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Modified Activated Carbons from Olive Stones for the Removal of Heavy Metals

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Abstract

The activated carbon "C" was obtained by carbonization followed by activation with steam at 40% of burn-off. Oxidized carbons C-N, C-P and C-H were obtained by oxidizing the activated carbon C with concentrated nitric acid, ammonium peroxysulfate and hydrogen peroxide, respectively. The textural properties of the carbons were determined from nitrogen adsorption at 77 K. The acidic surface functional groups were determined by pH titration, base neutralization capacity and electrophoretic mobility measurements. The cation exchange capacities of un-oxidized and oxidized carbons were determined by the removal of Cu(II) and Ni(II) from their aqueous solutions. The surface area and the total pore volume decreased but the pore radius increased by the treatment of activated carbon with oxidizing agents. These changes were more pronounced in case of oxidation with HNO_3. The surface pH of un-oxidized carbon was basic whereas those of the oxidized derivative were acidic. The removal of Cu(II) and Ni(II) was pH dependent and the maximum removal of the both ions was obtained at pH of 5-6. Cu(II) was more adsorbed, a phenomenon which was ascribed to its particular electronic configuration.

Keywords : *Activated carbon, Adsorption, Olive stones, Surface functional groups, Copper, Nickel*

1. Introduction

Heavy metals are of major concern because of their non-degradability and threat to human life and the environment. The heavy metals of most important concern are Hg, Pb, Cd, Cu, Zn, Cr and Mn [1-3]. A number of specialized processes have been developed for the removal of metals from waste discharges. These unit operations include: chemical precipitation, adsorption, coagulation/flocculation, ion exchange/ solvent extraction, cemnentation, complexation, membrane processes, biological and electrochemical operations [4-8].

Among various treatment technologies, adsorption onto activated carbons has proven to be one of the most effective and reliable physico-chemical treatment methodologies [9-11]. The interaction between the surface of active carbons (oxidized to enhance surface reactivity) and trace metal ions in aqueous media has been the subject of much recent research [12-14].

The selectivity and adsorptive capacity of conventional activated carbons towards heavy metals is rather low. However, metal sorption can be considerably enhanced by the introduction of weakly acidic functional groups through surface oxidation using different agents such as nitric acid, hydrogen peroxide and ammonium peroxysulfate [15]. The adsorption on oxidized activated carbons depends upon many variables including the metallic species to be removed, adsorbent surface chemistry and adsorption conditions [16, 17]. The proportion of weakly acidic surface functional groups as well as the concentration of individual groups are important factors in determining the selective removal of metal ion from solution [17].

The objective of the present investigation was to gain more understanding into the surface chemistry of steam-activated carbon "C" and three C-based oxidized carbons. Carbon "C" was obtained by carbonization followed by steam activation of olive stones at 40% of burn-off. Carbon "C-N" was obtained by oxidizing C with nitric acid; carbon "C-P" was obtained by oxidizing C with acidified ammonium peroxysulfate, whereas carbon "C-H" was obtained by oxidizing C with hydrogen peroxide. The physicochemical properties of carbon C and its oxidized derivatives were compared using different techniques for the characterization of adsorbents and for following their performance in adsorption from solutions. The capacities of C and its oxidized derivatives for the adsorption of Ni(II) and Cu(II) were investigated and discussed in relation to some physico-chemical properties of the carbons investigated.

2. Experimental

2.1. Materials

Carbon C was prepared as follows: Olive stones were

collected and then dried at 150ºC. The dried material was crushed to 2-4 mm size, washed with hot distilled water, and then carbonized in a muffle furnace at 600ºC for 1 h, in nitrogen atmosphere. Activation was applied by means of 1.0 kg/cm^2 pressure of steam at 900ºC for 1 h and the burn-off was determined to be 40 ± 0.5%.

C-N was obtained by oxidizing C with 30%(v/v) nitric acid at 90ºC for 12 h. The ratio of carbon to acid was 1:3 (v/v). Humic compounds formed were leached out of the carbon by washing with water followed by 2%(w/w) NaOH and finally with distilled water until the pH of the wash solution reached pH 9. Treatment with ammonium peroxy-sulfate to prepare C-P was as follows: carbon C was treated with a saturated solution of ammonium peroxysulfate in 2 M H_2SO_4 (1g C per 10 ml of solution) and left overnight. The oxidized sample was dried at 110ºC until no further SO_2 gas was evolved. Treatment with hydrogen peroxide to prepare C-H consisted of successive stages in which 5.0 g of C were out-gassed at 250ºC for 2 h, cooled to 30ºC in N_2 (purity > 99.998 vol.%) and treated with H_2O_2 solution of intermediate concentration (12.5 cm^3 of commercial H_2O_2 solution 33% w/v + 37.5 cm^3 of water) at pH 2.5 and a contact time of 2 h.

