



## INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY

### Removal of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup> Metals from Simulated Wastewater in Single and Competitive System Using Locally Porcelanite

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#### Abstract

The equilibrium uptake of lead (Pb<sup>2+</sup>), copper (Cu<sup>2+</sup>) and cadmium (Cd<sup>2+</sup>) ions, both singly and in combination, by locally Iraqi porcelanite rocks (PC) was studied in a batch system. The porcelanite rock was characterized using BET, and FTIR. Adsorption isotherms were developed for the single, and ternary-component systems and expressed by the mono- and multi-component Langmuir, Freundlich, Redlich–Peterson, Sips and Khan models. The model parameters were estimated by nonlinear regression method using Statistica version-6 software. To understand the action of metals uptake, factors influencing the adsorption of the heavy metals including pH, initial metal ion concentration, weight of the adsorbent, mixing speed, contact time and temperature were investigated. It was found that the mono- and multi-component adsorption equilibrium data fitted very well to the Langmuir model with high determination coefficient (R<sup>2</sup>). The maximum loading capacity (q<sub>max</sub>) was 76.104, 33.288 and 30.254 mg/g for Pb<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup> respectively. However, in ternary system the loading capacity decreased because of competition between ions to binding sites of adsorbent. Adsorption data were modeled using the pseudo-first and pseudo-second-order kinetic, Elovich and intraparticle diffusion models. It was seen that the pseudo-second-order kinetic equation could best describe the adsorption kinetics. Thermodynamic parameters showed that the adsorption of investigated heavy metals onto PC was exothermic, spontaneous in nature and the process is physisorption. The Fourier Transform Infrared spectroscopy (FTIR) analysis indicated that carbonyl (C=O) and hydroxyl (–OH) groups in PC played an important role in the adsorption process. In conclusion, PC was found suitable as an abundant adsorbent for removal of the selected metal ions from aqueous solutions.

**Keywords:** Adsorption; Porcelanite rocks (PC); Lead; Copper; Cadmium; Adsorption isotherms.

#### Introduction

Many industrial and metallurgical processes in addition to some human activities produce rapidly increasing amounts of wastewater containing heavy metals ions in appreciable concentration. At least 20 of these metal ions are classified as toxic [1]. In addition these ions are non-degradable and thus persistent, leading to both ecological and health problems even at low concentration [2]. For these reasons, the presence of heavy metal ions in the environment at concentrations above critical values is unacceptable and their removal from the wastewater is of primary importance. Removal of toxic heavy metals or decreasing their concentrations to the

permitted levels before discharge is important and is becoming more important with an increase in industrial activities [3]

There are many methods for the removal of heavy metals from aqueous solutions, such as adsorption, chemical precipitation, ion exchange, membrane processes, reverse osmosis, chemical oxidation, precipitation, etc. Adsorption is the most popular method in which activated carbon or ion exchange resins are usually applied. Activated carbon adsorption has been recommended by the USEPA as one of the best available technologies (BAT) [4] in removal of heavy metals and organic compounds, but

it is highly expensive especially for developing countries. In recent years, there has been a continuous search for locally available and cheaper adsorbents for the replacement of activated carbon for removal of a variety of heavy metals [5].

There is scope for developing adsorbents from low-cost materials. Many natural and synthetic materials are used for this purpose. Recently, natural materials have gained importance [6][7]. The choice of these materials depends on their availability, cost and adsorption capacity. Therefore, studies are now focusing on new natural adsorbents with low cost and local availability, such as Chitosan [8], bentonite [9], zeolite [10], clay minerals [11], olive mill residues [12], fly ashes [13], coal [14], rice husk [15], waste tea leaves [16], peanut hull pellets [17] and biosorbents [18].

