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Modified Activated Carbons from Tea Waste for the Removal of Cu(II) and Pb(II) Ions

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COLLOIDAL carbon was prepared from tea waste and then modified with H_2O_2. The physical and chemical properties were studied using N_2 adsorption at 77K, FTIR, SEM, effect of pH and base neutralization capacities. The adsorption of Cu(II) and pb(II) ions on the investigated sorbents was determined by kinetic and equilibrium measurements carried out at 303, 313 and 323K, respectively. Treatment of colloidal carbon with concentrated hydrogen peroxide, the surface area and micropore volume decreased but the total pore volume and mean pore radii increased. The adsorption capacity for both heavy metals ions was the highest at solution pH 5-6 for modified and unmodified sorbents, respectively. The kinetic data fits to pseudo-second order model and the adsorption is more controlled by intraparticle diffusion. The Langmuir adsorption isotherm model gave the better fit to the equilibrium adsorption data for both Cu(II) and pb(II) ions. The maximum adsorption capacities of Cu(II) and pb(II) ions per gram oxidized tea waste carbon were calculated as 1.385 and 1.750 mmol/g, respectively. The $\Delta G°$, $\Delta H°$ and $\Delta S°$ were calculated. It was found that the adsorption was spontaneous and endothermic, with favourable adsorption capacities being observed at higher temperatures. The sorption energy values obtained suggesting that the sorption mechanism may be a combination of electrostatic and physical sorption.

Keywords: Cu(II) & Pb(II) ions, Adsorption, Colloidal active carbon from tea waste, Isotherms, Kinetics and Thermodynamics.

The removal of toxic metal ions from aqueous solutions received a great deal of attention in the last years. Heavy metal ions are both stable and persistent environmental contaminants. Since, they cannot be degraded. The presence of excess metal ions levels in surface water may pose a health risk to human and to the environment. The heavy metals of most important concern are Hg, Pb, Cd, Cu, Zn, Cr and Mn[1-3]. The main sources of heavy metal pollution include mining, petroleum, textile, milling and surface finishing industries which discharge a variety of toxic metals into the environment. The conventional methods for the removal of heavy metal ions from water and waste water include reduction, oxidation, precipitation, membrane, filtration, ion-exchange and adsorption. Each of these processes has advantages and disadvantages based on simplicity, flexibility and effectiveness of the operation, cost, technical problems and maintenance.

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Adsorption has been found to be an efficient and economic process to remove heavy metal ions from waste water.

Due to the high cost of the active carbons, researchers have been encouraged to look for other types of low-cost sorbents. Carbonization of agricultural materials can be performed by dehydration with sulfuric acid resulting in colloidal porous active carbon at considerably lower cost compared with conventionally activated carbon[4-6].

Surface chemistry of carbons depends on the concentration of the surface functional groups may be modified by suitable chemical post treatments[7-10]. Some studies have demonstrated the ability of tea wastes to remove some types of heavy metal[11-15].

Here, using dried tea waste as precursor (sorbent 1). An Activated carbon is prepared by dehydrating tea waste with concentrated sulfuric acid (sorbent 2) and the resulting product is oxidized with concentrated H_2O_2 aqueous solution (sorbent 3). The characteristics of the porous structures and the oxygen surface functional groups of the investigated sorbents were estimated using N_2-adsorption at 77K and FTIR, Boehm method and SEM. All investigated sorbents were used for the adsorption of Cu(II) and Pb(II) ions from aqueous solution at different pH values,   the kinetic and equilibrium adsorption of these ions were also investigated at 303, 313 and 323K, respectively. These studies were performed to elucidate the relation between sorptive performed and the surface properties of these materials. The adsorption data were analyzed using the Langmuir, Freundlich and D-R equations. The kinetic characteristics of adsorption were studied with pseudo-first and second order equations and the intra-particle diffusion. The effect of the temperature on the adsorption of Cu(II) and Pb(II) ions was also studies.

Experimental

Material

Tea waste was collected from the cafeteria, washed thoroughly with hot distilled water and dried before usage. The dried tea waste (NTW) was crushed and sieved to 2.00 mm particle size. This gives sorbent 1, sorbent 2 "Colloidal carbon" was obtained by reaching sorbent 1 (20g) with sulfuric acid (12mol/L) in a 1:1 weight ratio at 303K for 24hr. The result black mixture was allowed to cool and then filtered. The carbonized product was washed several times with distilled water; the sorbent was soaked in a 1% sodium bicarbonate solution for 2 days to remove any remaining acid. The sample was then washed with distilled water until the pH of the wash water attained a value of 6 and did not give a precipitate with barium chloride solution. The carbonized product was dried at 373K for 24hr. Sorbent 3 (H_2O_2/HTW) was prepared by pre-oxidation of sorbent 2 with concentrated hydrogen peroxide, then 10g of the sorbent 2 (HTW) was treated for 24hr with 25ml of aqueous hydrogen peroxide (concentration 35%) in 20ml of

distilled water and oven-dried for 24hr at 373K. This treatment was designed to develop the greatest number of active sites on the surface of the investigated sorbents.

$Cu(NO_3)_2$ $3H_2O$ and $Pb(NO_3)_2$ were an analytical grade chemical and were prepared in deionized water.

Methods

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

The functional groups on the surface of sorbents 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 Pb(II) were measured using digital pH meter (Pope Model No. 1501). Surface morphologies of the sorbents 1, 2 and 3 were identified using JOEL JSM device.

The chemistry of the surface as determined from the surface pH and the relative concentration of different surface functional groups in the investigated sorbents were determined according to the Boehm's titration method[16]. Base neutralization capacities (BNC) were determined by the neutralization of 0.1M $NaHCO_3$, $Na_2(CO_3)$, NaOH and $NaOC_2H_2$ by the sorbent sample. Thus 0.25g of the sample was mixed with 50ml of the respective solution in 100ml (Guich fit polyethylene bottles) , the suspensions were flushed with nitrogen. Mechanical shaking was continued for 48hr. The residual concentration of each solution was determined by titrating the supernatant against 0.1M HCl.