2.2. Methods

Elemental analysis of the adsorbents was performed using an elementary analyzer (Perkin-Elmer Series II 2400). The estimated error for each element analyzed was ± 0.5%.

The textural properties (surface area and porosity) were determined from the adsorption of nitrogen at 77 K using a conventional volumetric apparatus, the carbon sample was degassed at 200ºC under a reduced pressure of 10^{-5} Torr.

The pH of the aqueous solutions of the nitrates of Ni(II) and Cu(II) and also of the aqueous suspensions or the aqueous slurry of carbons were measured using digital pH meter (Pope model No. 1501).

The chemistry of the surface as determined from the surface pH and the relative concentrations of different surface functional groups in the investigated carbons were determined according to the Boehm's titration method [18]. Base neutralization capacities (BNC) were determined by the neutralization of 0.1 M $NaHCO_3$, Na_2CO_3, NaOH and $NaOC_2H_5$ by the carbon sample. Thus 0.25 g of the carbon sample was mixed with 50 ml of the respective solution in 100 ml Quick fit polyethylene bottles, the suspensions were flushed with nitrogen. Mechanical shaking was continued for 48 h. The residual concentration of each solution was determined by titrating the supernatant against 0.1 M HCl.

pH titrations of the carbons investigated were carried out using a previously reported method [19]. A number of samples of the same carbon (0.1 g each-particle size less than 50 μm) were weighed into separate flasks. A set of samples was prepared with successively larger amounts of 0.1 M NaOH or HCl added to the different samples using a micro-pipette. 10 ml of 0.1 M NaCl solution was added to each flask to ensure a high background electrolyte concentration. A total batch volume of 15 ml was made up by adding distilled water to maintain the solution-to-sorbent weight ratio constant. A blank experiment with no carbon was also considered. The batches were equilibrated for 48 h after which the pH of the supernatant solution was recorded. Proton release uptake values as a function of equilibrium pH were recorded as follows: A pH vs (NaOH added) curve was plotted for the batch samples before adding the carbon sample to each flask. After equilibration, a new pH vs (NaOH added) curve was constructed. At a given pH, the difference between the two curves provided values of proton release vs uptake. PH titration data were fitted using a previously described method [20] that also allowed extracting acid-dissociation constants for the acidic sites.

Electrophoretic mobility measurements of the sorbent suspensions were determined as a function of pH at the time of pH titration experiments. After pH measurements sorbent suspensions were injected into the electrophoretic cell and zeta potential values were recorded using a Zeta meter (Laser Zee 3.0, Pen kem Inc.)

The adsorption of Ni(II) and Cu(II) was carried out as follows: defined amounts of the carbon sample were shaken for different periods of time (kinetic experiments) at 30ºC. Equilibria of metal ion sorption isotherms at 30ºC were obtained as follows: 0.10 g of granular carbon particles were accurately weighed out into 250 ml conical flasks. 200 ml of metal nitrate feed solutions (concentration range 0.02-0.80 m mol/l) were added to each flask. The flasks were shaken for 48 h using a Stuart Scientific flask shaker. After equilibration small aliquots of supernatant solutions were separated and analyzed for metal content using an atomic absorption spectrophotometer (Varian Spectra AA-200) in flame mode with an air-acetylene flame.

3. Results and Discussion

3.1. Elemental analysis

Table 1 gives the elemental analysis of the carbons investigated and depicts that: the un-oxidized carbons contain less than 1% oxygen whereas the oxidized derivatives contain much higher amounts of oxygen, i.e. 6.6, 5.9 and 5.6% for C-N, C-P and C-H, respectively. The considerable increase in the oxygen content in oxidized carbons is probably ascribed to the surface carbon-oxygen groups created by oxidation with nitric acid, ammonium peroxysulfate or hydrogen peroxide. Oxidation with nitric acid slightly increased the nitrogen content whereas oxidation with peroxysulfate slightly increased the sulfur content. Nitrogen or sulfur may react with oxygen-containing surface groups and/or with the