The aim of this study was to investigate the lead, copper and cadmium adsorption using porcelanite rock sample. Iraq is one of the major countries in porcelanite production. Langmuir, Freundlich, Redlich-Peterson, Sips and Khan models were applied to describe and predict the adsorption equilibrium. Four kinetic models including pseudo-first-order, pseudo-second-order, intraparticle diffusion and Elovich models were used to determine the mechanism of adsorption. The thermodynamic parameters such as standard free energy, enthalpy and entropy were also evaluated. In addition, the effect of various parameters affecting adsorption behavior of heavy metals such as contact time, pH, adsorbent dose, initial concentration, mixing speed and temperature are considered. Furthermore, specific surface area (BET), infrared spectra (FTIR), are verified for characterization of porcelanite adsorbent.

## Materials and methods

### Adsorbent preparation

The porcelanite rocks sample used in this study is supplied by the general company for geological survey and mineralogy-ministry of industry and minerals (GCGSM). The porcelanite rocks samples was ground in a mortar and sieved into mesh 0.6, 1 mm and geometric mean diameter was taken. Then the grounded sample was washed with distilled water to remove any non-adhesive impurities and small particles and then dried at 376 K for 24 h to remove moisture.

### Characterization of prepared PC

BET surface areas of the prepared porcelanite rocks was determined from N<sub>2</sub> adsorption isotherm data collected at 77 K (Autosorb-1-MP, Quantachrome Corporation, Boynton Beach, FL, USA). Prior to analysis, adsorbent samples were outgassed for 20 h at 423 K. The apparent density is determined using Hg picnometry analysis (Autotap, Quantachrome, USA). Micropore volume and mesopore volume were computed from N<sub>2</sub> adsorption isotherm data using the Density Functional Theory (DFT) with the N<sub>2</sub>\_carb1.gai kernel (PC software version 1.51, Quantachrome, Boynton Beach, FL). In addition, the mesopore volume was computed using the Barrett, Joyner, and Halenda (BJH) method because this method captures the entire mesopore range (20–500 Å) while the DFT method was only able to calculate a mesopore volume for pores with widths in the range of 20–360 Å. A more detailed description of the procedures used for adsorbent characterization is given elsewhere [19]. Chemical and Physical analyses of the PC are summarized in Table 1. Fourier Transform Infrared Spectroscopy (FTIR, Nicolet 6700, USA) was employed to determine the type of functional groups present on adsorbent's surface before and after adsorption.

**Table 1. General Characteristics of prepared porcelanite rocks adsorbent.**

Parameter	Value
Average particle diameter, mm	0.775
Bulk density, Kg m <sup>-3</sup>	816
BET Surface area, m <sup>2</sup> g <sup>-1</sup>	71.92
Particle porosity	0.532
Elemental Analysis	Weighted average, %
P <sub>2</sub> O <sub>5</sub>	1.98
CaO	10.75
MgO	2.1
TiO <sub>2</sub>	0.1
SiO <sub>2</sub>	70.4
Fe <sub>2</sub> O <sub>3</sub>	0.79
Na <sub>2</sub> O	2.59
K <sub>2</sub> O	0.12
Al <sub>2</sub> O <sub>3</sub>	1.75
Loss of ignition	9.42

### Batch adsorption studies

The aqueous solutions of metal ions used in the present investigation were prepared by using analytical grade chemicals. Individual stock metal ion solutions of 1000 mg/L concentration of Pb<sup>+2</sup> from Pb(NO<sub>3</sub>)<sub>2</sub>, Cu<sup>2+</sup> from CuSO<sub>4</sub>.5H<sub>2</sub>O and Cd<sup>2+</sup> from Cd(NO<sub>3</sub>)<sub>2</sub> respectively were prepared. In the case of

$Cd^{+2}$ , nitrate is used instead of sulphate to avoid metal precipitation, though the effect of the anion was negligible. These stock solutions were used to prepare dilute solutions of these ions by dilution with distilled water. The stock solutions were acidified to  $4 < pH < 6$  using concentrated  $HNO_3$  in order to prevent the formation of metal hydroxide and to return the metal ion to the dissolve state [20].