The batch adsorption of Cu(II) and Pb(II) was carried out as follows; defined amounts of the sorbent sample were shaken for different periods of time (Kinetic experiments) at 30°C. Equilibrium of initial ion sorption isotherms at 30°C were obtained as follows: 50mg of sorbent particles were accurately weighted out into 250ml conical flasks-100ml of metal nitrate feed solutions (concentration range (0.3-3.0)mmol/L and (0.2-2.0)mmol/L for Cu(II) and Pb(II), respectively were added to each flask. The flasks were shaken for 24hr using a Stuart scientific flask shaker. After equilibration small aliquots of supernatant solutions were separated and the concentration of Cu(II) and Pb(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 wave lengths of 324.8 nm and 217 nm were employed for the determination of copper and lead , respectively.

The amount adsorbed at equilibrium q_e or at time (t) q_t was determined from the corresponding initial concentration using Eq. (1) and % removal using Eq. (2)

$$q_e \, or \, q_t = \frac{(C_o - C_e \, or \, C_t)V}{m} \qquad (1)$$

$$\% \, removal = \frac{C_o - C_e}{C_o} \times 100$$

$$(2)$$

where, C_o, C_e and C_t are the initial, equilibrium and concentration at time t (mmol/L), respectively, V is the volume of the adsorption solution (L) and m is the mass of the sorbent (mmol).

Results and Discussion

Textural properties

The adsorption capacity of an adsorbent is determined by its texture (surface area and porosity) which is shown in Table 1. The adsorption of nitrogen at 77K on sorbent 1 (untreated) was too low to allow reproducible or trustful values for the textural parameter. Chemically-activated carbons are characterized by high surface area and wide range of pore size distribution. Colloidal carbons prepared by dehydrating cellulosic materials with concentrated sulfuric acid possess considerably lower surface areas and less developed pore structure.

The nitrogen adsorption isotherms of sorbents 2 and 3 are shown in Fig. 1, type II according to the BDDT classification[17], indicating the domination of mesoporous. The BET equation[18] 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 sample was also determined from the volume of nitrogen sorbed near saturation. The mean pore radius, $\bar{r}$ (nm) was calculated from the relationship.

$$\bar{r} = \frac{2V_T}{S_{BET}} \times 10^3 \qquad (3)$$

The volume of nitrogen adsorbed at relative pressure $= 0$ may be taken as a measure of the micropore volume V_{mic}, this allowed the determination of the ratio V_{mic}/V_T.
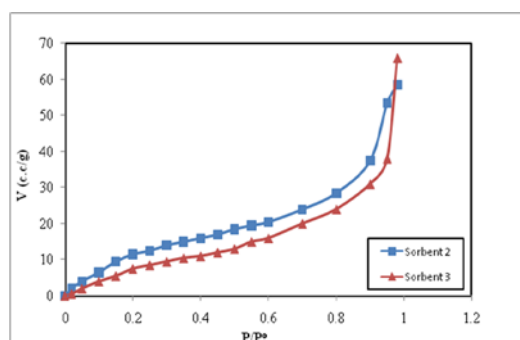

Fig. 1. Nitrogen adsorption isotherms at 77K onto sorbent 1 and sorbent 3 .

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

Sorbent	S_{BET} (m^2/g)	V_T ml/g	$\bar{r}$ (cm)	V_{mic} ml/g	V_{mic}/V_T dimension less
1	0.84	-	-	-	-
2	52	0.083	3.17	0.010	0.120
3	37	0.091	4.91	0.006	0.066

Inspection of Table 1 reveals that (i) sorbent 3 measured the lowest surface area and the largest total pore volume and mean pore diameter (ii) the microporosity in sorbents 2 and 3 represents small fractions of the total pore volume. The predominating pores are of mesoporous type.

Concentrated sulfuric acid acts as a hydrating 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 this carbon is considered as external surface area and other part is located in mesopores. The pre-oxidation of colloidal charcoal with hydrogen peroxide, the surface area of the latter is considerably lower and also most of their surface areas are located in mesopores.

The chemistry of the surface

The chemistry of the surface of an adsorbent is important in determining its adsorption capacity particularly from solution. The chemistry of the sorbent surface is due to the existence of carbon-oxygen groups of acidic and/or basic nature. The chemistry of the sorbent surface is determined from the base neutralization capacities (BNC)[16] expressed in (m.eq/g). The carbon-oxygen groups are listed in Table 2. The surface pH of the investigated samples is also given in Table 2.

TABLE 2. The carbon-oxygen groups on the surface of the investigated samples.

Sorbent	Carboxylic meq/g	Lactonic meq/g	Phenolic meq/g	Carbonyl meq/g	Total acidity meq/g	pH surface
1	0.80	0.20	0.29	0.18	1.29	6.42
2	1.8	0.40	0.76	0.24	2.96	6.06
3	2.6	0.54	0.80	0.22	3.94	5.40

The results given in Table 2 indicate that the sorbents 1, 2 and 3 contain considerable concentrations of surface-oxygen groups with their type in the order, carboxylic > phenolic > lactonic > carbonyl. These investigated samples contain very low concentration of surface carbon-oxygen groups of basic nature. The surface pH's of investigated samples lie on the acidic side and continuously shift to the lower pH's values with the increase of the amount of surface acidity. The Boehm's titration results show that the investigated samples possess acidic

surface functionalities in a form of non-carbonic (*i.e.,* carboxylic, lactonic and phenolic groups). The concentration of acidic groups on the surface sorbent 1 is very low. Tremendous increase in the concentration of these groups is observed for sorbents 2 and 3 due to treatment of sorbent 1, with H_2SO_4, or sorbent 2 with H_2O_2. Thus, oxidation with H_2SO_4, sorbent 2 brought about 2.2 fold increase of the total acidity and 3.0 fold increases for H_2O_2 oxidized sorbent 2 to sorbent 3.