Table 1. Elemental analysis of the carbons investigated

Carbon	Ash %	Elements					
		C	H	N	S	O*	Residue
C	3.4	88.5	0.60	0.52	0.82	0.99	8.57
C-N	2.5	84.5	0.58	0.88	0.06	6.60	7.38
C-P	3.2	84.9	0.59	0.55	0.98	5.90	7.63
C-H	3.1	85.2	0.58	0.53	0.03	5.60	8.06

*obtained by the difference between the percentage content.

mineral admixtures contained in the activated carbon. All the carbons investigated contain considerable amounts of inorganic matters (3.4-2.5%). Oxidation of the activated carbon was found to be associated with a decrease in the ash content with this decrease more pronounced for oxidation with nitric acid. Oxidation with nitric acid is more likely associated with a reaction of this acid with some inorganic constituents. Oxidation with peroxysulfate or with hydrogen peroxide involed also the use of dilute H_2SO_4 or HCl. These treatments may cause at least partially the digestion of some of the inorganic constituents. Most probably the residual ash in the oxidized is attributed to silica and silicate compounds. The major elements present in the ash include Si (13.8%), Al (12.8%), Fe (8.0%), Ca (2.8%), K (1.6%) and Na (1.4%). Similar results have been recently reported [21].

3.2. Textural properties

The adsorption of nitrogen at 77 K on C, C-N, C-P and C-H carbons proved to be rapid with the equilibrium attained within 20 min. However 30 minute intervals were allowed between successive adsorption points to ensure equilibrium condition. The rapid attainment of equilibrium may be taken as evidence for the absence of ultra-fine pores [22] in which adsorption of nitrogen at 77 K may be controlled by an activated diffusion process and refers also to the accessibility of the total porosity to nitrogen molecules [23]. Representative adsorption-desorption isotherms at 77 K (those of C and C-N) are shown in Fig. 1. The nitrogen adsorption isotherms of all the carbons investigated are of type IV showing hysteresis at high relative pressures [24].

Fig. 1 depicted that the nitrogen adsorption isotherm of C is characterized by steep initial region at low relative pressures ($P/P_o < 0.1$). This steep initial adsorption became less pronounced in the nitrogen isotherms of oxidized carbons. These isotherms are characterized by well defined inflection points (point B) indicating the completion of the mono-layer and the onset of multi-layer development. The isotherms obey the conventional BET equation [25] which allowed the determination of the mono-layer capacity and consequently the specific surface area S_{BET} (m^2/g), adopting the value of 0.162 nm^2 as the area occupied by nitrogen molecule. The total pore volume V_T (ml/g) could be obtained by converting

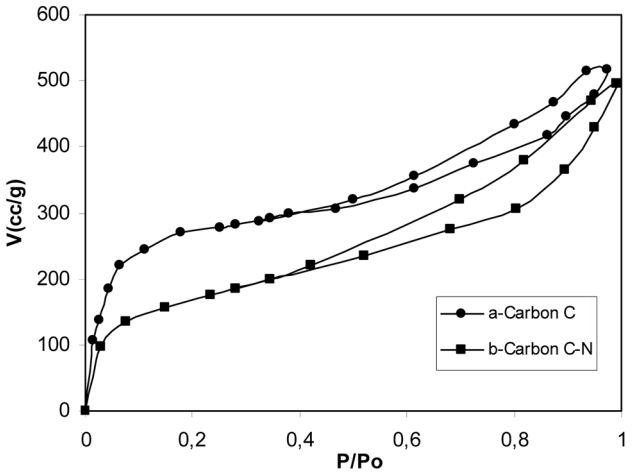

Fig. 1. Representative adsorption-desorption isotherms of nitrogen at 77 K.

the amount of nitrogen gas adsorbed at $P/P_o = 0.95$ into liquid. Another important textural parameter namely mean pore radius, r_m (nm), could be obtained from the relationship: $r_m = 2V_T/S_{BET}$, assuming cylindrical pore model [26]. S_{BET}, V_T and r_m of the carbons investigated are listed in Table 2. Included also in this table are the values of the BET-constant as determined from the BET equation is related to the heat of adsorption.

