Kinetic Study of Water Contaminants Adsorption by Bamboo Granular Activated and Non-Activated Carbon

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Abstract

The adsorptive capacity of metal ions from surface water with activated and non-activated carbon derived from bamboo was investigated. The validation of adsorption kinetics of Cl, PO_4 and Pb was done by pseudo-first and second order model while adsorption isotherms was proved by Langmuir and Freundlich isotherm model for activated and non- activated bamboo granular carbon. Generally, the amount of metal ions uptake increases with time and activation levels and the pH of bamboo granular carbon increase with activation. Similarly, the pore space of the activated carbon also increases with activation levels. The correlation coefficients (R^2) show that the pseudo-second order model gave a better fit to the adsorption process with 0.9918 as the least value and 1.00 as the highest value as compared with the pseudo-first order with 0.813 as the highest value and 0 as the least. The Freundlich isotherm was more favorable when compared with the Langmuir isotherm in determining the adsorptive capacity of bamboo granular activated carbon. The study has shown that chemical activation increases the pore space, surface area and the pH of bamboo granular carbon which ultimately increases the adsorption rate of metal ions in the contaminated surface water.

Keywords: adsorption, metal ions, activation levels, activated carbon, bamboo

1. Introduction

The contamination of surface water with metal ions is becoming a big challenge in Nigeria. This was attributed [1] to population growth and industrial development. Metal ions present in water lead to ecological and health problems [2]. They may, however, not be toxic to the human body if they play their basic roles as components of vital biochemical or enzymatic activities [3]. Ions like Cd, Pb, PO_4 and Cl can be toxic to human beings if they penetrate into the human organ and tissue [4]. Cadmium and Lead in particular have no beneficial biological importance in the human system. They are pollutants and their presence at elevated levels cause conditions that are similar to those of food poisoning and are also associated with kidney diseases and hypertension [5]. Metal ions can threaten aquaculture by reducing the level of dissolved oxygen [6]. There is, therefore, the need for structured measures to minimize ions in water bodies especially those meant for abstraction or human consumption. There is the need for improved techniques of water treatment in Nigeria aside the common ones. Such could be the adoption of local agricultural products which are renewable, readily available and abundant. One of such agricultural products is the non-timber forest plant called bamboo which is in large quantities in Nigeria, but is under-utilized compared to its use in countries like India and China [7].

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Researchers in Asia have confirmed the usefulness of bamboo to regulate blood circulation and prevent harmful electromagnetic fields in humans. Bamboo has been used as an electromagnetic shielding capacity and has also been adopted as an adsorbent in the environmental field in the form of activated carbon. Most of the research conducted lately in Nigeria on the use of agricultural products as adsorbent in removing heavy metals from water and wastewater include sawdust, coconut shell and palm kernel shell. Little has been done on the use of bamboo as an adsorbent. The use of bamboo as adsorbent in the purification of dyes, [8] and as adsorbent to reduce organic contaminants [9] has been reported. Both studies confirmed the efficacy of bamboo as adsorbent indicating potential for further usage as compared to the traditional uses. It was also observed to be better than other agricultural products earlier-on tried as adsorbent. This study investigated the adsorption capacity of bamboo for some ions and its conformity or otherwise to the pseudo-first and second order kinetic model as well as Langmuir and Freundlich adsorption models. The observation is restricted to the adsorption of Cl, PO_4 and Pb, ions from wastewater using activated and non activated bamboo granular carbon.

2. Materials and Methods

Waste bamboo was collected, reduced to smaller sizes and thereafter washed and soaked for 24hrs to remove waste particles adhered onto the surface during construction. The bamboo was subjected to pyrolysis with the aid of aluminum foil in a Gallenkamp muffle furnace at temperature range of 300-350°C for 2hrs. The charred bamboo was grinded and activated with chloride salt at various percentage weights of 0, 10, and 20. To ensure complete reaction of impregnation salt ($ZnCl_2$), the samples were subjected to temperature range of 200- 450°C for 6hrs. Thereafter, each GAC was washed with slightly boiled deionized water to remove zinc chloride and to stabilize the pH to neutral. They were then placed in the oven at 90°C for 24hrs and were removed to cool at room temperature. High energy electrons from Scanning Electron Spectroscopy with variety of signal were used to focus the surface of the GAC to get the micrographs (SEM, EVO/MA15: Sheda Science and Technology complex, Gwagwalada Abuja). The pore space and surface area were then read with java interactive software programme called image J.

