Lead Sorption by Carbon Nanofibers Grown on Powdered Activated Carbon — Kinetics and Equilibrium

Abdullah Al Mamun*,§, Yehya M. Ahmed†,
Ma'an Fahmi R. AlKhatib*, Ahmad Tariq Jameel*
and Mohammed Abdul Hakeem Abdul Rahman AlSaadi‡
*Nanoscience and Nanotechnology Research Group NANORG
Faculty of Engineering International
Islamic University Malaysia (IIUM)
Jalan Gombak, 53100, Kuala Lumpur, Malaysia

†Department of Civil Engineering
Faculty of Architecture and Built Environment
Limkokwing University of Creative Technology
63000 Cyberjaya, Malaysia

‡UMCiL, Department of Chemical Engineering
Faculty of Engineering, University of Malaya
50603 Kuala Lumpur, Malaysia
§mamun@iium.edu.my

Carbon nanofibers (CNFs) were synthesized by using a safe and less hazardous method, compared to using floating catalysts in chemical vapor deposition (CVD) process. This process used C_2H_2 as carbon source and oil palm kernel shell-based powdered activated carbon (PAC) as cheap solid substrate. Use of nickel (Ni^{2+}) impregnated PAC as fixed substrate for the synthesis of CNF is one of the novelties of the research work accomplished by the authors. The PAC–CNFs porous nanocomposite product was used for the sorption of lead ions (Pb^{2+}) from synthetic aqueous solution. Kinetics of Pb^{2+} adsorption and isotherms were investigated by varying initial concentration of lead and contact time. PAC–CNFs were found to remove Pb^{2+} better at acidic pH of about 5.5. Langmuir and Freundlich isotherms were applied to the sorption equilibrium data to find the best fitted model. Langmuir isotherm model with $R^2 = 0.965$ fitted the adsorption data better than the Freundlich isotherm. The kinetic processes of Pb^{2+} adsorption on CNFs were investigated by applying different kinetic models, namely zero-order, pseudo-first-order and pseudo-second-order. The pseudo-second-order rate equation exhibited the best results with $R^2 = 0.999$, $q_e = 74.79$ (mg/g) and $K_2 = 0.029$ (min · g/mg). The novel nanocomposite product seemed to have the potential to remove Pb^{2+} ions from aqueous solution.

Keywords: Adsorption; initial concentration; isotherms; Langmuir; pseudo-second-order.

1. Introduction

Heavy metals are of great concern due to their toxicity, resistance against decay and other harmful effects to the environment.[1,2] Because of their toxicity, the presence of any of these metals in excessive quantities will interfere with many beneficial uses of the water. Lead is one of the heavy metals which is used in various industries and is being discharged (intentionally or unintentionally) into the environment presents a special concern, since this metal is bounded to bioaccumulation and excessive concentrations of lead are associated with various diseases in humans and animals.[3,6,7] Several techniques have been applied to treat lead-containing wastewaters, including reverse osmosis, electrodialysis, ultrafiltration, ion exchange, chemical precipitation, adsorption, phytoremediation, etc. However, the major disadvantages of these techniques include incomplete metal removal, high reagent or energy requirements and toxic sludge generation.[4,5] As a consequence, the implementation of new alternative approaches became a necessity in the primary metal industries.

Sorption of metal from aqueous solution by sorbent is one of the easiest, safest and most cost-effective methods for the removal of the toxic metals.[8,9] Activated carbon is commonly and widely used as an adsorbent for removal of heavy metal pollutants from wastewater and has proven to be effective.[5,10,11] It can also be produced from cheap and locally available materials.[12–14] Ion exchange resins have also been used to remove heavy metals from wastewater.[15,16]

Equilibrium analysis is fundamental for the evaluation of the affinity or capacity of a sorbent. It is, therefore, important to determine how sorption rates depend on the concentrations of sorbate in a solution and how rates are affected by the sorption capacity or by the character of the sorbent in terms of kinetics.[17] Many attempts have been made to formulate a general expression describing the kinetics of sorption on solid surfaces for liquid–solid phase sorption systems. In recent years, sorption mechanisms have been reported and involved kinetic-based models. The most often cited literature involves first-order,[18] second-order-reversible reaction,[19] first-order,[20] second-order irreversible reactions,[21] pseudo-first-order[22] and pseudo-second-order reactions,[23] based on solution concentration. Equilibrium studies are described by a sorption isotherm and characterized by certain constants whose values express the surface properties and affinity of the sorbent.[24] In this research, Freundlich and Langmuir isotherms were applied against the equilibrium data to investigate their suitability to investigate the mechanism of lead sorption by a novel adsorbent "PAC–CNFs". Sorption kinetics were also investigated for further characterization of the composite nanoproduct.

