Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.835751

53 (2015) 126–138
January

Taylor & Francis
Taylor & Francis Group

Lead removal from aqueous solution using non-modified and nitric acid-modified charred carbon from the pyrolysis of used cigarette filters

Salman Masoudi Soltani[a,]*, Sara Kazemi Yazdi[a], Soraya Hosseini[b], Iman Bayestie[b]

[a]*Department of Chemical & Environmental Engineering, The University of Nottingham, Broga Rd,*
Semenyih 43500, Malaysia
Tel. +44 7831610837; email: smasoudis@gmail.com
[b]*Department of Chemical & Environmental Engineering, Universiti Putra Malaysia, Serdang 43400, Malaysia*

Received 15 April 2013; Accepted 14 August 2013

ABSTRACT

The efficiency of lead removal from aqueous solution using non-modified and nitric acid-modified charred carbon has been investigated. The charred carbon was obtained through the direct pyrolysis of used cigarette filters, one of the world's largest solid wastes. The effects of lead solution's pH, adsorbent dosage, initial lead concentration, and contact time on lead uptake from water by the two carbons were studied. It was revealed that the maximum lead uptake from water was at optimum pH values of 5 and 4 for non-modified and surface modified carbons, respectively. However, the effect of adsorbent dosage was almost identical for both carbons with an optimum value of 0.1 g. The equilibrium was reached after almost 24 h of contact time for both types of carbons. The adsorption data were fitted by the Freundlich and Langmuir adsorption isotherm models. The adsorption for both carbons was best explained by Freundlich adsorption isotherm. The kinetics of the adsorption were also investigated. Pseudo-second-order kinetic model could successfully fit the kinetic data implying the chemisorption adsorption mechanism being dominant for both carbons. At an initial lead concentration of 600 mg/l, the removal efficiency was measured to be 66 and 74.5 mg/g for non-modified and HNO_3-modified carbons, respectively.

Keywords: Charred carbon; Modified charred carbon; Lead adsorption; Adsorption isotherm

1. Introduction

1.1. Activated carbon in adsorption from solutions

Currently, there is quite a broad range of treatment technologies to treat water and wastewaters to remove the contaminants, including organic and inorganic matters. These techniques mainly include filtration, coagulation, oxidation, biological degradation, and ion-exchange. However, due to an increase in the variety and amount of hazardous materials in different streams, these conventional technologies have been sometimes made inefficient and even ineffective [1]. Moreover, these conventional methods are technically and economically confined when concentrations of heavy metals in wastewater are less than 100 ppm [2]. Activated carbons have been shown to be promising and effective in the removal of a wide range of

---

*Corresponding author.

materials from aquatic ecosystems. Due to this fact, activated carbons have been recommended to attain stringent, permissible limits of toxic metals and organic pollutants [3]. Many labs and field tests in many countries have suggested that currently adsorption with activated carbon is the best broad-spectrum approach to remove both organic and inorganic materials from water [1].

Quite recently, in streams industrial wastes containing heavy metal compounds have caused serious symptoms of poisoning and environmental damages [4]. The pollution brought about by cadmium, chromium, copper, lead, mercury, nickel, and arsenic is most critical to human body [5]. A concentration higher than 0.005 mg/l of lead will result in illness in humans [6]. The current USEPA drinking water standard for lead is 0.015 mg/l [7]. In humans, acute lead poisoning leads to serious damage to the kidneys, liver, brain, and nervous system [7]. Moreover, longer exposure to lead may result in sterility, abortion, and also neonatal death [8].

1.2. Mechanism of adsorption of inorganic compounds by activated carbon

There is no clear answer yet to explain the mechanism of metal removal by activated carbon. Ion-exchange and complex formation on heavy metal on carbon surface have been reported by some researchers [9]. Moreover, there have been reports on the interaction of the transition metal ions with the $\prod$ electrons of the carbons which exist as an electron cloud on carbon surface [10]. In the solution phase, the metal salt is first ionized and then hydrolyzed. This results in the creation of free and complex cationic and anionic species. However, the preponderance of any one or several cations or anions depends upon the concentration and the pH of the solution. For example, for a divalent metal salt MCl_2, the ionization of the salt produces M^{2+} cations, while its hydrolysis can produce $(MOH)^+$, $M(OH)_2$, $M(OH)_3^-$ and $M(OH)_4^{2-}$ ions. In addition, small amounts of multinuclear species such as $M_2(OH)_3^+$ and $M_4(OH)_4^{4+}$ may also be formed at high concentrations of the salt in the solution and at proper pH values [1].

It has been unanimously believed that the most important factors affecting the efficiency of metal ion removal from water are the surface carbon-oxygen groups and the pH of the solution. In addition, the solution's pH at which the surface of carbon possesses neutral charge i.e. zero electric charge is called pH_{PZC}. If the solution's pH is larger than the pH_{PZC}, the surface of carbon becomes negative. This provides a suitable environment for the adsorption of positively-charged species such as heavy metal ions on carbon surface. However, when the solution's pH is smaller than pH_{PZC}, carbon surface possesses a positive charge. The positive charge has been linked to the presence of basic surface groups while the negative surface charge at higher pH values has been associated with the ionization of acidic surface oxygen groups [1]. The degree of this ionization of acidic surface groups is very low at $pH < pH_{PZC}$ and is high at $pH > pH_{PZC}$. The ionization mechanisms of acidic surface groups are depicted in Fig. 1. Based on the reaction above, the H^+ ion is directed back into the solution which consequently leaves the carbon surface with a negatively-charged site for the adsorption of the positively-charged metal ions. The amount of acidic surface groups can be improved by a suitable oxidative post treatment technique. As a result, the number and concentration of the acidic surface groups will increase [1].

1.3. Modeling of the adsorption data

1.3.1. Adsorption isotherms

Maximum adsorption capacity (mg/g) of an adsorbent is the most important factor to be known. The adsorption capability is experimentally determined at constant temperature and then the equilibrium results are presented as isotherms [2]. Moreover, adsorption isotherms can allow the prediction of costs. There are many different models to describe the adsorption equilibrium. They include two, three, and four parameter models [2]. The most common mathematical model used to describe the experiments results of

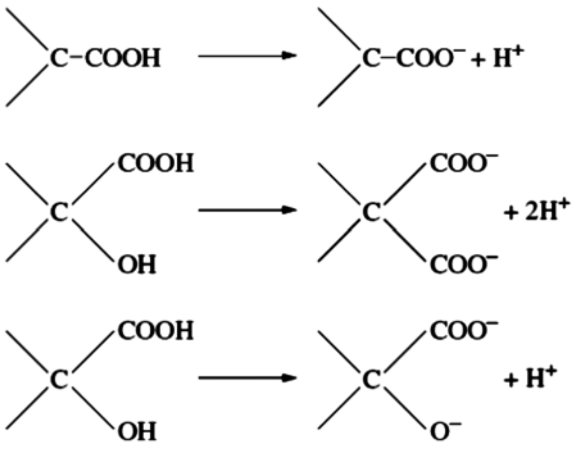

Fig. 1. Ionization of a typical acidic surface group in a solution [1].

adsorption from solutions with activated carbon were derived by Freundlich and Langmuir [11].