Table 2 reveals that: (i) the value of the BET-C constant of carbon C is the highest, i.e. 154, whereas that of C-N is the lowest, i.e. 46, those of carbons C-P and C-H are intermediate being 68 and 72, respectively. (ii) the surface area and total pore volume of the activated carbon C decreased as a result of oxidation with this decrease depending on the oxidizing agent used as a result of the contamination of the surface with the carbon oxygen groups which occupy a fraction of the surface [15]. (iii) Table 2 also depicts the oxidation of activated carbon is associated with pore widening as detected from the increase in r_m value. Generally the textural changes brought about by oxidation with nitric acid are more pronounced. Thus, for example r_m value of the activated carbon C was calculated to be 1.54 nm, i.e. lying in the region of micro-porosity, whereas r_m of C-N amounts to 2.2 nm lying thus in the region of mesoporosity. The increase in r_m values of C-P and C-H were calculated to be

Table 2. Textural characteristics of the carbons investigated

Carbon	S_{BET} (m^2/g)	V_T (ml/g)	r_m (nm)	BET-constant
C	960	0.744	1.55	154
C-N	620	0.680	2.22	46
C-P	691	0.718	2.08	68
C-H	682	0.699	2.05	72

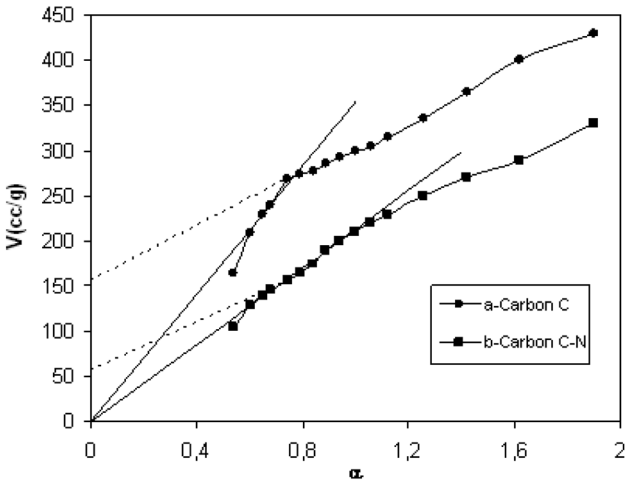

Fig. 2. Representative α-plots of nitrogen adsorption at 77 K.

2.08 and 2.05 nm, respectively. More knowledge on the texture of the carbons investigated could be obtained by considering the α-method [27] in analyzing the nitrogen adsorption results. The application of the α-method has been performed using the standard data reported [28]. This method is considered as an independent method for the determination of the specific surface area from nitrogen adsorption data. The method allows also the determination of some important textural parameters. These parameters are the area of micropores S^{α}_{mic} and the area of non-micropores S^{α}_{nonmic}.The volumes of micopores and of non-micropores V^{α}_{mic} and V^{α}_{nonmic} have been also determined. Fig. 2 shows representative α-plots (those of carbons C and C-N). The textural parameters determined by the α-method are listed in Table 3. Included also in this table are the total pore volume V_T and the BET-surface area S_{BET} for the subject of comparison. Table 3 depicted that: (i) comparable surface areas with difference not exceeding 2% are obtained from the α-method and the BET-method. This may be taken as an evidence for the reliability of the measurements. (ii) the surface area and the total pore volume of unoxidized activated carbons are higher than those of its oxidized derivatives. (iii) the volume and the surface area located in micropores decreased whereas those of non-micropores increased as a result of oxidation of the activated carbon. (iv) the textural changes depend among other factors on the oxidizing agent used.

3.3. Chemistry of the carbon surface

The chemistry of the surface of a carbon is equally important to its textural properties in determining its adsorption capacity particularly in adsorption from solution. The chemistry of the carbon surface is attributed to the existence of carbon-oxygen functional groups of acidic or basic character. The pH of the aqueous slurry of a carbon provides a convenient indicator on the acidity or basicity of this carbon. The functional groups on the surface of investigated carbons are listed in Table 4 together with the surface pH values.