2. Materials and Methods

Various amounts (3, 5 and 7% w/w) of nickel catalyst were dissolved in acetone and then mixed with oil palm kernel shell PAC. All these materials were sonicated in the ultrasonic bath for half an hour at room temperature and high speed for uniform impregnation of Ni^{2+} into PAC to be used as fixed substrate for CNF synthesis by chemical vapor deposition (CVD) method. The nickel-impregnated PAC was left at the water bath at a temperature of 56°C and sonicated for 12 h to ensure complete impregnation and evaporation of excess acetone.[31] Catalyst substrate was calcined by using nitrogen gas at 350°C by flowing at the rate of 200 mL/min for 1 h then reduced using hydrogen gas at 400°C and 120 mL/min flow rate for 2 h. The CNF growth process was carried out on the reduced catalyst in the CVD reactor at atmospheric pressure in the presence of C_2H_2/H_2 mixture (total flow rate, 20 mL/min and 100 mL/min) after the temperature was raised to 650°C.[32] The impregnated PAC substrate with 5% Ni^{2+} ion produced the best yield of the CNFs on the PACs.

Various standard tests such as, field emission scanning electron microscope (FESEM), transmission electron microscope (TEM), Fourier transform infra-red (FTIR) spectroscopy, energy dispersive X-ray analyzer (EDX), thermal gravimetric analysis (TGA), Zeta potential and Brunauer–Emmett–Teller (BET) were used to characterize the composite adsorbent.[31] The average surface area of the PAC–CNF composite was 837 m^2/g. The FTIR revealed that carbonyl and methyl groups were predominantly present in the composites. The zeta potential for the samples were negative and the peaks shifted toward zero point from PAC value (−30.9) to the PAC–CNF value (−24.9). High negative charges is an indication that the adsorbent is more hydrophilic in nature. The negative sign for

the zeta potentials was indicative of the hydrophilicity of the composite adsorbent. Scanning electron microscope (SEM) image of the nanocomposite and typical diameters of the CNFs for 5% Ni^{2+} catalysts are shown in Fig. 1.

Various initial concentrations of Pb^{2+} (5, 10, 15, 20, 40 and 70 mg/L) were employed to perform adsorption equilibrium isotherm experiments at room temperature. The samples were tested in duplicate and the mean values were used for the results and discussion. Reproducibility of the synthesis and laboratory test results were considered acceptable if the mean variation did not exceed 10% of the test results. The adsorption tests were conducted at pH 5.5, dose of PAC–CNFs 0.25 g/L, agitation speed 200 rpm and various time intervals (2, 5, 15, 30, 60 and 120 min). The optimum pH of 5.5 was determined at the laboratory by face cantered central composite design (FCCCD) using the Design Expert™ Software. Aqueous solution of Pb^{2+} was prepared and pH was controlled as mentioned above; then 20 mL volume of this solution was mixed with the adsorbent in 50 mL conical flask and fixed on the shaker which was operated at speed 200 rpm for various time intervals. Then the solution was filtered using 45 μm membrane filter. The Pb^{2+} concentration of the filtrate was measured using Perkin Elmer 300 AAS, USA. Adsorption capacities of the selected PAC–CNFs to lead at time t, q_t, were calculated using Eq. (1):

$$q_t = (C_0 - C_t)v/m, \tag{1}$$

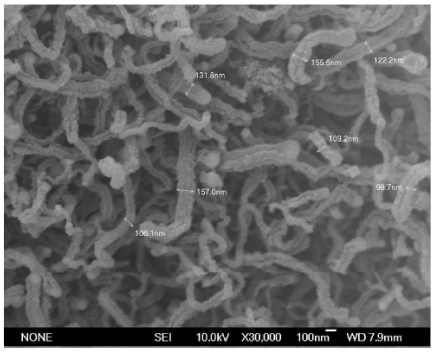

Fig. 1. SEM Image of the CNFs grown on the PAC substrate at 5%w/w nickel (the adsorbent used for the isotherm and kinetics study).