The water samples used in the adsorption experiment were analyzed according to WHO and EC standards. A fixed adsorption bed experiment was set-up and valves were opened slowly such that the water flowed from the reservoir into the adsorption filter bed by gravity. The water samples were retained in each of the filters for 60mins before flowing down the filtering bed and this was repeated five times. The effluents collected were subjected to physico-chemical analysis. The adsorptive capacity of the bamboo GACs were then evaluated with the use of pseudo- first and second order kinetic model while the adsorptive isotherms were done by means of Langmuir and Freundlich isotherms. The amount of metal ions adsorbed was the difference between the initial and final concentration in the contact time ranging from 60 to 300 min.

3. Results and Discussion

Table 1 pH and temperature values for progressive adsorption of ions by Zinc Chloride Activated Carbon derived from Bamboo

	% Activation		
Parameters	0	10	20
pH	7.1	7.7	7.8
Temperature(°C)	27	27	27

Table 2 Progressive adsorption of ions by zinc chloride activated carbon derived from bamboo

	Cl			PO_4			Pb		
	% Activation								
Contact Time (min)	0	10	20	0	10	20	0	10	20
0	25	25	25	15	15	15	0.12	0.12	0.12
60	9.0	10.5	10.7	5.0	7.8	9.0	0.1	0.11	0.1
120	9.6	10.8	11.2	6.0	8.5	10.0	0.1	0.11	0.11
180	10.0	11.3	11.3	6.0	8.5	10.6	0.1	0.11	0.11
240	9.5	11.2	11.5	5.6	9.0	10.6	0.1	0.11	0.11
300	9.5	11.3	12.7	6.0	9.1	10.6	0.1	0.11	0.11

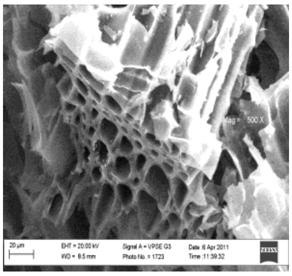
All parameters in mg/L
Note 0% implies no activation

Increasing temperature could affect the surface of the adsorbent and leave the surface inactive, rendering some active part destroyed due to bond ruptures hence weakening the force of attraction between the adsorbate and adsorbent [10]. From Table 1 the temperature of the activated GAC is held constant so that the effect of temperature is inconsequential in the adsorption of ions studies.

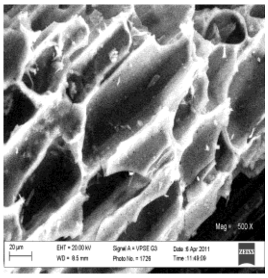
An increase in pH will increase the ligands negatively hence raising the binding effect of cations [11]. In Table 1 as the activation of carbon increases the pH values also increases. This may be due to the fact that zinc chloride has the ability to attack metal oxide in the carbon to give a derivative. Similarly in Table 2 the rate of metal adsorption increases with activation. This gave the indication that an increase in pH will increase the negative charge on the surface, thus facilitating metal uptake thereby increasing adsorption greatly [12].

Another factor that influenced the amount of ions adsorbed by the adsorbent in Table 2 was the amount of pore spaces and surface areas of each Bamboo GAC which in turn are closely related to the $ZnCl_2$ activation levels. Irrespective of the contact time, the amount adsorbed increases with activation level. Initially, the amount adsorbed increased with contact time but showed marginal increase at high contact time for some ions. The result is not conclusive for removal of Pb as all values remained practically the same irrespective of the activation level and the contact time.

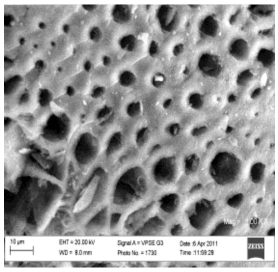
The trend at which adsorbate are absorbed by the different adsorbent could be explained based on pore size and surface area derived from impregnation and non-impregnation levels of $ZnCl_2$. This trend of adsorption is confirmed by what reported was in [13] that carbon pore size must be larger than that of the contaminant for it to adsorb impurity. This was also shown in the micrographs of bamboo GAC (Fig. 1).



0% $Zncl_2$ at 500x



10% $Zncl_2$ at 500x



20% $Zncl_2$ at 500x

(SEM, EVO/MA15: Sheda Science and Technology Complex, Gwagwalada Abuja.)