Surface functionality of the sorbents 1, 2 and 3, FTIR spectra are shown in Fig. 2. As shown in the figure, sorbent 2 showed spectra intermediate between those exhibited by sorbent 1 and sorbent 3. This may be taken as evidence that oxidation with sulfuric acid of biosorbent materials, concentrates the acid functionality on the surface of resulted carbonized product. The H_2O_2-treated carbon shows a significantly different trend in the FTIR spectra. The FTIR spectra of the sorbent 3 in Fig. 2 exhibited strong and broad bands in the 3600-3000 cm^{-1} region (O-H stretching vibration). The appearance of a sharp absorption peak at 1740-1648 cm^{-1} indicates the abundant introduction of carboxyl, carbonate structure. The band at 1730 cm^{-1} for sorbent 3 is due to stretching vibration of carboxyl groups on the edges of layer plane. The weak bands appearing at 1540, 1434, 1384 and 1355 cm^{-1} are due to formation of highly conjugated (C=O stretching, C=O stretching in carboxylic groups and carboxylate moieties. Figure 2 also shows that the intensity of peaks at 1648 cm^{-1} increased from 67.9 to 86.4 (27%) after modification of sorbent 2 with hydrogen peroxide indicating the increases in the number of – C=O – groups. The weak band near 1628 cm^{-1} for sorbent 3 indicates the conversion of -OH groups to peroxo-groups[19]. In fact, it has been reported that treatment of sorbent 2 with H_2O_2 promotes the conversion of –OH group to peroxo-groups. However, the present results agree with those previously reported[19].
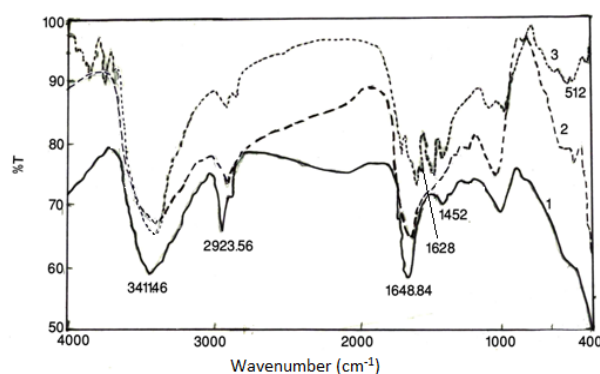

Fig. 2. Fourier transforms infrared spectra of (1) Sorbent 1 (2) Sorbent 2 (3) Sorbent 3.

The scanning electron microscope (SEM) micrographs clearly reveal the surface texture. SEM micrographs of the sorbents 1, 2 and 3 are shown in Fig. 3 (a, b & c). The surface morphology of sorbent 1(3a) is different from that of

sorbent 2 (3b) or sorbent 3 (3c). After being treated with sulfuric and then oxidized with H_2O_2, respectively, more irregular and more porous structure than sorbent 1 and therefore a larger surface area of sorbent 2 and then decrease in surface area after oxidation with H_2O_2 with increase of the mean pore radii. The SEM micrographs obtained at magnification of x1000 clearly indicate the porous structure of the activated carbons.
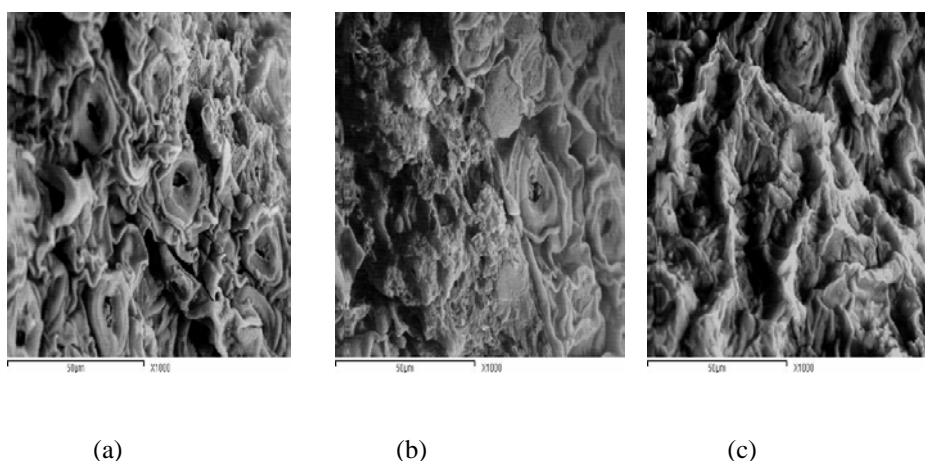

(a)   (b)   (c)

Fig. 3. SEM for (a) sorbent 1 (b) sorbent 2 and (c) sorbent 3.