1.3.1.1. Langmuir adsorption isotherm model. Langmuir equation has been widely used in the evaluation of adsorption results from solutions. This equation has been suggested based on the following assumptions [12]:

1. The adsorption takes place at specific homogeneous sites within the adsorbent.
2. Only one molecule occupies each available site.
3. The adsorbent has finite capacity for the adsorbate.
4. All sites are energetically identical and homogeneous.

Based on the above assumptions, Langmuir equation is written as [12]:

$$\frac{x}{m} = q_e = \frac{K_L C_e}{1 + a_L C_e} \tag{1}$$

In this equation, x is the amount of adsorbed matter (mg), m is the amount of adsorbent used (g), $C_e(\frac{mg}{l})$ and $q_e(\frac{mg}{g})$ are the liquid and solid phase equilibrium concentrations of the adsorbate. $K_L\left(\frac{l}{g}\right)$ and $a_L\left(\frac{1}{mg}\right)$ are the Langmuir isotherm constants. The transformed version of this equation into a linear form is:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \tag{2}$$

By plotting $\frac{C_e}{q_e}$ against C_e, a straight line is produced with a slope of $\frac{a_L}{K_L}$ and an intercept of $\frac{1}{K_L}$. The straight line characterizes the applicability of the Langmuir equation for the data obtained. It is also mentionable that the theoretical monolayer capacity q_{max} of the adsorption is equal to $\frac{K_L}{a_L}$.

1.3.1.2. Freundlich adsorption isotherm model. Freundlich equation, another common and equally important adsorption isotherm model is written as [12]:

$$q_e = K_F C_e^{\frac{1}{n_F}} \tag{3}$$

where q_e is the equilibrium adsorbate concentration (mg/g). C_e is the equilibrium concentration of the adsorbate in the solution containing the activated carbon (mg/l). K_F is the Freundlich constant (l/g) which is related to bonding energy. $\frac{1}{n_F}$ is the heterogeneity factor. This parameter is of great importance. If n_F is equal to unity, the adsorption is linear, if it is below unity, the adsorption process is chemical and if it is larger than unity, the adsorption process is a physical process. Freundlich equation has been extensively applied in the adsorption isotherms of solutions [1]. The simplest method to evaluate the two-factor models' constants is to transform the equilibrium equation into a linear format. Linear regression is commonly used to assess the model parameters [2]. The alternative logarithmic form of the equation is written in a linear form as:

$$\ln q_e = \ln K_F + \left(\frac{1}{n_F}\right) \ln C_e \tag{4}$$

By plotting $\ln q_e$ against $\ln C_e$, a straight line is drawn with a slope of $\frac{1}{n_F}$ and an intercept of $\ln K_F$.

This allows us to estimate the highest adsorption capacity of one specific solute for a given initial concentration of the adsorbate in solution.

1.3.2. Adsorption kinetics

1.3.2.1. Pseudo-first-order kinetic model. Kinetic parameters allow us to understand the rate of adsorption process [2]. The kinetics of the adsorption is often expressed either by applying pseudo-first-order and pseudo-second-order kinetic models to assess and predict the kinetic of adsorption. The first-order model is expressed as [12]:

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \tag{5}$$

In this equation, q_t is the amount of the adsorbed adsorbate ($\mathrm{mg\,g^{-1}}$) at time t, q_e is the maximum (equilibrium) adsorption capacity ($\mathrm{mg\,g^{-1}}$) and k_1 is the first-order rate constant ($\mathrm{min^{-1}}$). After integration and applying the boundary conditions, the integrated form of the Eq. (5) becomes:

$$\log\left(\frac{q_e}{q_e - q_t}\right) = \frac{K_1}{2.303} t \tag{6}$$

The linear form of the above equation then is:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{7}$$

If $\log(q_e - q_t)$ is plotted against t, a straight line should be drawn in case of the validity of the pseudo-first-order model. This model is most applicable when the adsorption rate is controlled through the diffusion mechanism. If the data cannot be explained by pseudo-first-order model, the adsorption is not diffusion-controlled. In that case, $k_1(q_e - q_t)$ does not represent the number of available adsorption sites and log q_e is not equal to the intercept of the plot of log $(q_e - q_t)$ vs. t [12].

1.3.2.2. Pseudo-second-order kinetic model. The kinetic of the adsorption may be similarly explained by pseudo-second-order model that is written as [12]:

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \tag{8}$$

where q_e is the equilibrium adsorption capacity (mg g^{-1}), q_t is the amount of adsorbate adsorbed at time t and k_2 is the equilibrium rate constant of pseudo-second-order adsorption (g mg^{-1} min^{-1}).

Integrating Eq. (8) together with applying the boundary conditions gives:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \tag{9}$$

The rearrangement of the above equation leads to the following linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{10}$$

The intercept and slope can be easily obtained by plotting $\frac{t}{q_t}$ vs. t. If the pseudo-second-order kinetic is applicable, the graph shows a linear relationship.

1.4. Lead removal with acid-modified and non-modified activated carbon

Nadeem et al. [13] used activated carbon synthesized through the first step pyrolysis of husk and pods of Moringa oleifera. They noticed a 79.43% total lead removal from water. They also observed that contact time, initial metal concentration, adsorbent dosage and pH were among the most influencing factors in the adsorption efficiency. They could successfully increase the total removal percentage by modifying their carbon with sulfuric and phosphoric acids to 91.8 and 96.58%, respectively. Their adsorption data were fitted by pseudo-second order kinetic model and Langmuir isotherm.

Gercel et al. [8] investigated the application of activated carbon derived from a renewable plant material (Euphorbia rigida) in lead removal. They studied the effects of adsorbent dosage, contact time, initial lead concentration, temperature and pH on the adsorption efficiency. Their data also was fitted into a Langmuir isotherm model. The maximum lead removal was reported to be 1.35×10^{-3} mol g^{-1} (279.72 mg g^{-1}) which was at an optimum pH value of 5. The kinetic of adsorption also was best explained by a pseudo-second-order model.

Ornek et al. [14] studied the equilibrium and kinetics of adsorption of lead onto sulfuric-acid treated carbon. Langmuir equation and pseudo-second-order models were best fit into the data. The equilibrium was reached after 120 min of contact time which was independent of initial lead concentration. Their removal efficiency was between 14.1 and 99.3 mg/g corresponding to initial lead concentrations of 30–300 mg/l.

Tao and Xiaoqin [15] used nitric-acid modified carbon to remove lead from water. The data were also best explained using Langmuir model. The modified carbon was able to remove 35.5 mg/g of lead from water. The improved removal efficiency with nitric acid-modified carbon was attributed to the pore widening, increased cation-exchange capacity by oxygen groups and enhanced hydrophilicity of carbon surface.

Baniamerian et al. [16] investigated the adsorption of lead from water by nitric acid-modified activated carbon. They reported that the optimum pH value was between 6.5 and 8. Their data were also best fit using Langmuir and pseudo-second order models.

Mohammadi et al. [17] used the sea-buckthorn stones activated carbon to remove lead from solution. The maximum removal was reported to be 51.81 mg/g when the precursor was treated with phosphoric acid before activation. They also observed a strong dependency of the removal efficiency on the lead removal. Pseudo-second-order kinetic was known to be the best possible fit.