Fig. 1 Micrographs of bamboo GAC at 0%, 10% and 20% activation levels at 500 magnification(x) levels

3.1. Adsorption Kinetics

The adsorption kinetics theory depends on the interactions between the adsorbate, adsorbent and the system conditions. The resident time required for completing the adsorption reactions depend on solute uptake rate and it is enumerated from kinetic analysis. To investigate the rate of metal ions uptake, the pseudo-first and second order model [14, 15] was employed. The laboratory experimental data and model predicted values of adsorption rate were gotten from correlation coefficients "R^2" and regression equations. The values of R^2 must be less than or equal to 1. A high value indicates that the model conforms to kinetics of adsorption.

3.2. The pseudo-first order equation

The Pseudo-first order rate of equation derived by [15] can be expressed mathematically as

$$\frac{d_{qt}}{dt} = K\,(q_e - q_t)^2 \tag{1}$$

where q_m and q_t (mgg^{-1}) are the adsorption capacities at equilibrium and at time t respectively. K (min^{-1}) is the rate constant of pseudo-first order adsorption. Thus, applying first-order model of adsorption, the plot of log (qe-qt) against (t) gave a linear relationship from which values of q_e and k were determined from the slopes and intercepts of the plots. Figs. 2-4 show the plots of metal ions adsorption with Bamboo GAC impregnated at 0%, 10% and 20% activation levels. First order model adsorption kinetics for Cl, Pb and PO_4 ions removal with varying $ZnCl_2$ levels.

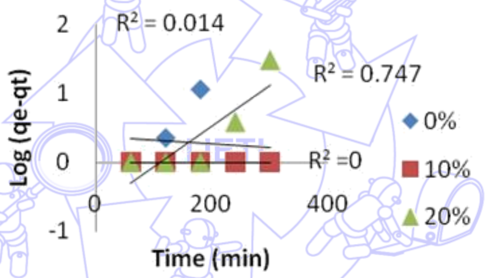


Fig. 2 First order model adsorption kinetics for Cl

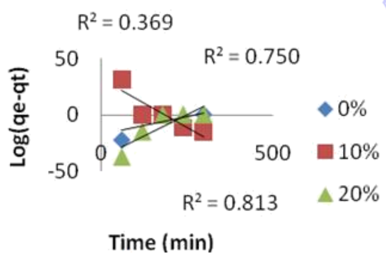


Fig. 3 First order model adsorption kinetics for PO_4

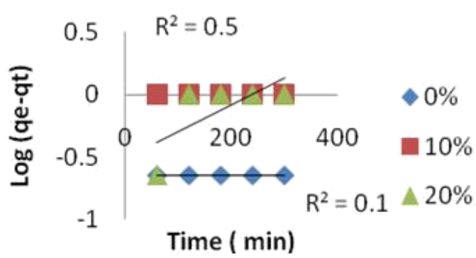


Fig. 4 First order model adsorption kinetics for Pb

Table 3 The kinetic adsorption constants for pseudo-first order model

Metal ions	Pseudo- first order constant					
%	0%		10%		20%	
	qe	K_1	qe	K_1	qe	K_1
Cl	0	0	0	0	48000	6.7E-10
PO_4	0	0	3600	6.4E-10	0	0
Pb	0	0	0	0	6000	5.4E-10

The plot for activated and non- activated bamboo GAC for all metal ions gave a fairly straight line as shown in Figs. 2-4. The correlation coefficients R^2 on the plot gave a least value of 0 for 10% activation levels in the adsorptions of Cl while the higher value was 0.813 was recorded for 20% activation level in the adsorption of Cl. The lower values of R^2 indicated poor correlation.

The values of qe and K_1 in Table 3 are gotten from the slopes and intercept of plots in Figs. 2-4. The values indicate that the pseudo-first order model is not applicable in describing the adsorption of metal ions onto bamboo activated and non-activated GAC.

3.3. The pseudo-second order equation

The rate of sorption as second order mechanism was described in [14]. The second order model is a chemisorptions kinetic rate equation and was expressed as

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

where q_e and q_t are the sorption capacity at equilibrium and at time t, respectively in mg/g and k, the rate constant of pseudo-second order of sorption (g/mg/min). If equation 2 is integrated and rearranged with h_o (mg/g/min) as the initial adsorption rate, when $q_t/t \rightarrow 0$ equation 2 becomes

$$\frac{t}{q_t} = \frac{1}{h_o} + \frac{1}{q_e\,t} \tag{3}$$

since $h_o = kq_e^{\,2}$

Hence, applying second-order model of adsorption, the plot of t/q_t against t gave a linear relationship from which values of q_e and k are determined from the slopes and intercepts of the plots. Figs. 5-7 show the plots of metal ions adsorption with Bamboo GAC impregnated at 0, 10 and 20% activation levels. Second order model adsorption kinetics for Cl, Pb and PO_4 ions removal with varying $ZnCl_2$ levels.