Inspection of Table 4 reveals that: (i) the surface pH of the activated carbon C is basic whereas those of its oxidized derivatives are acidic. However, surface acidic and basic functional groups are existing in all the investigated carbons. Which of these functionality dominates depends on the methods of preparation, activation and/or modification. (ii) the Boehm's titration results show that the carbons possess acidic surface functionalites in a form of non-carbonyl (i.e., carboxylic, lactonic and phenolic groups) and carbonyl groups. The concentration of the acidic groups on the surface of carbon C is very low. Tremendous increase in the concentration of these acidic groups is observed due to treatment of this carbon with oxidizing agents. Thus, oxidation with nitric acid brought about 9.1-fold increase in the overall exchange capacity, 8.3-fold increase of the total exchange capacity was determined for peroxysulfate-oxidized carbon (C-P) and 7.0-fold increase for H_2O_2-oxidized carbon (C-H). (iii) the increase in the individual types of acidic

Table 3. Some textural parameters as determined by the α-method and the BET-method

Carbon	S_{BET} (m^2/g)	S^{α} (m^2/g)	S^{α}_{mic} (m^2/g)	S^{α}_{nonmic} (m^2/g)	V_T (ml/g)	V^{α}_{mic} (ml/g)	V^{α}_{nonmic} (ml/g)
C	960	980	532	448	0.744	0.296	0.448
C-N	620	610	274	336	0.680	0.140	0.540
C-P	691	685	322	363	0.718	0.223	0.495
C-H	682	675	308	367	0.699	0.250	0.449

Table 4. Surface functional groups (meq/g) and the pH of the carbons

Carbon	Carboxylic	Lactones	Phenolic	Carbonyl	Surface pH
C	0.04	0.09	0.01	0.15	8.6
C-N	0.80	0.40	0.50	0.95	3.8
C-P	0.62	0.48	0.50	0.80	4.6
C-H	0.55	0.38	0.45	0.65	4.2

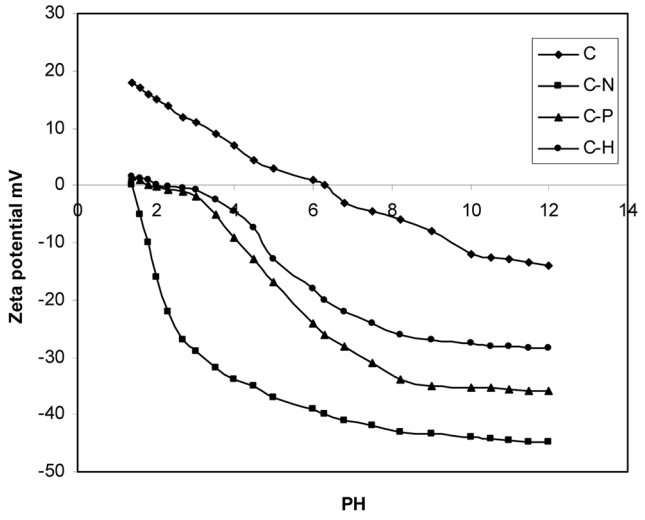

Fig. 3. Zeta potential curves for the carbons investegated.

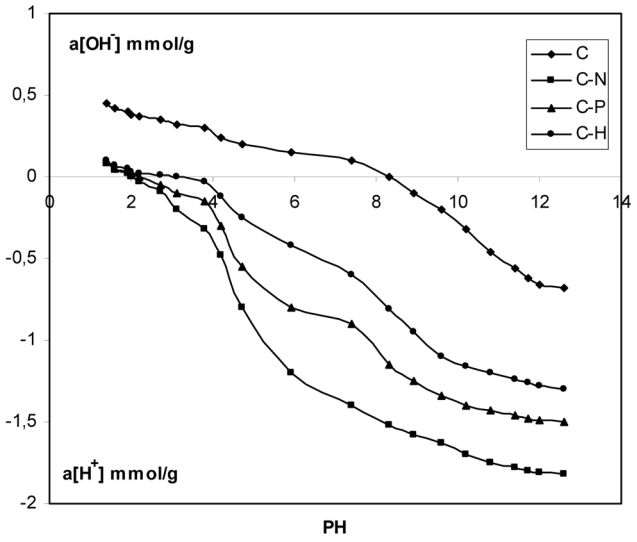

Fig. 4. Proton-binding curves for the carbons investigated.

groups after oxidation did not occur in equal proportion, but the relative concentration of noncarbonyl acidic groups followed the same order in all oxidized carbons, i.e., carboxylic > phenolic > lactonic.

3.4. Electrophoretic mobility

Active carbons are characterized by the existence of carbon-oxygen groups of varying amount and nature on their surface. Active carbons are therefore considered as amphoteric sorbents for which the pH of an aqueous solution is the dominant factor in determining their adsorption properties, particularly of charged ions. An important parameter in considering the adsorption of charged species from aqueous solution by activated carbon is the isoelectric point (IEP). This is the point at which the electrokinetic potential of the sorbent (Zeta potential) equals zero.