Effect of solution pH on Cu(II) and Pb(II) ions uptake

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 Pb(II) ions was studied using a dosage of 50mg sorbent and initial metal ion solutions of 50mg/L. The initial metal ion solution, *i.e.* before the addition of the sorbent was adjusted at different pH values (ranging from 2 to 8) via the addition of dilute NaOH or HNO_3 solutions. After agitating for a period adequate for reaching equilibrium adsorption, the equilibrium concentration of the metal ions was determined. Figure 4 (a & b) shows, the variation of the adsorption percent of Cu(II) and Pb(II) ions onto sorbents 1, 2 and 3 with pH. It is shown that for Cu(II) and Pb(II) ions adsorption onto sorbent 1 (Fig. 4 (a & b)), The percent removal increased with the increase of pH from 2 to show maximum percent removal at pH=6 and then slightly decreased with the further increase of the solution pH to 8, *i.e.* the adsorption of both metal ions onto the sorbent 1, its maximum percent removal around neutral conditions (pH=6). For sorbents 2 and 3, (Fig. 4 , a & b), the maximum percent removal of Cu(II) and Pb(II) ions is exhibited at pH value 5 which may be attributed to a change in the charge on the treated tea waste surface with the change in the pH values. The % removal of these metal ions considerably decreased at higher pH which may be due to the formation of soluble hydroxyl complexes.
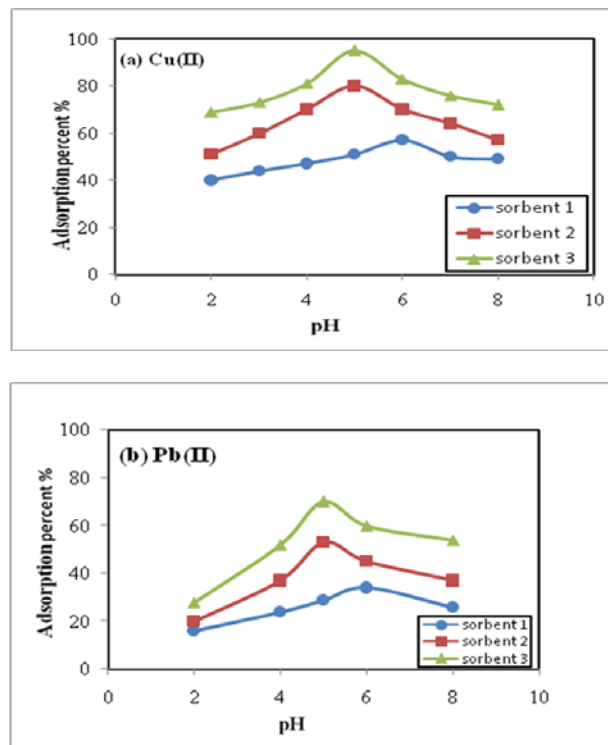
Fig. 4. Effect of pH on adsorption of (a) Cu(II) and (b) Pd(II) ions onto sorbent 1, 2 and 3.

Effect of the contact time and adsorption kinetics

After determining the optimum pH at which Cu(II) and Pb(II) ions sorption should be followed. The kinetic experiments on the adsorption from aqueous solution are important to decide the order of the reaction, its rate constant as well as to determine the equilibrium time that should be allowed to study the equilibrium adsorption. One and the same initial concentration of an adsorbate was used for its adsorption onto the sorbents investigated. Thus, an initial concentration of 3.15 mmol/L and 1.88 mmol/L were used for Cu(II) and Pd(II) ions, respectively. The kinetic adsorption curves of Cu(II) and Pb(II) ions at 303K and pH 5 for sorbent 1 and pH 6 for sorbents 2 and 3 are shown in Fig. 5 (a & b), respectively.

Figure 5 (a & b) depicted that (i) Sorbent 3 exhibited the highest adsorption capacity for two adsorbates (ii) It is evident also that Cu(II) is more adsorbed than Pb(II). This is true for all investigated sorbent. (iii) Treatment of sorbent 1 with sulfuric acid increased the leaching of organic matters from tea waste, such modified sorbent had larger sorption efficiencies for Cu(II) and Pb(II) ions than the sorbent 1. The higher adsorption also may be attributed to a change on the

carbon surface, the metal ions replaced hydrogen ions on the carbon surface at pH = 5 leading to an increase in the extent of adsorption. (iv) Moreover, the greater capacity for Cu(II) or Pb(II) ions adsorption by sorbent 3 (HTW/H_2O_2) relative to sorbant 2 or sorbent 1 may be related to concentration of hydroxyl groups, as supported by the Infra-red spectroscopic data. In other words, the adsorbed amount by the biomass materials simply reflected the affinity of the metal ions to the surface –OH groups present in the bio-materials.
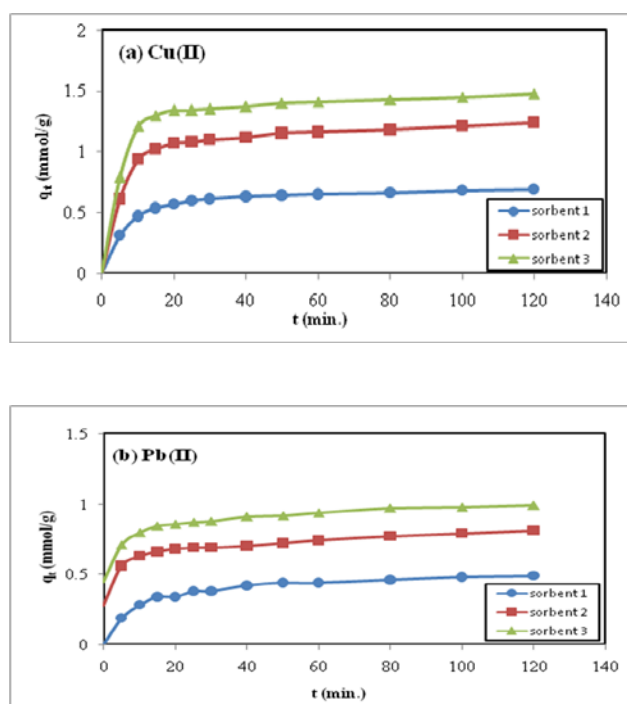

Fig. 5. Adsorption kinetics for (a) Cu(II) and (b) Pb(II) ions at 303K onto sorbent 1, 2 and 3.