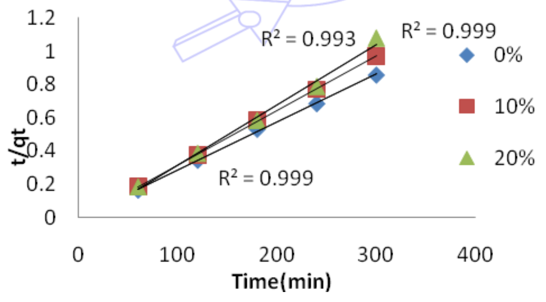


Fig. 5 Second order model adsorption kinetic for PO4

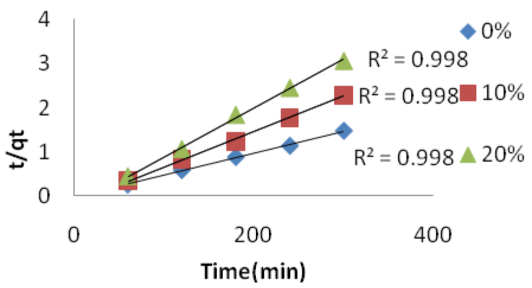


Fig. 6 Second order model adsorption kinetic for Cl

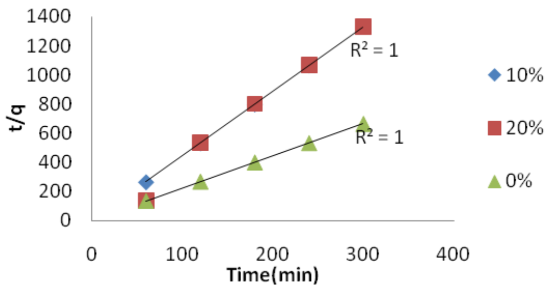


Fig. 7 Pb Second order model adsorption kinetic for Pb

Table 4 The kinetic adsorption constants for pseudo-second order model

Metal ion	Pseudo-second order								
	0%			10%			20%		
	q_e	K	h_o	q_e	K	h_o	q_e	K	h_o
Cl	120000	0	0	80000	1.04E-8	66.59	80000	3.06E-8	19.607
PO_4	36000	4.06E-8	5.28E1	22500	1.20E-8	6.06	16363.6	1.71E-8	4.57
Pb	54.15	9.8E15	2.9E15	27.09	1.1E19	7.7E21	24.602	5.688	3292.7

The plot for both activated and non activated bamboo GAC for all the metal ions gave a good straight line. The 20% activation level has a higher rate of adsorption as compared to 0 and 10% activation level, although initial adsorption starts from the same level. In Fig. 7, the trends of Pb adsorption differ from those of Cl and PO_4.

The R^2 values are detailed on the plots in Figs. 5-6 for the pseudo second-order equation while Table 4 shows the values of q_e, K and h_o. The value of R^2 shows that the pseudo-second order model gave a better fit to the adsorption process with 0.992 as the least value for Pb adsorption at 20% activation and 1.00 as the highest for Pb adsorption at 0 and 10% activation.

The values of k and h_o for all ions adsorbed are higher for 10% as compared to 0 and 20% $ZnCl_2$ activation. This is contrary to the trend observed initially, but still corroborates the fact that activated bamboo GAC has more pore space after activation thus aiding adsorption. The non-activated bamboo GAC has a higher value of q_e for all metal ions adsorbed. This is in agreement with [16] that if the value of k is higher, adsorption rate will be greater while q_e will be lower at greater adsorption. It then means that the higher the value of q_e the lesser the adsorption rate.