Fig. 3 presents the zeta potential of the carbons investigated as a function of pH. The zeta potential curves of the oxidized carbons are very different compared with that of the unoxidized carbon, the IEP of the latter was detected at pH=6.3. A considerable shift was found for oxidized carbons. Thus, the IEP of C-N was shifted to pH 1.4 whereas those of C-P and C-H were detected at pH 1.8 and 2.0, respectively. The high concentration, mutual arrangement and the high dissociation constants of various surface functional groups on one hand, and the electron-donating properties of the carbon matrix on the other hand, explain the low values of IEP's of oxidized carbons [29]. Beyond the pH values of the IEP the surface charge of the oxidized samples remains negative up to pH~12, the highest pH value investigated. Fig. 3 together with Table 4 show the existence of minor quantities of weak acidic groups which dissociate at high pH values [30].

3.5. pH titration

The proton-binding pH titration curves of the carbons investigated are shown in Fig. 4. Basic properties are dominated in unoxidized carbon C, up to pH 8.3. On the other hand, C-N exhibited acidic properties above pH 2.0, C-P and C-H exhibited acidic properties at slightly higher pH values, i.e., 2.7 and 3.1, respectively. The titration curve of carbon C indicates very low cation exchange capacity although high anion exchange capacity may be exhibited by this carbon. The titration curves of the oxidized carbons are continuous indicating their polyfunctional nature, but the existence of some inflections in these curves may be attributed to the considerable difference between the dissociation constants of the functional groups. The titration curves of the oxidized carbons show shallow descents in the pH range between 2 and 4 (this phenomenon is more obvious for C-N), which may be ascribed by the suppressed dissociation of surface functional groups. With the increase of the pH, the gradients of the titration curves of oxidized carbons increased up to pH values between 9 and 11. Beyond these pH values weaker functional groups (lactonic and phenolic etc.) begin to dissociate and to contribute to the total cation exchange capacity. It remains now to point out to the fact that the dissociation constants of acid functional groups in the carbon investigated exhibited, greatly, different values between 10^{-3} and 10^{-11}. An additional evidence for the polyfunctional nature of the carbons investigated is obtained from the dissociation constants of acid functional groups as depicted in Table 5.

The crossover point of the titration curves with the pH axis is the point of zero charge (PZC) at which cation and anion exchange processes are at equilibrium. PZC occurred at low

Table 5. Electrophoretic mobility and dissociation constants of the carbons

Carbon	PH_{IEP}	PH_{PZC}	PH_{PZc} - pH_{IEP}	PK_{a1}	PK_{a2}	PK_{a3}	PK_{a4}
C	6.5	8.3	1.8	–	–	9.1	10.8
C-N	1.4	2.0	0.6	3.6	5.7	7.5	9.9
C-P	1.8	2.7	0.9	4.0	5.9	7.8	10.1
C-H	2.0	3.1	1.1	4.6	6.2	8.1	10.1

pH in case of oxidized carbons whereas it occurred at high pH ~ 8.3 in case of unoxidized carbon. Oxidation of activated carbon is a diffusion controlled process due to the wide range of the pore size distribution of activated carbons. The alkalimetric titration process is also a diffusion controlled process because it involves transfer of protons and OH^- ions between the bulk phase and the solid surface. Based on this, the PZC measurements represent the net total surface charge of the particle. On the other hand, electrophoretic mobility measurements detect the potential of the electric double layer at a plane adjacent to the external surface [31]. Hence, the IEP values are only representative of the external surface charges of the carbon particles in aqueous solutions. The difference between ZPC and IEP can therefore be taken as a measure of the charge distribution of porous carbons. Higher pH_{PZC}–pH_{IEP} values indicate a more negatively charged external than internal particle surface. Lower values suggest a more homogeneous distribution of the surface charges. Table 5 gives the PZC and IEP values of the carbons investigated.

3.6. Metal sorption

It is well established that sorption from solution depend to a great extent on the pH of that solution. Preliminary experiments have been carried out to determine the pH at which maximum adsorption of Cu(II) and Ni(II) was obtained. Evidently, un-measurable adsorption of these metal ions was found at pH lower than 2. The amount adsorbed was found to increase with increasing pH to reach to a maximum at pH 5 which continued at pH 6. At pH < 2, the $[H^+]$ is high and competition between this ion and Cu(II) and Ni(II) for the sorption sites is expected. At pH > 7 precipitation of metal ions may take place and continue to increase with further increase of pH. In this investigation all metal ion adsorption measurements were made at pH 6.