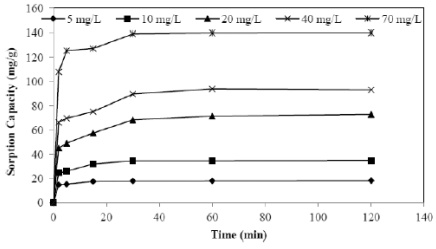

Fig. 2. Equilibrium sorption capacity for various Pb^{2+} concentrations.

where, C_0 and C_t (mg/L) are the liquid-phase initial concentrations of lead and at time t, respectively, v (L) volume of lead aqueous solution and m (g) is the mass of dry PAC–CNFs used. The concentrations were plotted against time to get the equilibrium concentration.

Langmuir isotherm for the adsorption of lead on the PAC–CNFs was studied by plotting the relation between equilibrium concentration C_e (mg/L) of Pb^{2+} in the x-axis and C_e/q_e in the y-axis [Eq. (2)].

$$C_e/q_e = 1/K_L q_m + C_e q_m, \tag{2}$$

where, q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), q_m (the maximum sorption capacity, mg/L) and K_L (Langmuir constant) were determined from the slope and intercept of the straight line of C_e/q_e versus C_e graph.

Fruendlich isotherm for the adsorption of lead on the PAC–CNFs was also studied by plotting the relation between $\log C_e$ in the x-axis and $\log q_e$ in the y-axis from the following linear equation [Eq. (3)].

$$\log q_e = \log K_F + (1/n) \log C_e, \tag{3}$$

where, q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium concentration of solute in the bulk solution (mg/L), K_F is a constant, indicative of the relative adsorption capacity of the adsorbent (mg/g) and the constant $1/n$ indicates the intensity of the adsorption.

The following equations [Eqs. (4)–(8)] were used to investigate the mechanism of lead adsorption: zero-order, pseudo-first-order and pseudo-second-order kinetic models[25–30]

$$C_0 - C = K_t, \tag{4}$$

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

$$dq_t/d_t = K_2(q_e - q_t)^2, \tag{6}$$

where, C_0 and C (mg/L) are the initial concentration and concentration at time t, respectively; q_t and q_e are Pb^{2+} sorption capacity at time t and equilibrium, respectively; t is time (min) and K is the rate constant.

3. Results and Discussion

3.1. *Adsorption isotherms*

The relations between contact times (min) and sorption capacity q_t (mg/g) for different Pb^{2+}

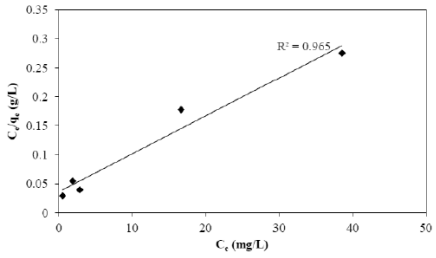

Fig. 3. Langmuir adsorption isotherm for Pb^{2+} sorption (adsorbent dose = 0.25 g/L, pH = 5.5, agitation = 200 rpm and ambient temperature = 28 ± 2°C).

concentrations are shown in Fig. 2. It was observed that in case of the samples having concentrations from 5 mg/L to 20 mg/L, more than 85% of Pb^{2+} was removed within the first 60 min of sorption process. Whereas, about half of the lead ions (Pb^{2+}) were removed within the same period for the samples with initial concentrations of 40 mg/L and 70 mg/L (high concentrations). Removal of high amount of the Pb^{2+} was due to increase in mass transfer driving force leading to higher lead adsorption rates.[33–35] It was also observed that the adsorption process was fast, and it reached equilibrium in 30 min to 60 min based on initial concentration of Pb^{2+}. The equilibrium solid-phase concentration of Pb^{2+} (q_e) increased with increasing the adsorbate concentration, which mainly attributed to the availability of more adsorption sites for the adsorption process. Such observation was also reported by other researchers.[36–38] The pH values were not recorded for every time interval used for the equilibrium study (Fig. 2). The initial and final pH values were recorded, which indicated that pH values at the end of the sorption processes increased depending on the initial concentrations of the Pb^{2+} ions. The mean pH value increased from 5.5 to 6.85.