Batch experiments for optimization of process parameters were carried out in 250 ml round bottom flasks with working volume of 100 ml at 125 rpm in an incubator cum orbital shaker (Heidolph, No.549-59000-0-0, Germany). All the experiments were carried out in triplicates and average results were used. The range of various process parameters was varied as pH: 1-6, adsorbent mass: 0.1-1.4 g, contact time: 0- 360 min, initial concentration: 25-100 mg/L, and temperature:  $10^\circ C$ - $60^\circ C$ .

### Metal analysis

The concentration of remaining  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Cd^{2+}$  in solution after adsorption was determined as follow: Samples (40 ml) were transferred into a micro centrifuge tube and centrifuged at 3000 rpm for 5 minutes, to remove suspended materials in the samples. Supernatant (10 ml) was transferred to 100 ml volumetric flask and acidified with 90 ml of 10% nitric acid ( $HNO_3$ ) to get a standard solution of 100ml. These samples were stored in a freezer to terminate the reaction until measurement [12]. These samples were analyzed using Atomic absorption Spectrophotometer (AAS, Buck, Accusys 211, USA). The capacity uptake  $q_{eq}$ , adsorbed amount adsorbate onto unit weight of adsorbent, and removal percentage ( $E_r$ , %) were calculated, respectively, using the following equations:

$$q_{eq} = \frac{V_L(C_o - C_{eq})}{M} \quad (1)$$

$$E_r = \frac{C_o - C_{eq}}{C_o} \times 100 \quad (2)$$

Where  $C_o$  and  $C_{eq}$  is the initial and final equilibrium concentration of the metal ion respectively (mg/L),  $V_L$  the volume of solution (L) and  $M$  is the adsorbent mass (g).

### Adsorption isotherm

#### Single component isotherm models

Five models for single system have been tested: Langmuir model, Freundlich model,

Redlich–Peterson model, Sips model and Khan Model [21]:

$$\text{Langmuir model: } q_{eq} = \frac{q_{max} b C_{eq}}{1 + b C_{eq}} \quad (3)$$

Where  $q_{eq}$  is the amount of pollutant bound to per g of PC at equilibrium (mg/g) and  $C_{eq}$  is the residual (equilibrium) pollutant concentration left in solution after binding (mg/L).  $q_{max}$  is the maximum amount (maximum loading capacity) of pollutant per unit weight of adsorbent to form a complete monolayer on the surface bound at high  $C_{eq}$ (mg/g), and  $b$  (L/mg) is a constant related to the affinity of the binding sites.

$$\text{Freundlich model: } q_{eq} = k_F C_{eq}^{1/n} \quad (4)$$

Where  $K_F$ (mg/g)(L/mg) $^{1/n}$  and  $n$  are the mono-component Freundlich constants characteristic of the system.

$$\text{Redlich–Peterson model: } q_{eq} = \frac{K_{RP} C_{eq}}{1 + a_{RP} C_{eq}^\beta} \quad (5)$$

Where  $K_{RP}$ (mg/gL/mg),  $a_{RP}$  (L/mg) $^\beta$  and  $\beta$  are the Redlich–Peterson parameters.

Sips model (Combination of Langmuir-Freundlich Model) :

$$q_e = \frac{b q_m C_{eq}^{1/n}}{1 + b C_{eq}^{1/n}} \quad (6)$$

where  $b$  (L/mg) is a constant related to the affinity of the binding sites and  $n$  are the mono-component Freundlich constants characteristic of the system

$$\text{Khan model: } q_e = \frac{Q_{max} b_k C_e}{(1 + b_k C_e)^{a_k}} \quad (7)$$

Where,  $Q_{max}$  (mg/g),  $b_k$  (l/mg) and  $a_k$  represent the model parameters.