In another study, activated carbon from bamboo was used in the removal of lead from water [4]. The studied parameters included solution's pH, carbon dosage, and contact time. The optimum pH value was reported to be between 5.81 to 7.86 and 7.10 to 9.82 for Moso and Ma bamboo, respectively. The optimum contact time was understood to be 2–4 h by Maso bamboo activated carbon and 1 h by Ma bamboo activated carbon.

Momcilvoic et al. [7] used pine cone activated carbon to remove lead from water. They studied the effects of pH, contact time, initial concentration of lead and adsorbent dosage on the removal efficiency. Langmuir model was best to describe the equilibrium data with a maximum adsorption capacity of 27.53 mg/g. The kinetic data were also best explained using pseudo-second-order model.

2. Materials and methodology

2.1. Materials

Charred carbon was prepared by direct pyrolysis of used cigarette filters at 900˚C for 3 h at a heating rate of 5˚C/min under a constant nitrogen gas with a flow rate of 100 cm^3/min in a steel tube furnace (Carbolite Co.). The nitric acid-modified carbon was prepared by treating the pre-weighed 0.2 g (Mettler Toledo Co, AB204-S/FACT) of the previously synthesized charred carbon with 5 M nitric acid solution for 5 h in a continuous contact on a manual shaker. The treated sample was then washed with hot distilled water (70˚C) until the filtrate showed a pH value of around 7. The washed sample was then dried in an oven at 105˚C overnight and kept in a desiccator for the future use. The physical and chemical properties of non-modified and nitric acid-modified carbons have been tabulated in Table 1. A thorough discussion on the synthetic procedure, the pyrolysis setup and the physical/chemical properties of the synthesized charred carbon are found in the authors' earlier paper [18].

Lead nitrate (II) was supplied by Ajax Finechem Co. (purity 99%). All other chemicals were provided by Merck and were of analytical grade.

2.2. Methodology

To study and compare the adsorption capacity of the non-surface-modified carbon and the nitric acid-modified carbon for lead, adsorption experiments was carried out according to standard methods.

Initially, a stock solution of lead with a concentration of 1,000 mg/l was prepared using $Pb(NO_3)_2$ salt [19]. The stock solution was kept at room temperature in completely capped glassware. This stock solution was later used to prepare dilute solutions of lead in water.

A solution of $Pb(NO_3)_2$ with specific lead concentration was first prepared by carefully adding specific volume of the as-prepared lead stock solution with known volumes of ultrapure distilled water. The pH of the produced solution was next adjusted to a desired value (2–8) by slowly adding HNO_3 (1 N) and NaOH (1 N) and was measured immediately using the online digital pH meter (Trans Instruments Co.). Next, 80 ml of the diluted solution was added to a small glass bottle which was immediately capped. Then, a prescribed and carefully weighed amount of powdered and pre-sieved carbon (0.02–0.12 g) was added to the as-prepared lead solution. The tightly capped glass bottle was then placed on a manual shaker for kinetic studies. At specified intervals (1, 2, 4, 6, 8, 10, …, 24 h), 0.5 ml of the in-contact lead solution was removed by means of an automatic micropipette and was then brought to 50 ml volume with ultrapure distilled water. Next, its concentration for lead was immediately measured using an atomic adsorption spectrometer (AAS) (PerkinElmer^{TM}, AAnalyst 400). The AAS which was equipped with a lead lamp (PerkinElmer^{TM}, Lumina^{TM} Lamp) and a flame atomizer (C_2H_2 gas + air), was first calibrated using standard solutions of lead. The AAS was operated using WinLab32 software. The displayed Pb concentration value was then converted to the original sample concentration according to its dilution factor. For each set of experiments, a separate calibration graph was initially drawn for the maximum measurements' accuracy. All experiments were run in triplicates.

3. Results and discussion

3.1. Point of zero charge

Point of zero charge (PZC) is identified as the point at which the density of the electrical charge on the solid surface is zero and so the surface has net electrical neutrality [16]. This point is dependent on the solution's pH. To detect the PZC, carbon samples are placed inside the solutions with different initial pH values and the solutions' final pH values are

Table 1
Physical and chemical properties of non-modified and HNO_3-modified charred carbons

	Total surface area (m^2/g)	Micropore area (m^2/g)	Mesopore area (m^2/g)	Total pore volume (cm^3/g)	Micropore volume (cm^3/g)	Average pore diameter (nm)	Surface acidity (mmol/g)	Basicity (mmol/g)
Non-modified	597	453	144	0.33	0.23	3.32	0.7671	0.0116
HNO_3-modified	439	306	133	0.24	0.16	3.24	1.23047	0.00986

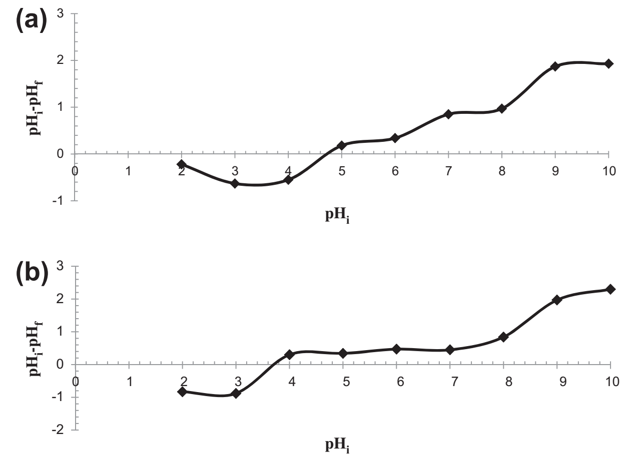

Fig. 2. Determination of point of zero charge: (a) non-modified carbon (b) nitric acid-modified carbon.

recorded after 24 h when no further change in the pH was observed. PZC is the point at which the initial and final pH values are identical. Fig. 2(a) and (b) illustrates the graphs used in the determination of PZC for the non-modified and nitric-acid modified carbons, respectively. Fig. 2(a) and (b) shows that at a pH value of around 4.8 and 3.6 for non-modified and nitric acid-modified carbons, there would be no change in the solution's pH after 24 h of contact time, respectively.

A comparison between the pH_{pzc} of the non-modified carbon (4.8) and that of the nitric acid-modified carbon (3.6) shows a decrease of 25%. The same lowering in pH_{pzc} when carbon was modified with nitric acid has been reported by Chingombe et al. [10]. This suggests that acidic properties are more dominant in the nitric acid-modified carbon. This is a consequence of the presence of more acidic surface functional groups such as carboxyl, lactone, and phenol on carbon surface [10]. The quantity and quality of these functional groups were reported in the authors' earlier work [18].

3.2. Effect of adsorbent dosage on Pb uptake from water

The effect of adsorbent dosage on the lead adsorption has been depicted in Fig. 3(a) and (b). For both types of carbons, the graphs show that the adsorption capacity of the carbon increases with adsorbent dosage. There is almost a gradual rise from about 12 mg/g to around 27 mg/g and from about 14.8 mg/g to around 27.8 mg/g when adsorbent mass has increased from 0.02 to 0.1 g for non-modified and modified carbons, respectively. From this point forward, there is no significant increase in the removal efficiency with an increase in the adsorbent mass for both types of carbons. This is due to the unsaturation of adsorption sites through the adsorption process [20]. This phenomenon may also be explained by particle interaction such as aggregation which is a consequence of high adsorption dosage. When such aggregations take place, total surface area may decrease with an increase in diffusion path length [14]. Therefore, we can conclude that the optimum adsorbent dosage is 0.1 g for both the carbons. In all the subsequent experiments, this optimum adsorbent dosage has been used to investigate the effect of other parameters.