The Langmuir and Freundlich models are the most frequently employed models. In the present work, both models were used. The Langmuir equation [Eq. (2)] relates solid-phase adsorbate concentration (q_e), the uptake, to the equilibrium liquid concentration (C_e) and q_m are calculated from the slope and intercept of the straight lines of C_e/q_e versus C_e graph. The lead sorption isotherm followed the linearized Langmuir model as shown in Fig. 3.

It can be seen that the isotherm data fits the Langmuir equation well ($R^2 = 0.965$). The values of K_L and q_m were determined from the plot and were found to be 0.17 L/mg and 166.66 mg/g, respectively.

The relation between the lead uptake capacity (q_e) in mg/g of adsorbent and residual lead concentration C_e in mg/L at equilibrium is given by Eq. (3). K_F and n were determined from the slope and intercept of the linear plot of $\log q_e$ versus $\log C_e$ (Fig. 4).

The values of K_F and n were determined from the plot and were found to be 28.97 mg/g and 2.2 mg/g, respectively. It can be seen that the isotherm data also fits the Freundlich equation ($R^2 = 0.903$). The q_m, K_L, R_1^2 (correlation coefficient for Langmuir isotherm), K_F, n and R_2^2 (correlation coefficient for Freundlich isotherm) are given in Table 1.

A relatively high R^2 value is an evidence that the adsorption of lead is well fitted to both Langmuir and Freundlich models although, from the value of R_1^2 and the scatter of the plotted points, the Langmuir model is better than Freundlich. Good fit of

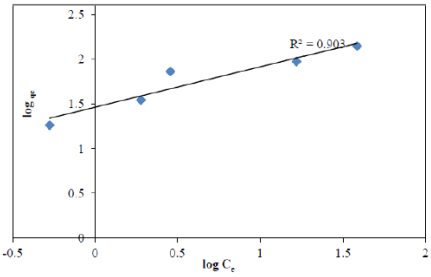

Fig. 4. Freundlich adsorption isotherm for Pb^{2+} sorption (adsorbent dose = 0.25 g/L, pH = 5.5, agitation = 200 rpm and ambient temperature = 28 ± 2°C).

pH values were recorded, which indicated that pH values at the end of the sorption processes increased depending on the initial concentrations of the Pb^{2+} ions. The mean pH value increased from 5.5 to 6.85.

The Langmuir and Freundlich models are the most frequently employed models. In the present work, both models were used. The Langmuir equation [Eq. (2)] relates solid-phase adsorbate concentration (q_e), the uptake, to the equilibrium liquid concentration (C_e) and q_m are calculated from the slope and intercept of the straight lines of C_e/q_e versus C_e graph. The lead sorption isotherm followed the linearized Langmuir model as shown in Fig. 3.

It can be seen that the isotherm data fits the Langmuir equation well ($R^2 = 0.965$). The values of K_L and q_m were determined from the plot and

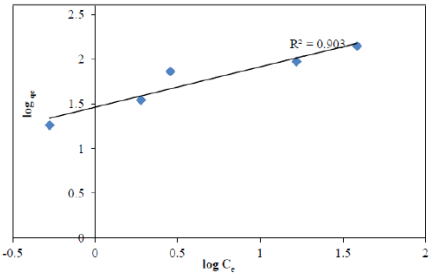

Fig. 4. Freundlich adsorption isotherm for Pb^{2+} sorption (adsorbent dose = 0.25 g/L, pH = 5.5, agitation = 200 rpm and ambient temperature = 28 ± 2°C).

Link to Full-Text Articles :

http://www.worldscientific.com/doi/abs/10.1142/S1793292015500174?af=R