3.4. Adsorption Isotherms

The most common adsorption isotherms used in describing the adsorption of wastewater contaminant and water treatment are the Langmuir and Freundlich which reflect the capacity of activated carbon in adsorbing waste [17]; it also gives the description of functional dependence of capacity on the concentration of pollutants [18]. It further shows how adsorbate reacts with adsorbents and is very important in adsorption optimization [4, 10]. The mathematical expression of Langmuir and Freundlich can be stated as

$$\frac{Ce}{qe} = \frac{1}{Q_m K_L} + \frac{Ce}{Q_m} \tag{4}$$

and

$$\log q_e = \log K_f + \frac{1}{n}(\log C_e) \tag{5}$$

respectively, where q_e is the metal ion concentration on the adsorbent at equilibrium (mg/g), C_e is the equilibrium metal ion concentration in the solution (mg/l), q_m is the monolayer adsorption capacity of the adsorbent (mg/g) and K_L is the Langmuir adsorption constant(l/mg). For the Freundlich equation, q_e is the equilibrium metal ion concentration on the adsorbent (mg/g dry weight), C_e is the equilibrium metal ion concentration in the solution (mg/L), K_f is a constant that describes the adsorption capacity of the adsorbent and n is an empirical parameter which dictates the intensity of the adsorption.

The constants Q_m and K_L in Table 5 indicate Langmuir monolayer saturation capacity and Langmuir isotherm constant, and these were obtained from the intercepts and slopes of the linear plots in Figs. 7-9. The value of the correlation coefficients R^2 for Cl and PO_4 for all bamboo GAC used is 1, indicating that the adsorbent is very good in adsorption of these metals and also a perfect order of adsorption. For Pb, the R^2 values are very low.

This shows that bamboo GAC did not optimize the adsorption of Pb. High values of Qm and K_L show that it is more favorable for the ions in question; hence greater efficiency [4,19]. The values of Qm and K_L for tested bamboo GAC in Table 5 are low, indicating unfavorable adsorption condition.

The Freundlich Isotherm gives a contrite view in adsorption process when compared with Langmuir. The adsorption process is considered favorable when the value of 1/n is between 0.1 and 1.0 [4]. If high, it indicates a larger change in effectiveness over different equilibrium concentration. If it is greater than 1.0 the change in adsorbed concentration is higher than change in solute concentration [17]. The adsorption constant K_f and1/n was obtained from the slopes and intercepts of the plots in Figs. 10-12. The1/n values for Cl, PO_4 and Pb as shown in Table 6 are between 0.1 and 0.7 with the exception of PO_4 at 10% activation level. To this end, the Freundlich isotherm is found more applicable in describing the bamboo GAC capacity in adsorption of wastewater contaminant.

Table 5 Adsorption isotherms constant for Langmuir model

Metal ion	Langmuir Constants											
	0%				10%				20%			
	Ka	Qm	K_L	R^2	Ka	Qm	K_L	R^2	Ka	Qm	K_L	R^2
Cl	349.6	0.0028	1.5E-5	1	1028	0.0032	3.9E-7	1	278.1	0.004	0.0004	1
PO_4	338.3	166.7	1.9E-8	1	146.6	0.0007	0.0005	1	97.67	0.01	0.0006	1
Pb	0.19	41.7	0.98	0.01	3.65	4.96	0.69	0.11	2.71	0.69	0.75	2E-13

Table 6 Adsorption isotherms constant for Freundlich model

Metal ion	Freundlich constants								
	0%			10%			20%		
	1/n	K_f	R^2	1/n	K_f	R^2	1/n	K_f	R^2
Cl	0.165	0.715	1E-13	0.599	2.387	2E-1	0.211	1.51	1E-1
PO_4	0.741	1.051	3E-1	0.046	1.21	1E-1	0.396	0.182	1E-1
Pb	0.412	1.445	0.41	0	1	0	0.777	2.159	2E-1