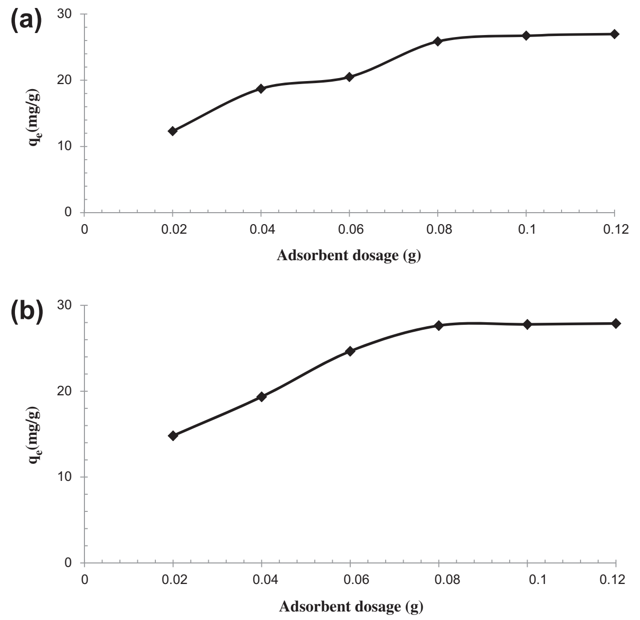

Fig. 3. Effect of adsorbent dosage on the lead uptake from lead solution: (a) non-modified carbon and (b) nitric acid-modified carbon (pH = 5, initial Pb concentration = 100 mg/l, contact time = 24 h, and temperature = 30℃).

3.3. Effect of lead solution's pH on Pb uptake from water

The pH of the solution plays a determining role in the efficiency of the entire adsorption process. The solution's pH defines carbon surface charge in terms of concentration. This is due to the degree of ionization of carbon surface functional groups. In addition, solution's pH dictates the degree of ionization of the salt present in the solution as well [12]. The effect of solution's pH on the lead uptake by carbon is illustrated in Fig. 4(a).

Based on the graph, lead removal efficiency increases with increasing solution's pH up to a value of 5. The lead uptake increases from around 4.5 mg/g to approximately 26.2 mg/g when the solution's pH rises from 2 to 5. The lead uptake is lower at lower pH values. However, this increase in lead removal is more noticeable when pH is raised from 2 to 3 than when pH is elevated from 3 to 5. This can confirm that the ionization of surface oxygen complexes on carbon surface is more pH-sensitive at lower pH values. The maximum lead removal is achieved at pH = 5 which is slightly above the pH_{PZC} value of non-modified carbon ($pH_{PZC} = 4.8$). At this pH, carbon surface is negatively charged and is a suitable medium for positively-charged lead ions. Fig. 4(a) shows that when the pH is further increased beyond 5, the removal efficiency decreases accordingly. At pH values above 6, lead precipitation in the form of $Pb(OH)_2$ occurs which is due to the presence of excess amount of OH^- ions in the adsorption medium [14]. This is due to the fact that at this pH the ionic product of $[(Pb^{2+})\cdot(OH^-)^2]$ becomes greater than the solubility constant of $Pb(OH)_2$ and thus lead precipitation takes place. The optimum pH value is selected based on the pH value at which the lead removal efficiency is maximum i.e. pH = 5. This pH value is in agreement with the adsorption capacity of the most heavy metal ions removal being reported to be best at pH values of less than 7 [4].

Due to the nature of the existing surface functional groups on the carbon surface such as carboxyl and the positively charged Pb^{2+} ions with two protons, each lead ion can be positioned within two adjacent carboxyl groups which can donate two pairs of electrons to the Pb^{2+} ion. This is followed by four coordination number compound and the release of two hydrogen ions, H^+, into the solution [14].

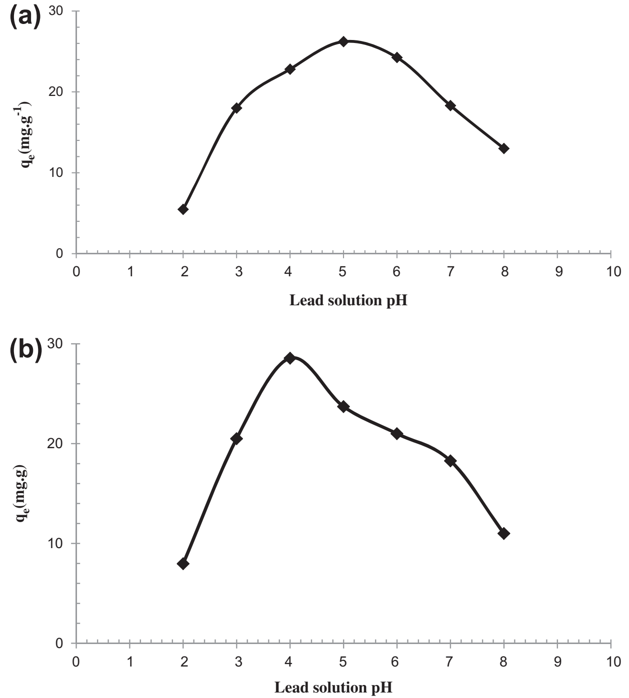

Fig. 4. Effect of lead solution's pH on the lead uptake from lead solution: (a) Non-modified carbon (initial Pb concentration = 100 mg/l, contact time = 24 h, adsorbent dosage = 0.1 g, and temperature = 30°C) (b) HNO_3-modified carbon (initial Pb concentration = 100 mg/l, adsorbent dosage = 0.1 g contact time = 24 h, and temperature = 30.

The mechanism of lead adsorption in aqueous solutions has been explained by Ormek et al. [14]. At lower pH values, the concentration of H^+ in solution is high and thus Pb^{2+} ions should compete with hydrogen ions to sit on the adsorption sites on carbon surface. In a certain pH range, lead may exist in an aqueous medium in various forms including Pb^{2+}, $Pb(OH)^+$, and $Pb(OH)_2$. At lower pH values, Pb ions in competition with H^+ may be adsorbed onto the carbon surface by ion-exchange mechanism. However, at elevated pH values, lead ion neutral species may also be adsorbed by hydrogen bonding together with the presence of ion-exchange mechanism. The ion-exchange mechanism has been illustrated below [14]:

$$2(R-COH) + Pb^{2+} \rightarrow (R-CO)_2Pb + 2H^+ \tag{11}$$

$$R-COH + Pb(OH)^+ \rightarrow R-COPb(OH) + H^+ \tag{12}$$

It is, however, notable that the exact adsorption mechanism on a typical carbon surface based on the information derived from literature is difficult to interpret. It is due to the fact that various carbons are synthesized from different precursors. Moreover, the comparison may be wise to make if the chemical and physical natures of the to-be-compared carbons are approximately identical.