In fact, it has been reported that treatment of sorbent 2 with H_2O_2 promotes the conversion of –OH group to peroxo- groups. However, the present results agree well with those previously[19] reported. It is also predicted from Fig. 5 (a & b) that the initial adsorption is rapid and that after 30 min insignificant increase of adsorption with time was observed. Several adsorption kinetic models have been developed to understand the adsorption kinetics and the rate limiting step[20-22]. The following models have been widely used; Lagergen pseudo-first-order model can be expressed by Eq: 4 & 5.

$$dq/dt = K_1(q_e - q_t) \tag{4}$$

$$\ln(q_e - q_t) = \ln q_e - K_1 t \tag{5}$$

The pseudo-second-order model is given by Eq. 6 & 7

$$dq/dt = K_2(q_e - q_t)^2 \tag{6}$$

$$t/q = \frac{t}{q_e} + \frac{1}{K_2 q_t^2} \tag{7}$$

where q_t and q_e are the amount of metal adsorbed per unit weight of adsorbent (mmol/g) at time t, and at equilibrium, respectively and K_1 and K_2 are the adsorption rate constants.

The results obtained for adsorption of Cu(II) and Pb(II) ions onto investgated tea waste sorbents was fitted to Eq. (7). The plots of t/q_t versus t for the linear second order model are shown in Fig. 6 (a & b). The kinetic parameters calculated are shown in Table 3. Pseudo-second-order model provides better correlation than pseudo-first-order model and all the values of $q_{e\ ca}$ thereby obtained were virtually equal to $q_{e\ exp}$.
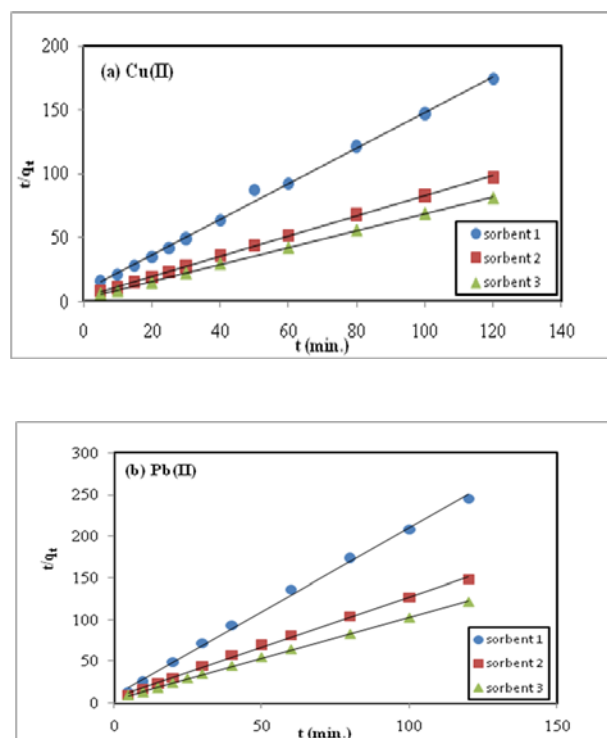

Fig. 6. Linear plots of kinetic second-order of (a) Cu(II) and (b) Pb(II) ions sorption at 303K onto sorbent 1, 2 and 3.

The pseudo-second-order model assumes that chemisorption occurs and consequently, the close fit observed between the values of model and the experimental data indicates that Cu(II) and Pb(II) adsorption onto investigated samples occurred in a chemical manner. Thus, the negative charge of the carboxyl group (-COO⁻), hydroxyl group -OH⁻ and other oxygenated (peroxo species) groups on the surface of the tea waste samples interacts with the positive Cu(II) and Pb(II) ions existing in solution. This suggests that the main mechanism for the adsorption behavior of Cu(II) and Pb(II) ions onto tea waste samples was ion exchange. It is also shown that K_2 of sorbent 1 are considerably higher than those determined for sorbents 2 and 3. This is true for both Cu(II) and Pb(II) uptake. This may be attributed to the difference in nature of these sorbents. Sorbent 1 is a biomass matter on which adsorption takes place on the external surface since no pores are existing. On treatment of sorbent 1 with concentrated sulfuric acid to have sorbent 2, one would expect partial carbonization and development of some porosity in which the rate of adsorption decreased. K_2 for Cu(II) and Pb(II) ions sorption by sorbent 3 is low compared with this calculated for sorbent 2 and 1. This may be taken as an additional evidence for the same explanation. Sorbent 2 was treated with H_2O_2 hydrogen peroxide which may be related to a higher concentration of hydroxyl groups as supported by the infrared data.

If intra-particle diffusion is assumed to be the rate-limiting step in the adsorption process, the corresponding equation may be written as the equation of Weber and Morris[22], viz.

$$q_t = K_{id}t^{0.5} + C$$

(8)

where K_{id} is the intra-particle diffusion rate constant [g/mmol min$^{1/2}$] and C is a constant that provides information regarding the thickness of the boundary layer, *i.e.* the larger the value of C the greater is the boundary layer effect. The values of K_{id} and C for the Cu(II) and Pb(II) sorbent surface systems investigated are listed in Table 3. Figure 7 (a & b) shows the initial curved portions followed by linear portions. The initial curved portions of the plots refer to boundary layer diffusion, whereas the linear portions correspond to intraparticle diffusion. However, the linear portion does not pass through the origin, indicating that intra-practical diffusion is not the only process controlling heavy metal ions sorption. The values of K_{id} and C in Table 3 indicate that sorbent 2 and sorbent 3 resulted in an increase in the value K_{id} and C with the increase of the solute sorption. This indicates that adsorption on these sorbents is more controlled by intraparticle diffusion.
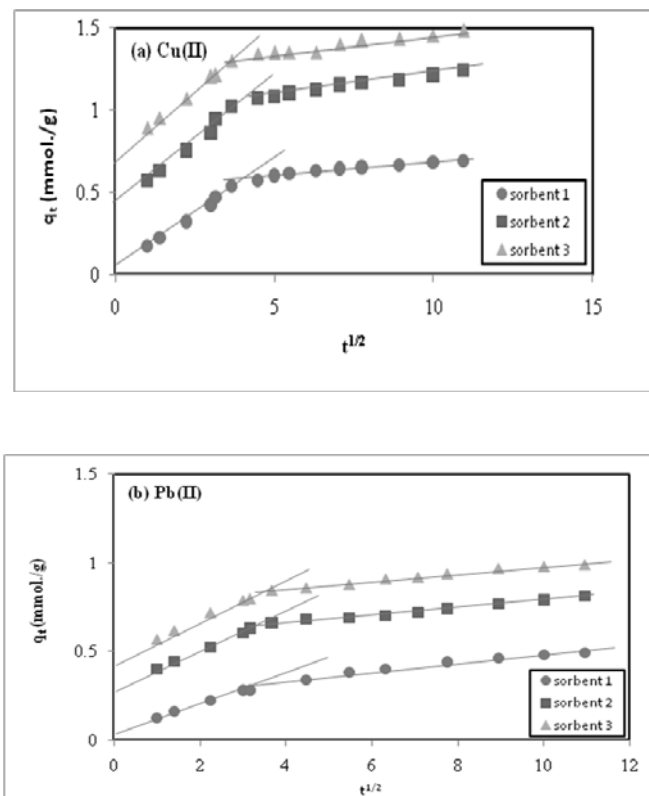
Fig.7. Linear plots of intraparticle diffusion of (a) Cu(II) and (b) Pb(II) ions sorption at 303K onto sorbent 1, 2 and 3.