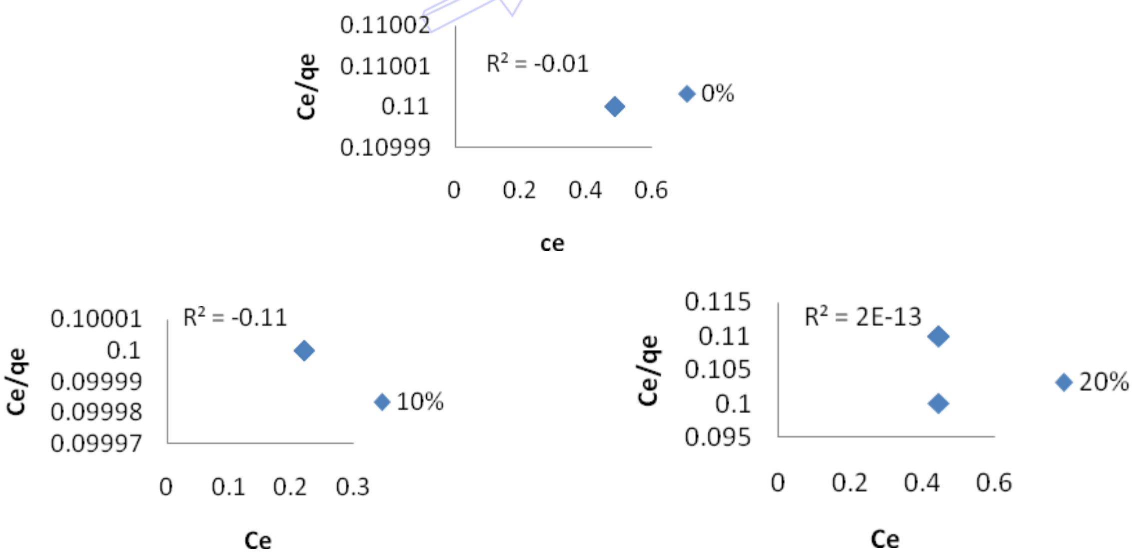


Fig. 7 Langmuir isotherms for lead on activated and non-activated bamboo GAC

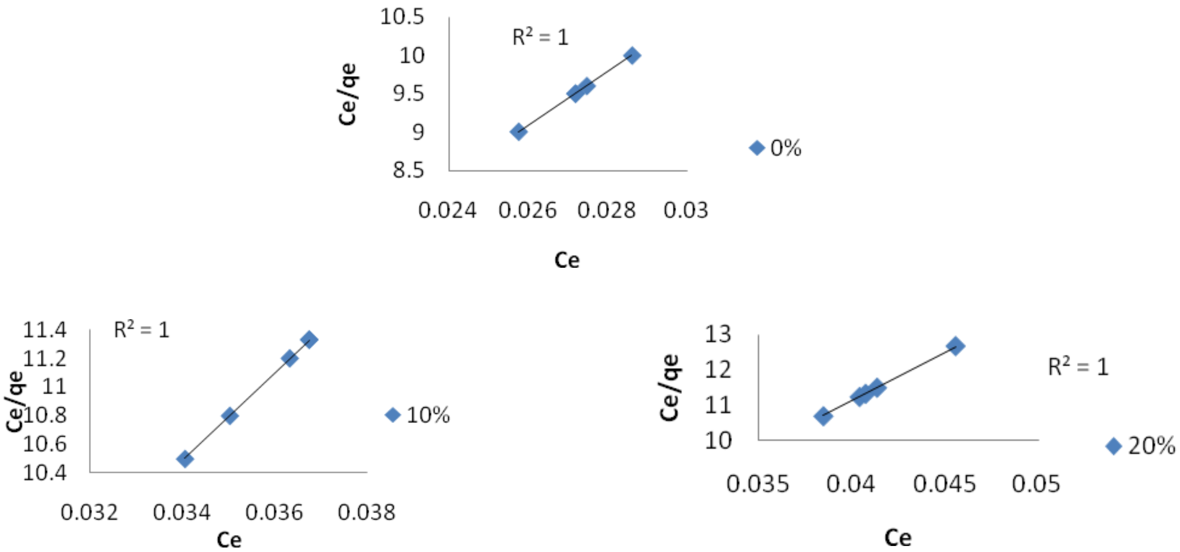


Fig. 8 Langmuir isotherms for PO_4 on activated and non-activated bamboo GAC

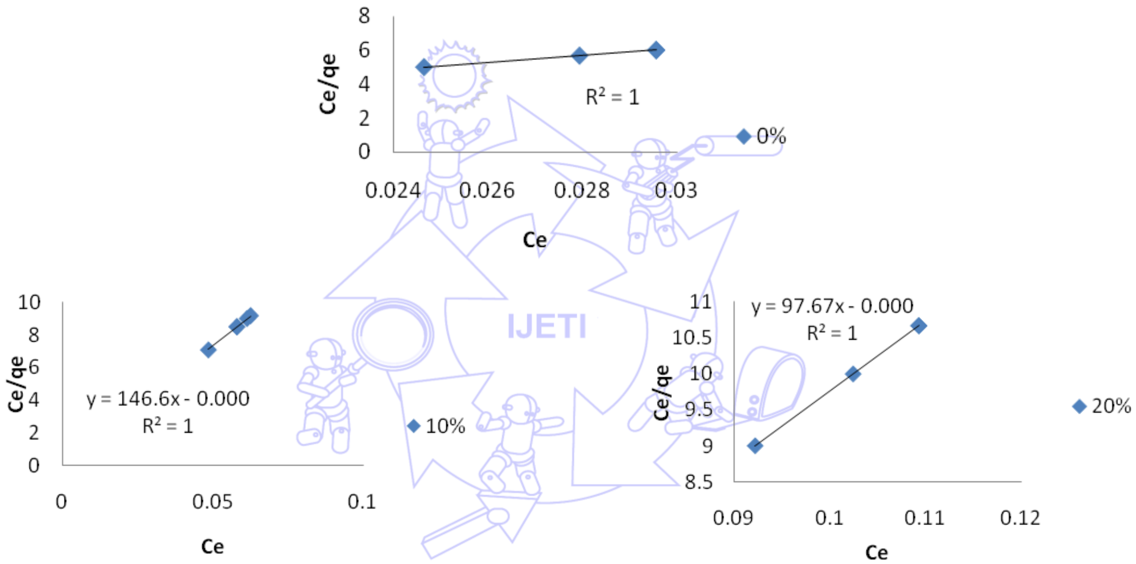


Fig. 9 Langmuir isotherms for Cl on activated and non-activated bamboo GAC

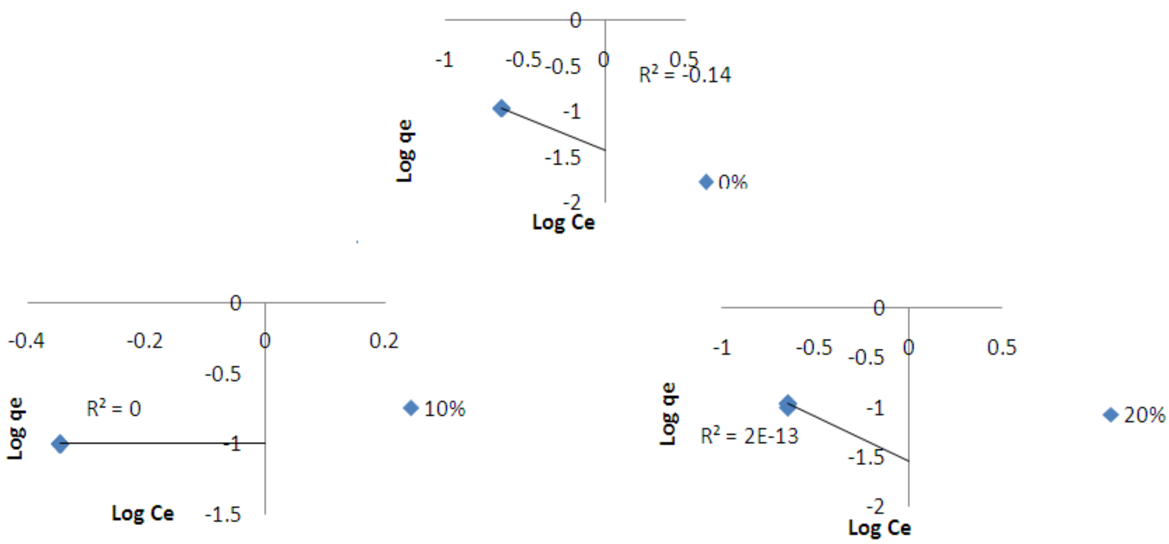


Fig. 10 Freundlich isotherms for Pb on activated and non-activated bamboo GAC