The effect of lead solution's pH on the lead uptake by nitric acid-modified carbon is depicted in Fig. 4(b). For the nitric acid-modified carbon, the optimum pH value at which the Pb adsorption is maximum is 4 which is slightly above the pH_{PZC} for this carbon. Lead adsorption by carbon at lower pH values is much lower. When solution's pH is increased from 2 to 4, the lead uptake by carbon has been enhanced from around 8 to a maximum of 28.5 mg/l. Similarly, this increase is due to the higher degree of ionization of surface complexes by increasing the solution's pH. However, by further increasing the pH of the solution, no further enhancement in the lead removal efficiency is observed. Moreover, the lead uptake by the adsorbent begins to constantly dip to a minimum value of about 11 mg/l at a pH value of 8. This phenomenon has been reported by other researchers and has been attributed to the fact that lead ions begin to precipitate at higher pH values and specifically in alkaline environments [13]. Based on these observations, we can conclude that the optimum pH value corresponding to maximum Pb removal is 4. This value is slightly lower than the optimum value obtained for non-modified carbon i.e. pH = 5. This can be as a result of increased concentrations of surface acidic groups and the release of more free hydrogen ions at lower pH values. Similarly, Nadeem et al. [13] compared the effect of surface modification with acid sulfuric, phosphoric, and non-modified carbons. However, they reported a small change in the optimum pH value for non-modified and modified carbons.

3.4. Effect of lead initial concentration and contact time on Pb uptake from water

The effect of initial concentration of lead and the contact time is illustrated in Fig. 5(a).

It was observed that the lead adsorption onto carbon follows two separate stages. Initially the adsorption rate is high. This fast adsorption of lead ions continues during the first 8 h of the contact time. However, from this point on, the adsorption process enters a slow interval during which the removal efficiency remains almost unchanged or with only a slight increase. The equilibrium is reached after approximately 24 h of contact time. The fast higher adsorption tendency during the initial period of the reaction is due to the abundant unsaturated adsorption sites on the surface of carbon. However, as time passes, lead ions begin to saturate these sites, which consequently leaves fewer chances for Pb ion species to be coupled to the carbon surface and thus the adsorption rate slows down until all adsorption sites are occupied and the equilibrium has been reached.

The initial concentration has shown to affect the adsorption process in two distinct ways. Firstly, the adsorption rate becomes higher when the initial lead concentration is increased. This is confirmed by considering the sharper slopes at higher initial concentrations. This can be attributed to the higher influx of Pb ions to the carbon pores from the solution bulk as a result of higher concentration gradients. Moreover, when initial Pb concentration is elevated, the final adsorption capacity has also improved. It is well justified by knowing the fact that when higher initial Pb concentrations involve, the concentration gradient is much higher compared to lower initial concentrations. This provides the Pb ions a longer time for the boundary layers to be stabilized. This consequently results

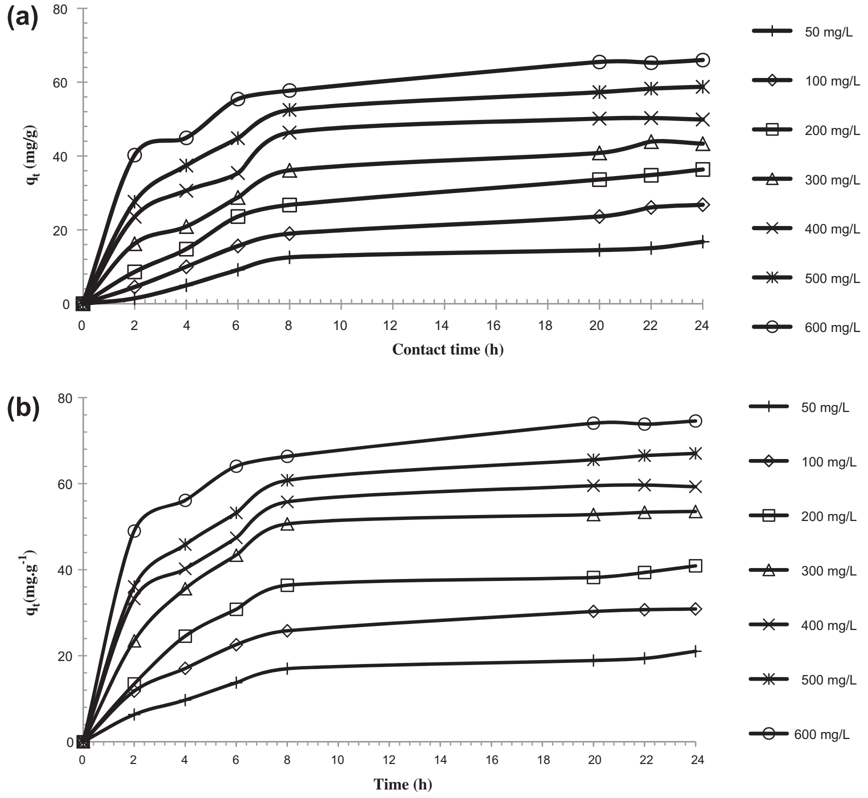

Fig. 5. Effect of initial concentration and contact time on Pb adsorption: (a) Non-modified carbon (pH = 5, adsorbent dosage = 0.1 g, temperature = 30˚C) (b) HNO_3-modified carbon (pH = 4, adsorbent dosage = 0.1 g, and temperature = 30˚C).

in an enhanced uptake of adsorbate from the solution bulk. It was seen that when the initial lead concentration increases from 50 to 600 mg/l, the adsorption capacity increases by a factor of about 3.94.

The effect of initial concentration of lead and the contact time for modified carbon is depicted in Fig. 5 (b). Similarly, the adsorption of lead species onto the modified surface of pores takes place in two distinguishable stages. Initially, the adsorption goes through a rapid process rate. Almost for all initial concentrations, this phase ends after the first 8 h of contact time. During this interval, stronger available driving force as a result of virgin adsorption sites which are completely unsaturated, results in the high influx of Pb ions species onto the carbon surface. During this period, a minimum removal of around 17 mg/g and a maximum uptake of 66 mg/g of lead are measured for the initial concentrations of 50 and 600 mg/l, respectively. As it is expected, at higher initial concentrations there exists a stronger concentration driving force. This can be simply justified by the sharper slopes of the line graph at higher initial lead concentrations. After around 20 h of the contact time, there exist slight changes in the lead uptake from water indicating the maximum capacity of the adsorbent to be almost satisfied. The maximum lead uptake from water is approximately 21 and 74 mg/l for the initial concentrations of 50 and 600 mg/l of lead after a contact time of 24 h.

3.5. Adsorption of lead from water using non-modified carbon

3.5.1. Adsorption kinetics

Figs. 6 and 7 illustrate the curve-fitting plots of pseudo-first-order and pseudo-second-order models, respectively.

The parameters corresponding to pseudo-first-order and second-order adsorption kinetics models have been tabulated in Tables 2 and 3, respectively. The best models were selected based on their corresponding R^2 values [21].

The adsorption data were best described by pseudo-first-order model only in the initial period of adsorption process during which rapid adsorption took place i.e. first 500 min of the adsorption. It suggested that the entire adsorption period cannot be considered for the application of pseudo-first-order model. This has been in agreement with various other reports [12].