TABLE 3. Kinetic parameters for the adsorption of Cu(II) and Pb(II) ions onto sorbents 1, 2 and 3.

Model/parameters sorbent	Cu(II) ion			Pb(II) ion		
	1	2	3	1	2	3
Pseudo-first-order						
K_1 (1/min)	0.07	0.1	0.1	0.014	0.045	0.10
$q_{e\,ca}$ (mmol/g)	0.46	0.921	0.927	0.105	0.30	0.57
R^2	0.889	0.891	0.899	0.911	0.955	0.962
Pseudo-second-order						
K_2(g/(mmol min)	0.211	0.193	0.156	0.444	0.26	0.153
q_{2ca} (mmol/g)	0.725	1.321	1.464	0.45	0.80	1.043
R^2	0.996	0.999	0.999	0.996	0.997	0.999
Intra-particle diffusion						
K_{id} (mmol/gmin$^{1/2}$)	-0.125	0.145	0.150	0.08	0.105	0.110
C mmol/g	0.05	0.43	0.74	0.04	0.30	0.47
R^2	0.992	0.995	0.992	0.996	0.997	0.995

Equilibrium adsorption and the effect of temperatures

Fig. 8 (a & b) shows the adsorption isotherms of Cu(II) and Pb(II) ions from aqueous solution onto sorbents 1, 2 and 3 at 303K and at pH=6 for sorbent 1 and pH=5 for sorbent 2 and 3. It is shown also from the kinetic curves (Fig. 5, a & b) that beyond 20 min contact, no significant increase in the sorption capacity with time was observed. However, the sorbents were soaked for 24hr to ensure the attainment of equilibrium 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[23].
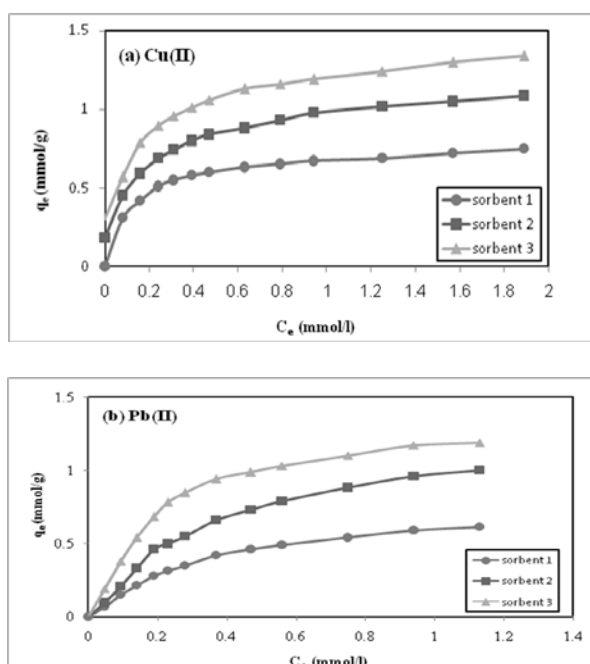

Fig. 8. Adsorption isotherms at 303K for (a) Cu(II) and (b) Pb(II) ions onto sorbent 1 at pH=6 and sorbent 2 and 3 at pH=5.

According to the Giles classification, all the isotherms obtained in the study had shapes which conformed to the L2 type Giles and Smith[24]. Many model sorption isotherm expressions have been applied to sorption experimental, especially those obtained for heavy metal ions. These models are the Langmuir isotherm model and the Freundlich isotherm model and may be expressed as:

Langmuir isotherm
$$q_e = \frac{q_{max}bC_e}{1+bC_e}$$
(9)

Freundlich isotherm
$$q_e = K_F C_e^{1/n}$$
(10)

where q_e is the amount of Cu(II) or Pb(II)ions adsorbed per unit mass of adsorbent at equilibrium (mmol/g), C_e is the equilibrium concentration of Pb(II) or Cu(II) ions in solution (mmol/L), q_{max} is the maximum sorption capacity per unit weight of sorbent mmol/g and b is a constant related to the sorption energy (L/mmol).

The linear form of the Langmuir isotherm is given by the following equation:

$$C_e / q_e = \frac{1}{q_{max}b} + \frac{1}{q_{max}} C_e \qquad (11)$$

Finally, the Langmuir constant K_L is obtained from the following equation:

$$K_L = q_{max}b \qquad (12)$$

The quantities K_F and 1/n are the Freundlich constants, with K_F corresponding to the relative sorption capacity of the sorbent while n represents the degree of dependence of sorption on the equilibrium concentration of heavy metals ions. These two constants can be used to determine whether the nature of the sorption process is favorable or unfavorable.