After determining the pH at which sorption of Cu(II) and Ni(II) should be followed, the kinetics of sorption of these ions must be determined. Meanwhile, the change of sorption with time allows the determination of the time required to attain equilibrium which is essential to construct the adsorption isotherms.

3.6.1. Kinetic measurements

The kinetics of sorption of Cu(II) and Ni(II) at 30°C on C and C-N carbons are shown in Fig. 5. It is evident that the adsorption capacity of C-N for Cu(II) and Ni(II) are very high compared to the capacity of C. This indicates that the textural parameters are not important factors in determining the adsorption behavior of heavy metal ions from aqueous solution on activated carbons. Carbon C possesses higher surface area and porosity compared with C-N although the latter exhibited higher capacities for the metal ions. It is also predicted from Fig. 5 that the initial adsorption is rapid and that after 120-180 minutes insignificant increase in the metal ion uptake was observed. The uptake of Cu(II) and Ni(II) was found to vary linearly with the half power of time ($t^{0.5}$), in the initial stages (the plots are not illustrated).

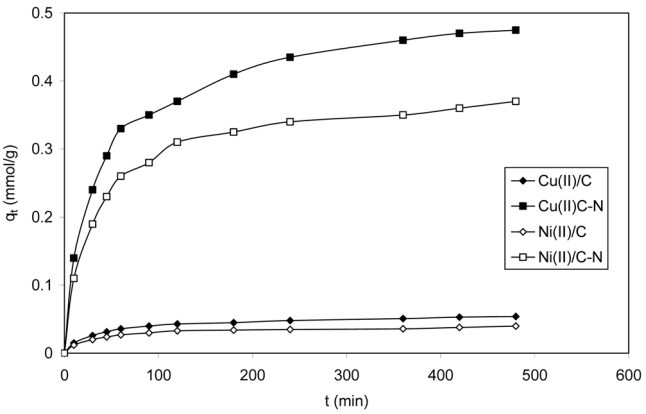

Fig. 5. Kinetics of (i) Cu(II) sorption at 30°C onto carbon C, (ii) Cu(II) onto carbon C-N, (iii) Ni(II) onto carbon C and (iv) Ni(II) onto carbon C-N.

The kinetic adsorption data of Cu(II) and Ni(II) onto were analyzed assuming pseudo second order kinetics [32]. The linear form is :

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

where q_t and q_e are the amounts adsorbed at time t and at equilibrium, respectively and K_2 is the overall rate constant. The kinetic adsorption data gave satisfactory straight lines when values of t/q_t were plotted versus t (Fig. 6). For Cu(II) adsorption on C-N, K_2 and q_e were determined to be 0.075 g min/mmol and 0.452 mmol/g, respectively. Ni(II) adsorption on the same carbons gave 0.086 g min/mmol and 0.393 mmole/g for K_2 and q_e, respectively. Higher K_2 values (0.74 and 0.81 g min/mmol) were calculated for Cu(II) and Ni(II)

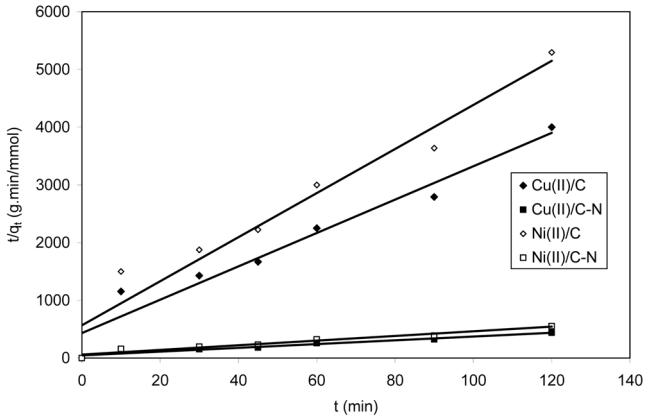

Fig. 6. Pseudo second order of Cu(II) and Ni(II) sorption on C and C-N carbons at 30°C.

adsorption on C, the q_e values of Cu(II) and Ni(II) were determined to be 0.055 and 0.042 mmol/g, respectively.