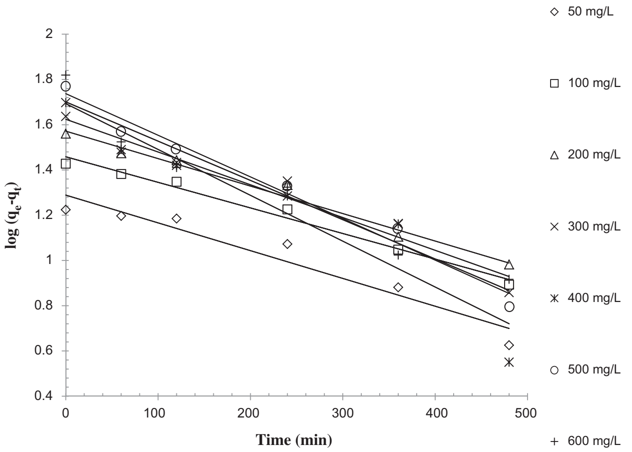

Fig. 6. Adsorption kinetics for Pb ions: Pseudo-first-order model (non-modified carbon).

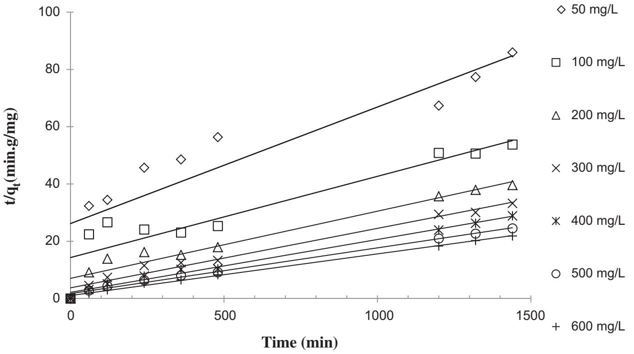

Fig. 7. Adsorption kinetics for Pb ions: Pseudo-second-order model (non-modified carbon).

Table 2
Pseudo-first-order kinetic model parameters: non-modified carbon

Pseudo-first-order kinetic model				
C_0 (mg/l)	R^2	K_1 (min^{-1})	$q_{e,\text{ model}}$ (mg/g)	$q_{e,\text{ exp}}$ (mg/g)
50	0.9306	0.0028	19.4536	16.757
100	0.9835	0.0025	27.9145	26.784
200	0.9814	0.0028	37.2735	36.347
300	0.9517	0.0032	42.092	43.335
400	0.8957	0.0046	49.3174	49.872
500	0.9771	0.0041	54.6135	58.75
600	0.9402	0.0039	50.2227	65.989

The R^2 values obtained for both models show that the pseudo-second-order kinetic model can best describe the adsorption kinetic data for the concentrations of 200–600 mg/l. However, for the low concentrations of 50 and 100 mg/l, the pseudo-first-order model resulted in a relatively better R^2 value. Such dependencies in the values of R^2 on the initial

Table 3
Pseudo-second-order kinetic model parameters: Non-modified carbon

Pseudo-second-order kinetic model				
C_0 (mg/l)	R^2	K_2 (g/mg min)	$q_{e,\ model}$ (mg/g)	$q_{e,\ exp}$ (mg/g)
50	0.8084	6.33E−05	24.57	16.757
100	0.8586	4.13E−07	35.71	26.784
200	0.9830	7.78E−05	42.735	36.347
300	0.9771	0.000116	48.077	43.335
400	0.9899	0.000159	54.054	49.872
500	0.9932	0.000148	62.5	58.75
600	0.9965	0.000198	68.966	65.989

concentration of the solute have been similarly reported by Azizian [22]. In general, it can be understood that the pseudo-second-order kinetic model can best describe the kinetic data for a well wider range of initial concentration over the entire adsorption period. It is therefore concluded that the adsorption is due to chemisorption based on the theory behind the pseudo-second-order kinetic model [12].

3.5.2. Adsorption isotherms

There are different forms of adsorption isotherms with which the adsorption data can be interpreted. These mainly include Langmuir, Freundlich, Toth, Temkin, Redlich–Peterson, Sips, and Dubinin–Radushkevich isotherms. However, among these models, the two most common types are the Langmuir and Freundlich models [12]. The obtained data are, therefore, evaluated based on these two models.

The Langmuir and Freundlich curve-fittings are shown in Figs. 8 and 9, respectively.

The isotherm parameters corresponding to Langmuir and Freundlich adsorption isotherm models are tabulated in Table 4.

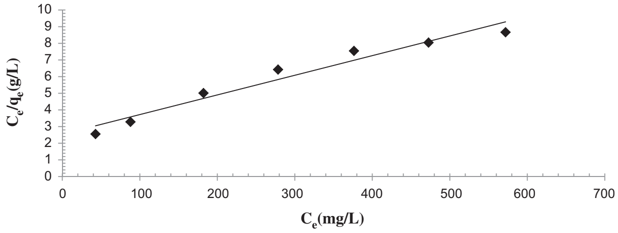

Fig. 8. Langmuir isotherm curve fitting to the lead adsorption experimental data: Non-modified carbon.

Table 4
Langmuir and Freundlich isotherm models parameters: non-modified carbon

Langmuir		Freundlich	
a_L	0.0091	$1/n_F$	0.5036
K_L	0.39341	K_F	2.62479
R^2	0.956	R^2	0.993

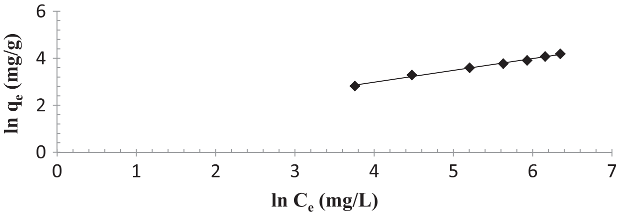

Fig. 9. Freundlich isotherm curve fitting to the lead adsorption experimental data: Non-modified carbon.

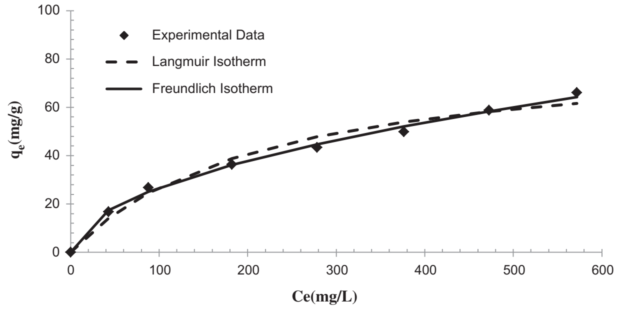

Fig. 10. Comparison of Langmuir and Freundlich models in fitting the experimental data: non-modified carbon.

Based on the table and the R^2 values calculated for the two models, Freundlich isotherm is understood to be the best model to fit the experimental data. This empirical model is employed to describe the heterogeneous systems [12]. This confirms the non-uniform distribution of the active sites on the surface of the carbon unlike the Langmuir isotherm which assumes a homogeneous distribution of the active sites on the carbon surface.

A comparison between the experimental data and Langmuir and Freundlich models is shown in Fig. 10.

3.6. Adsorption of lead from water using nitric acid-modified carbon

3.6.1. Adsorption kinetics

Figs. 11 and 12 illustrate the curve-fitting plots of pseudo-first-order and pseudo-second-order models, respectively.