Another model used in the present study, *i.e.* the Dubinin-Raduskevich (D-R) isotherm. The D-R isotherms may be written as:

$$q_e = q_{max} \exp^{(\beta\varepsilon^2)} \qquad (13)$$

where q_m is the D-R isotherm constant corresponding to the theoretical sorption capacity while the constant β is related to the mean free energy of sorption per mole of the sorbate (mol^2/KJ^2). The polanyl potential, ε is equal to $RT \ln(1 + 1/C_e)$, where R is the gas constant and T (K) is the absolute temperature.

The experimental data were modeled using the Langmuir, Freundlich and D-R isotherms models and the isotherm constants calculated from the slopes and intercept of the corresponding plots are summarized in Table 4. The data for the adsorption of Cu(II) and Pb(II) ions onto investigated sorbent samples were well fitted by the Langmuir isotherm model Fig. 9, as demonstrated by the high correlation coefficients obtained (R^2=0.9890) compared to that for the application of the Freundlich isotherm model and D-R isotherm models (not shown). This might be due to the homogeneous distribution of active sites on the surface of the all investigated sorbents.
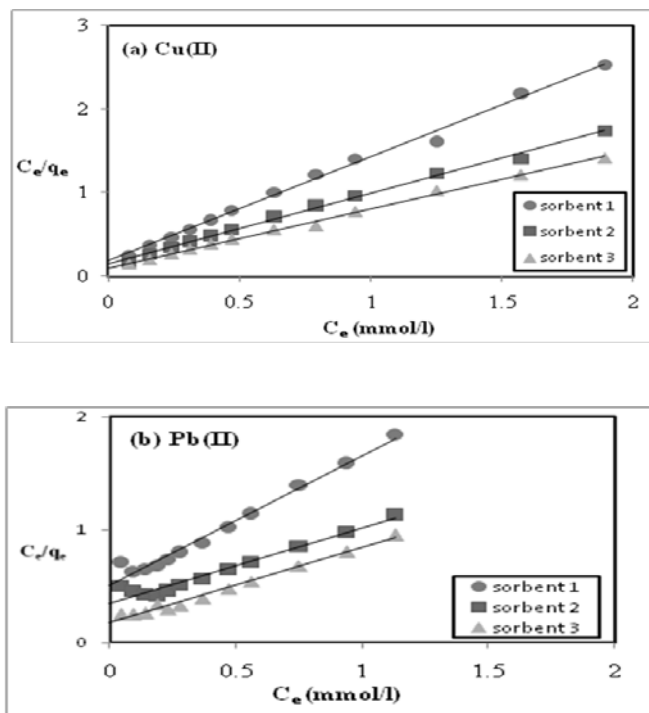
Fig. 9. Linear Langmuir plots of (a) Cu(II) and (b) Pd(II) ions sorption sorption at 303K onto sorbent 1, 2 and 3.

TABLE 4. Langmuir, Freundlich and D-R equation coefficient for Cu(II) and Pb(II) sorption onto investigated sorbents at 303K.

Sorbent	Langmuir Parameters		Freundlich parameters		D-R parameters	
	K_L	q_{max}	n	K_F	q_{max}	E_a
			Cu(II)			
1	7.35	0.8	5.71	0.67	0.69	1.64
2	7.49	1.07	4.53	0.96	10.6	1.54
3	9.02	1.385	5.38	5.93	1.27	1.58
			Pb(II)			
1	2.67	0.833	3.6	0.63	0.644	1.12
2	2.96	1.300	2.22	0.99	1.062	1.12
3	3.17	1.750	4.09	1.17	1.270	1.27

The correlation coefficients R^2 for applicability of Freundlich sorption isotherm are less than 0.8, indicating less fitting of the adsorption data to the Freundlich model. This can be taken as evidence that the adsorption of Cu(II) and Pb(II) ions by the investigated sorbents is chemical adsorption.

For D-R adsorption isotherm model, the sorption energies of the investigated samples were between 1.12 and 1.64 KJ. $mol^{-1}K^{-1}$. The sorption energy values provide information about the sorption mechanism, *i.e.,* where there it involves ion exchange or physical adsorption. Thus, if the value of adsorption energy is between 8-16 $KJmol^{-1}$, the sorption process corresponds to ion-exchange process. The sorption energy values obtained in the present study were less than those expected for a typical ion-exchange process thereby suggesting that the sorption mechanism may be a combination of electrostatic and physical sorption. At the start of the sorption process (*i.e.,* during the formation of monolayer), ion-exchange and Vander Waal's interactions are predominantly responsible for the process.

Thermodynamics parameters of Cu(II) and Pb(II) adsorption the better fitting Langmuir plots were used to make estimation of the changes in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) during the adsorption of Cu(II) and Pb(II) ions onto sorbent 1 and sorbent 3. For such calculations, the following relationships were employed.

The free energy change of the sorption reaction is given by the following equation:

$$\Delta G^{o} = -RT \ln b \tag{14}$$

where R is the gas constant (8.314 J $mol^{-1}K^{-1}$) and T is the temperature (K). The thermodynamic parameter ΔH° and ΔS° to be described by Van't Hoff's equation.

$$\ln b = \frac{-\Delta H^{o}}{RT} + \frac{\Delta S^{o}}{R} \tag{15}$$

The Slope and intercept of Van't Hoft plot are equal to $\dfrac{-\Delta H^{o}}{R}$ and $\dfrac{\Delta S^{o}}{R}$, respectively.