3.6.2. Equilibrium adsorption

The adsorption isotherms of Cu(II) and Ni(II) at 30ºC on the carbons investigated are shown in Fig. 6. The isotherms are of Langmurian type (L type) with relatively steep initial portions and with a plateau starting at relatively low solution concentration, the plateau covers a wide range of solution concentration. The adsorption data were analyzed by using the linear form of Langmuir equation [33]:

$$C_e/q_e = C_e/q_m + 1/bq_m$$

Where C_e the equilibrium concentration (mmol/l), q_m the monolayer capacity (mmol/g), and b the adsorption equilibrium constant (1/mmol). The linear Langmuir plots are shown in Fig. 7 and the equilibrium sorption data are listed in Table 6.

Table 6 predicts that the values of the adsorption equilibrium constants are comparable (11.9-15.0). This may be

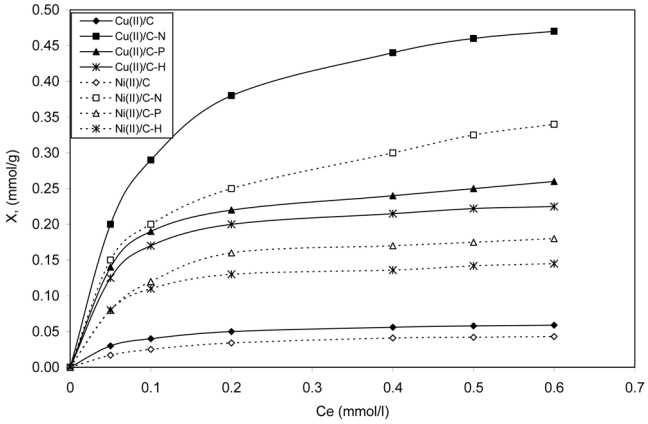

Fig. 7. Adsorption isotherms at 30°C of (a) Cu(II) and (b) Ni(II) onto the carbons investigated.

Table 6. Monolayer capacities and adsorption equilibrium constants of Cu(II) and Ni(II)

Carbon	Cu(II)		Ni(II)	
	q_m(mmol/g)	b (l/mmol)	q_m(mmol/g)	b (l/mmol)
C	0.067	15.0	0.050	12.9
C-N	0.542	12.5	0.374	13.9
C-P	0.265	14.8	0.200	15.0
C-H	0.242	13.3	0.143	14.5

attributed to the similarity of the sorbent-sorbate systems. Concerning the values of q_m, unoxidized carbon C measured low adsorption capacities for Cu(II) and Ni(II) compared with oxidized carbons. It is also depicted from Table 6 that oxidation of activated carbons is associated with a considerable increase in metal ion uptake. However, oxidation with nitric acid brought about the maximum effect. It is also evident that for all the carbons investigated, Cu(II) is more adsorbed than Ni(II).

The diversity of the surface functional groups in carbons may cause the metal ions to react differently with the surface. The bond between the metal ion and the carbon surface will depend on the nature of the metal ion. Thus, for example, the interaction of alkali metal ion (Na^+) with the carbon surface may be purely ionic interaction. Heavy metal ions are not similar to alkali metal ions and therefore their interaction with the surface is not purely ionic. Transition metal ions capable of forming complexes are expected to interact with the carbon surface where ionic bonds may substantially lose their hetero-polarity and become coordinate covalent in nature such as M^{2+}-O-C. The high uptake of Cu(II) by carbons compared with Ni(II) may be ascribed to its particular electronic configuration. Cu(II) ions have the electronic configuration d^9 which is susceptible to Jahn Teller distortion [34], with the six metal-ligand bonds in the octahedral Cu(II) complexes are not of the same strength. Distorted Cu(II) octahedral complexes are relatively more stable [35], favoring thus the adsorption of this particular metal ion.

4. Conclusions

Oxidation of activated carbon with oxidizing agents was associated with a decrease of surface area and total pore volume but, with an increase in the pore dimensions.

Basic properties are dominant for untreated steam-activated carbon. This is in contrast to the oxidized carbon which exhibited acidic properties. Treatment of activated carbons with oxidizing agents concentrated the acidic surface functionalities depending on the oxidizing agent and on the degree of oxidation.

The removal of Cu(II) and Ni(II) from their aqueous

solution is pH dependent with the maximum removal of both ions exhibited at pH=5-6. At low pH values the adsorption of metal ions is retarded by the high concentration of hydrogen ions. Cu(II) is more adsorbed than Ni(II) although the ionic radius of the latter is smaller. The electronic configuration is a prominent factor in determining the adsorption of heavy metal ions.

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