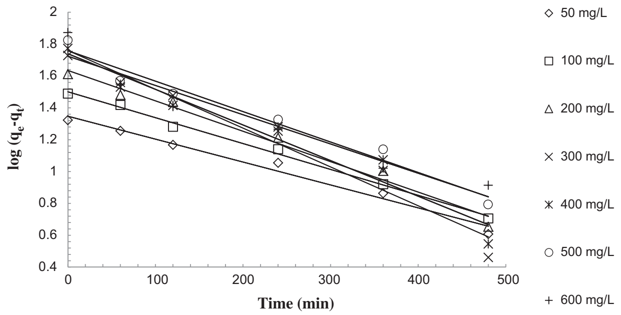

Fig. 11. Adsorption kinetics for Pb ions: Pseudo-first-order model (HNO_3-modified carbon).

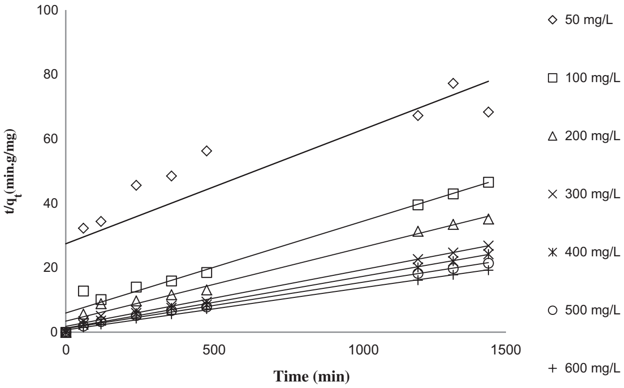

Fig. 12. Adsorption kinetics for Pb ions: Pseudo-second-order model (HNO_3-modified carbon).

The parameters corresponding to pseudo-first-order and second-order adsorption kinetics models have been tabulated in Tables 5 and 6, respectively. The best models were selected based on their corresponding R^2 values [21].

The R^2 values obtained for both models show that the pseudo-second-order kinetic model can best describe the adsorption kinetic data for the concentrations of 200 to 600 mg/l. However, for the low concentrations of 50 and 100 mg/l, the pseudo-first-order model produced a better R^2 value. Such dependencies in the values of R^2 on the initial concentration of the solute have been similarly reported recently by Azizian [22]. In general, it can be understood that the pseudo-second-order kinetic model can best describe the kinetic data for a well wider range of initial concentration over the entire adsorption period.

3.6.2. Adsorption isotherms

The Langmuir and Freundlich curve-fittings are shown in Figs. 13 and 14, respectively.

Table 5
Pseudo-first-order kinetic model parameters: HNO_3-modified carbon

Pseudo-first-order kinetic model				
C_0 (mg/l)	R^2	K_1 (min^{-1})	$q_{e,\text{ model}}$ (mg/g)	$q_{e,\text{ exp}}$ (mg/g)
50	0.9805	0.003224	22.26384	21.03915
100	0.9954	0.003685	31.67379	30.8793
200	0.9813	0.004376	43.16184	40.90083
300	0.9598	0.005527	57.54399	53.54345
400	0.9451	0.005067	54.91614	59.28062
500	0.9691	0.004376	57.38521	67.02031
600	0.9311	0.004145	52.99074	74.568

Table 6
Pseudo-second-order kinetic model parameters: HNO_3-modified carbon

Pseudo-second-order kinetic model				
C_0 (mg/l)	R^2	K_2 (g/mg min)	$q_{e,\text{ model}}$ (mg/g)	$q_{e,\text{ exp}}$ (mg/g)
50	0.733	2E−05	42.55319	21.039
100	0.9698	1.3E−06	355.8719	30.879
200	0.9829	0.00015	44.24779	40.901
300	0.9923	0.00016	57.47126	53.543
400	0.9954	0.00019	62.89308	59.281
500	0.9958	0.00011	70.42254	67.02
600	0.998	0.00022	76.92308	74.568

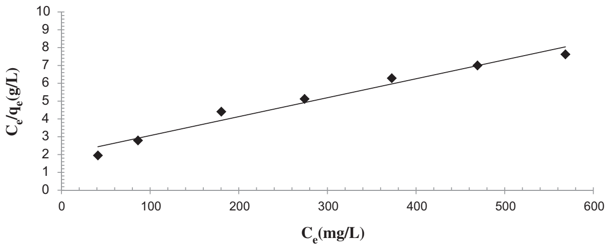

Fig. 13. Langmuir isotherm curve fitting to the lead adsorption experimental data: HNO_3-modified carbon.

The isotherm parameters corresponding to Langmuir and Freundlich adsorption isotherm models are tabulated in Table 7.

Based on the table and the R^2 values calculated for the two models, Freundlich isotherm is understood to be the best model to fit the experimental data. A comparison between the experimental data and Langmuir and Freundlich models is shown in Fig. 15.

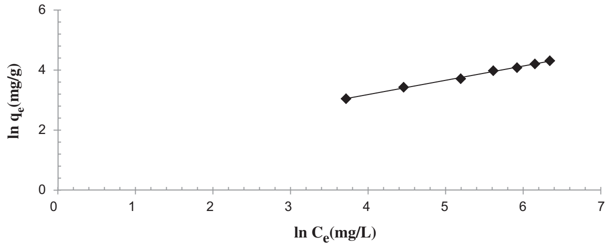

Fig. 14. Freundlich isotherm curve fitting to the lead adsorption experimental data: HNO_3-modified carbon.

Table 7
Langmuir and Freundlich isotherm models parameters: HNO_3-modified carbon

Langmuir		Freundlich	
a_L	0.0053	$1/n_F$	0.4749
K_L	0.49975	K_F	3.62118
R^2	0.9699	R^2	0.997

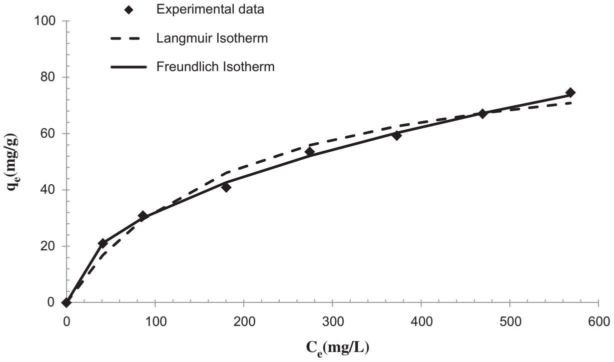

Fig. 15. Comparison of Langmuir and Freundlich models in fitting the experimental data: HNO_3-modified carbon.

4. Conclusions

For the first time, adsorption of lead ions and lead species in water has been studied using non-modified porous charred carbon and nitric acid-modified carbon obtained through the direct pyrolysis of used cigarette filters. The adsorption data for both carbons best followed a Freundlich isotherm model. The kinetics of both carbons were also best explained by fitting a pseudo-second-order model to the adsorption data which favors the chemical mechanism of adsorption. It was observed that the lead adsorption capacity for both carbons increased with increasing the initial concentrations of the lead solution. However, when the nitric acid-modified carbon was contacted with the lead solution, lead uptake capacity was enhanced. This increase was around 30 and 13% with initial lead concentrations of 50 and 600 mg/l, respectively. This increase in lead uptake from water was expected as a result of the increased number of surface functional groups due to acidic modification of the carbon surface.

