each one stands for one of the two metal ions investigated. The values of the regression coefficients and the passage of the lines through the origin may indicate that the total surface acidity is the dominant if not the only sites on which metal sorption takes place via ion exchange and complex formation.

3.3.4. Column experiments

In practice, the treating plants used column-type operation because experiments cannot give accurate scale-up data to be used for flow columns. Applicability of ACs for column operations was also studied. The solution concentration for each metal ion was 2.0 mmol/dm^3 , the pH was 6.0 and the columns were maintained at 303 K.

The breakthrough curves of SN30, SN45 and SN60. Figs (11 and 12) show the concentration of Pb(II) and Cd(II) ions in the eluant versus bed volumes (bv), the bv was 5 cm^3 and the flow rate was 20 bv/h. The curves are more or less symmetric and indicate the high capacity of the columns for lead compared with cadmium. It remains now to point out that the breakthrough capacities determined from column experiments differ from the corresponding monolayer capacities obtained from the equilibrium adsorption experiments. For the determination of the monolayer capacity q_m equilibrium time was allowed whereas column operation involves dynamic conditions. Breakthrough capacities of 0.954, 1.23 and 1.85 were calculated for Pb(II) uptake on SN30, SN45 and SN60, respectively. For Cd(II), breakthrough capacities of 0.337, 0.511 and 0.746 were exhibited by SN30, SN45 and SN60 columns, respectively.

4. Conclusions

Steam-activated carbon S developed from pecan shells exhibited surface area of $872 \text{ m}^2/\text{g}$ and a total pore volume of 0.482 ml/g . However, a large fraction of this area is located in micropores. Oxidation of activated carbon with nitric acid brought about drastic decrease in surface area and remarkable pore widening. Treatment with nitric acid increased also the surface acidity of activated carbon as a result of creation of new carbon-oxygen groups of acidic character. Nitric acid-oxidized carbons exhibited high adsorption capacities for Pb(II) and Cd(II) with this adsorption following pseudo-second order model and the rate of the reaction depends on the concentration of the metal ions and the surface concentration of the acidic sites. The total surface acidity is the dominant if not the only factor determining the adsorption capacity of oxidized carbons for metal ions. Symmetric breakthrough curves indicating good breakthrough capacities for Pb(II) and Cd(II) were obtained from the column experiments.

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