Table 5 summarized the values of ΔG°, ΔH° and ΔS° for sorbent 1 and sorbent 3 sorbent adsorbate system. It is predicted from Table 5, that all the values of standard free energy change ΔG° are negative at all temperature studied suggesting thus the spontaneous nature of the sorption of Cu(II) and Pb(II) ions of the sorbent 1 and the sorbent 3 and meanwhile refers to the feasibility of the sorption process. The free energy of the process changed with the rise in temperature. Fig. 10 (a & b) shows a plot of ΔG° versus T was linear. The change of the standard free energy decreases with increasing temperatures regardless of the nature of adsorbent. This indicates that a better adsorption is actually obtained at higher temperatures. The negative values of the standard enthalpy change (ΔH°) indicate that the interaction of Cu(II) and Pb(II) with the investigated sorbent is exothermic in nature, thereby demonstrated that the process is stable energetically. All the value of ΔH° is negatively low compared with heats evolved in chemisorptions process. The values of ΔH° may ascribe specific

interaction between the adsorbed ion and the sorbent surface. The positive ΔS° values for Cu(II) and Pb(II) ions indicate that the pollutant ions in water are caged by solvation molecules (Water molecules) and also give evidence of the weak adsorption forces between the sorbent surface and the pollutant ions[25].
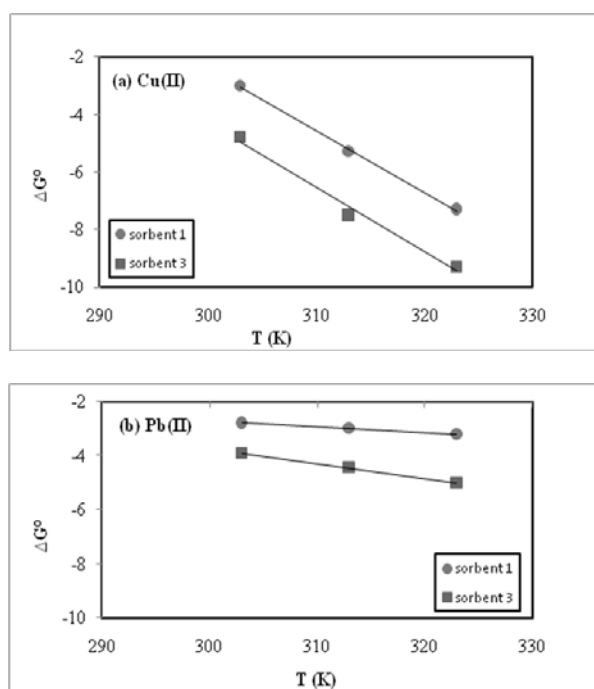

Fig. 10. A plot of ΔG° against T for (a) Cu(II) (b) Pd(II) ions onto sorbent 1 and sorbent 3.

TABLE 5. Thermodynamic parameters of Cu(II) and Pb(II) sorption onto investigated sorbents.

Sorbent	Temperature (K)	ΔG^{o} KJ/mol	ΔH^{o} KJ/mol	ΔS^{o} KJ/mol
		Cu(II)		
1	303	-3.0		
	313	-5.1	-59.86	29
	323	-7.2		
3	303	-4.8		
	313	-7.2	-41.85	34
	323	-9.2		
		Pb(II)		
1	303	-2.8		
	313	-3.0	-83.00	10.4
	323	-3.2		
3	303	-4.8		
	313	-7.3	-62.36	9.6
	323	-9.1		

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Conclusions

Treatment of tea waste with sulfuric acid at 303K is a simple low cost technique to product carbonaceous materials of developed porosities and relatively high surface areas.

The carbonaceous materials produced by treating tea waste with sulfuric acid and then oxidizing with H_2O_2 at 303K exhibited high adsorption capacities for Cu(II) and Pb(II) ions from their aqueous solution where it is found 1.385 mmol/g for Cu(II) and 1.750 mmol/g for Pb(II). The adsorption of Cu(II) and Pb(II) ions at 303K proved to be rapid and the dynamic adsorption data were applicable to pseudo-second-order kinetic and the adsorption on sorbents 2 and 3 is more controlled by intraparticle diffusion.

The equilibrium adsorption data obeyed Langmuir equation. For D-R adsorption isotherm, the sorption energies of the investigated samples were between 1.12 and 1.64 $KJ.mol^{-1}K^{-1}$, thereby suggesting that the sorption mechanism may be combination of electrostatic and physical sorption. The thermodynamic parameters of the adsorption of Cu(II) and Pd(II) on the sorbents investigated have been evaluated, The negative values of ΔG^o indicates the spontaneous nature and the feasibility of the sorption process. The negative values of (ΔH^o) demonstrate that the process of sorption is stable energetically. The positive values of ΔS^o may be attributed to the weak adsorption forces between the sorbent surface and the pollutant ions.

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كربون منشط ومطور من مخلفات الشاي لإزالة أيونات النحاس والرصاص

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تم في هذا البحث تحضير كربون منشط من مخلفات الشاي وتطوير سطح الكربون بمعالجته بفوق أكسيد الهيدروجين المركز. تم التعرف على الخواص الفيزيائية والكيميائية لسطح الكربون المطور وغير المطور. كما تم قياس الإمتزاز الإتزاني لأيونات النحاس (II) Cu الرصاص Pb(II) عند 303، 313، 324 كلفن، هذا وقد تم تعيين كيناتيكية الإمتزاز لهذين العنصرين على سطح الكربون المطور وغير المطور. وتبين أن مساحة السطح والحجم الكلي للمسام يقلان ولكن الحجم الكلي للمسام ومتوسط سعتها يزدادان. بلغت كفاءة إمتزاز هذين العنصرين القيم القصوى عند pH=6-5 بالنسبة لكل من الكربون المطور وغير المطور. وتبين أن منحنيات الإمتزاز الإتزاني يتبع معادلة لنجمير. كما يتبع نتائج معادلات الحركة الرتبة الثانية الكاذبة Pseudo-Second-order. كما أتضح أن قدرة الكربون المؤكسد أكبر بكثير من غير المؤكسد وذلك على إمتزاز أيونات النحاس والرصاص. كما استنتج من حساب طاقة الإمتزاز أن الإمتزاز إحتمال أن يكون الكتروستاتيكى إلى جانب الفيزيائي.