Table 8
Monolayer adsorption capacity (q_e (mg/g)) for the adsorption of lead using different adsorbents [16]

Adsorbent	q_e (mg/g)
Chitosan nanoparticle	398
Tannin gel	190
Activated phosphate	155
Chitosan	115.5 (0.558 mmol/g)
Natural phosphate	115
Tannin resin	114.9
Modified rice husk	108
Peat	103.1
Sawdust activated carbon (SDAC)	93.36 (0.451 mmol/g)
Charred carbon from used cigarette butts modified with nitric acid	*74.5*
Zeolite	70.58
PHEMA/chitosan membranes	68.81
Charred carbon from used cigarette butts	*66*
Gelidium algae	64
Commercial activated carbon	54.65 (0.264 mmol/g)
Activated carbon (Sorbo-Norit)	54.10
Bacteria modified activated carbon	54.10
Modified peat-resin particles	47.39
Algal waste	44
Live biomass	35.69
Activated carbon (Merck)	21.50
Carbon nanotubes	17.44
Sawdust	12.63 (0.061 mmol/g)
Groundnut shells	12.21 (0.059 mmol/g)
Cone biomass of Pinus sylvestris	11.38
Goethite	11.04
Montmorillonite	10.40
Waste tea leaves	2.096

The pH of the lead solution was seen to be a very critical parameter for both non-modified and modified carbons. For both carbons the optimum pH was reached at a maximum point in the graph of pH vs. lead uptake. Any further increase in the pH value resulted in a subsequent decrease in the removal efficiency. The optimum pH was observed to be at a value of 5 and 4 for non-modified and modified carbons, respectively. Any further increase in pH beyond around 6 resulted in precipitation of lead in the solution affecting the total lead removal efficiency. Adsorbent dosage had also a significant effect of the lead uptake from water. As more amounts of adsorbents were contacted with a fixed concentration of lead solution, more lead ions and species were removed due to an increase in the available adsorption sites. However, when the adsorbent mass was increased beyond 0.1 g, no significant lead uptake from water was observed for both types of carbons.

The removal efficiencies of the non-modified and modified carbons were of an acceptable range, though not very high, compared to several recently-studied adsorbents used in the adsorption of lead from water. For comparison, Table 8 has tabulated the lead adsorption capacity of several adsorbents from water.

According to Table 8, the removal efficiencies of both types fall in the middle range of the table.

References

[1] R.C. Bansal, M. Goyal, Activated Carbon Adsorption, Tayler & Francis Group, Boca Raton, FL, 2005.

[2] A. Witek-Krowiak, R.G. Szafran, S. Modelski, Biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent, Desalination 265 (2011) 126–134.

[3] J.D. Celis, N.E. Amadeo, A.L. Cukierman, In situ modification of activated carbons developed from a native invasive wood on removal of trace toxic metals from wastewater, J. Hazard. Mater. 161 (2009) 217–223.

[4] S.F. Lo, S.Y. Wang, M.J. Tsai, L.D. Lin, Adsorption capacity and removal efficiency of heavy metal ions by meso and ma bamboo activated carbon, Chem. Eng. Res. Des. 90(9) (2011) 1397–1406.

[5] World Health Organization. Guidelines for Drinking-Water Quality, 3rd ed., vol. 1, WHO Library Cataloguing-in-Publication Data, Geneva, 2004.

[6] K. Kawarada, K. Haneishi, T. Iida, Pore structure and performance for drinking water treatment of activated carbon prepared from sugi thinning from water source forest in Tokyo, Wood Industry 60 (2005) 398–401.

[7] M. Momcilovic, M. Purenovic, A. Bojic, A. Zarubica, M. Randelovic, Removal of lead (II) ions from aqueous solutions by adsorption onto pine cone activated carbon, Desalination 276 (2011) 53–59.

[8] O. Gercel, H.F. Gercel, Adsorption of lead (II) ions from aqueous solutions by activated carbon prepared from biomass plant material of Euphorbia rigida, Chem. Eng. J. 132 (2007) 289–297.

[9] V.J. Strelko, D. Malik, Characterization and metal sorptive properties of oxidised active carbon, J. Colloid Interf. Sci. 250 (2000) 213–220.

[10] P. Chingombe, B. Saha, R.J. Wakeman, Surface modification and characterization of coal-based activated carbon, Carbon 43 (2005) 3132–3143.

[11] F. Rodriguez-Reinoso, A. Sepulveda-Escribano, Porous carbons in adsorption and catalysis. in: H.S. Nalwa (Ed.), Handbook of Surfaces and Interfaces of Materials, vol. 5, Academic Press, San Diego, CA, 2001, pp. 309–355.

[12] G. Crini, H.N. Peindy, F. Gimbert, C. Robert, Removal of C.I. basic green 4 from aqueous solutions by adsorption using cyclodextrin-based adsorbent: Kinetic and equilibrium studies, Sep. Purif. Technol. 53 (2007) 97–110.

[13] M. Nadeem, A. Mahmood, S.A. Shahid, S.S. Shah, A.M. Khalid, G. McKay, Sorption of lead from aqueous solution by chemically modified carbon adsorbents, J. Hazard. Mater. B138 (2006) 604–613.

[14] A. Ornek, M. Ozacar, A.I. Sengil, Adsorption of lead onto formaldehyde or sulphuric acid treated acron waste: Equilibrium and kinetic studies, Biochem. Eng. J. 37 (2007) 192–200.

[15] X. Tao, L. Xiaoqin, Peanut shell activated carbon: Characterization, surface modification and adsorption of Pb^{2+} from aqueous solution, Chinese. J. Chem. Eng. 16(3) (2008) 401–406.

[16] M.J. Baniamerian, S.E. Moradi, A. Noori, H. Salahi, The effect of surface modification on heavy metal ion removal from water by carbon nanoporous adsorbent, Appl. Surf. Sci. 256 (2009) 1347–1354.

[17] S.Z. Mohammadi, M.A. Karimi, D. Afzali, F. Mansouri, Removal of Pb (II) from aqueous solutions using activated carbon from sea-buckthorn stones by chemical activation, Desalination 262 (2010) 86–93.

[18] S. Masoudi Soltani, S.K. Yazdi, S. Hosseini, Effects of pyrolysis conditions on the porous structure construction of mesoporous charred carbon from used cigarette filters, Appl. Nanosci., doi: 10.1007/s13204-013-0230-0.

[19] V. Bhole, D.S. Ramteke, Preferential adsorption of heavy metals on activated carbon, Bangladesh J. Sci. Ind. Res 46(2) (2011) 211–218.

[20] S. Shukla, Y. Zhang, P. Dubey, J.L. Margrave, S.S. Shukla, The role of sawdust in the removal of unwanted materials from water, J. Hazard. Mater. B95 (2002) 137–152.

[21] M. Malekbala, S. Hosseini, S.K. Yazdi, S. Masoudi Soltani, M. R. Malekbala, The study of the potential capability of sugar beet pulp on the removal efficiency of two cationic dyes, Chem. Eng. Res. Des. 90 (2012) 704–712.

[22] S. Azizian, Kinetic models of sorption: A theoretical analysis, J. Colloid Interf. Sci. 276 (2004) 47–52.