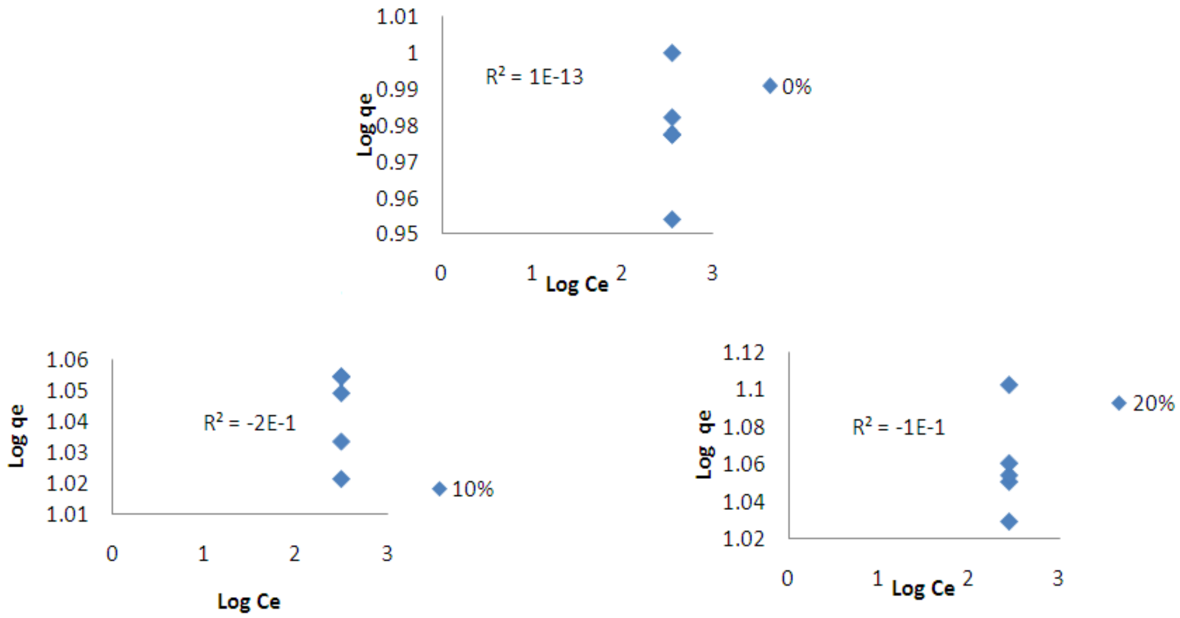


Fig. 11 Freundlich isotherms for Cl on activated and non-activated bamboo GAC

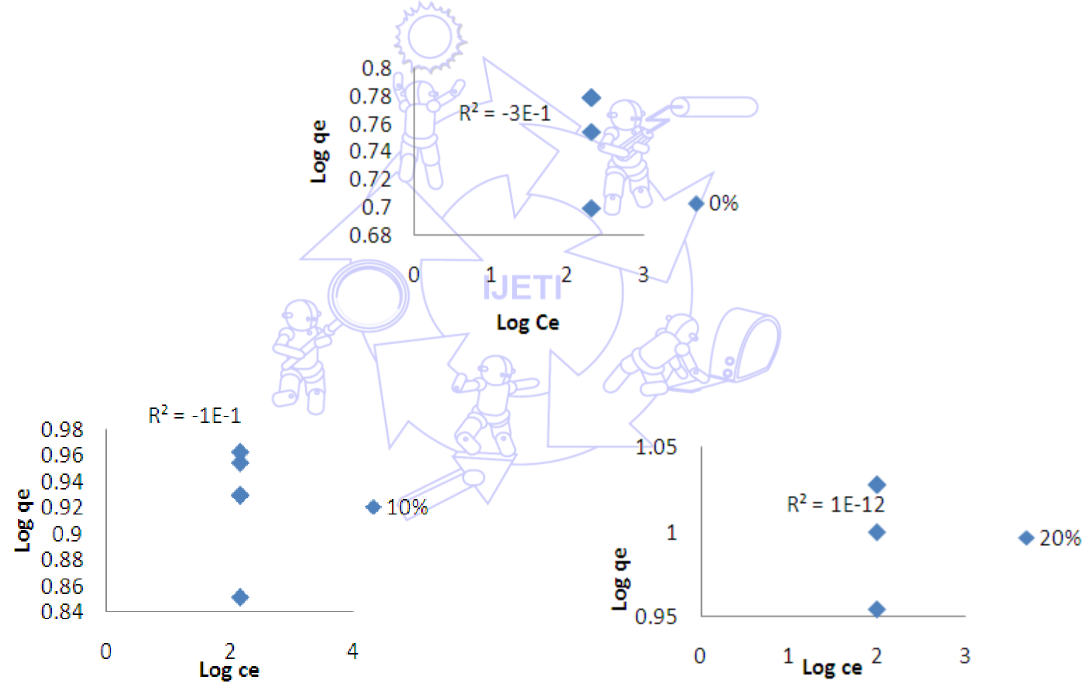


Fig. 12 Freundlich isotherms for PO_4 on activated and non-activated bamboo GAC

4. Conclusion

This study has shown that bamboo granular carbon can adsorb ions from surface water. Its adsorption performance is enhanced when activated with $ZnCl_2$ because of the enlargement of the pore space of the adsorbent. The adsorption of ions is time dependent. The 20% activation level adsorbs more ions than the 0 and 10% levels. The pseudo-second order kinetic model describes the adsorption of ions by the non-activated as well as the activated granular activated carbon. The correlation coefficient of Langmuir isotherm for Cl and PO_4 gave a perfect adsorption, but the Freundlich isotherm is more applicable in describing the bamboo GAC capacity in adsorption of wastewater contaminant.

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