#### Multicomponent isotherm models

One of the difficulties in describing the adsorption of pollutants from waste streams is that wastewaters contain not one, but many kinds of pollutants. When several components are present, interference and competition phenomena for adsorption sites occur and lead to a more complex mathematical formulation of the equilibrium. Therefore, competitive isotherms attempt to express relationships between the adsorbed quantity of one component and the concentrations of all other components, either in solution or already adsorbed. Several isotherms have been proposed to describe equilibrium and competitive adsorption for such a system. The long and tedious experimental method

for obtaining competitive adsorption data has rapidly given rise to the idea of predicting multi-component isotherms from the single component ones only and competitive non-modified adsorption models were developed:

$$\text{Extended Langmuir model: } q_{e,i} = \frac{q_i \max b_i C_{eqi}}{1 + \sum_{j=1}^N b_j C_{eqj}} \quad (8)$$

Where  $C_{eqi}$  and  $q_{eqi}$  are the unadsorbed concentration of each component in the mixture at equilibrium and the adsorbed quantity of each component per g of adsorbent at equilibrium, respectively,  $b_i$  and  $q_{i\max}$  are derived from the corresponding individual Langmuir isotherm equations [22].

Extended Freundlich model:

$$q_{eqi} = \frac{K_{Fi} C_{eqi}^{n_i+n_1}}{C_{eqi}^{n_1} + \sum_{j=1}^N b_j C_{eqj}^{n_j}} \quad (9)$$

Where  $C_{eqi}$  and  $q_{eqi}$  are the unadsorbed concentration of each component in the mixture at equilibrium and the adsorbed quantity of each component per g of adsorbent at equilibrium, respectively,  $K_{Fi}$  and  $n_i$  are derived from the corresponding individual Freundlich isotherm equations [22].

Redlich-Peterson model:

$$q_{eqi} = \frac{K_{RPi} C_{eqi}}{1 + \sum_{j=1}^N a_{RPj} (C_{eqj})^{\beta_j}} \quad (10)$$

Where  $K_{RPi}$ ,  $a_{RPj}$  and  $b_i$  are the Redlich-Peterson parameters derived from the corresponding individual Redlich-Peterson isotherm equations (Aksu and Akpinar, 2000).

Combination of Langmuir and Freundlich model:

The competitive Langmuir-Freundlich model related to the individual isotherm parameters is expressed in the following equation [23].

$$q_{e,i} = \frac{q_{m,i} b_i C_{e,i}^{1/n_i}}{1 + \sum_{i=1}^N b_i C_{e,i}^{1/n_i}} \quad (11)$$

### Study of adsorption kinetics

Kinetic studies of adsorption for  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Cd^{2+}$  onto porcelanite rocks were carried out at the initial concentration of 50 mg/L (in 250 mL flask during shaking at 250 rpm) for contact times in the

range of 30 to 360 min. For understanding the mechanism of adsorption process and determining the rate of dominating step, the adsorption data were analyzed using four simplest kinetic models such as pseudofirst-order, pseudo-second-order, Elovich and intraparticle diffusion model [24][25]:

Pseudo-First Order:

$$\log(q_{eq} - q_t) = \log q_{eq} - \left(\frac{k_L t}{2.303}\right) \quad (12)$$

where  $q_{eq}$  is the amount of  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Cd^{2+}$  adsorbed at equilibrium (mg/g);  $q_t$  is the amount of  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Cd^{2+}$  adsorbed at time  $t$  (mg/g); and  $k_L$  is the equilibrium rate constant of pseudo-first sorption ( $\text{min}^{-1}$ ).

$$\text{Pseudo-Second Order: } \frac{t}{q_t} = \frac{1}{k_s q_{eq}^2} + \frac{t}{q_{eq}} \quad (13)$$

Where  $K_s$  (g/mg.min) is the rate constant of adsorption.

$$\text{Intraparticle diffusion model: } q_t = k_{id} t^{1/2} + C \quad (14)$$

Where  $K_{id}$  ( $\text{mg/g min}^{1/2}$ ) is the rate constant of intraparticle diffusion,  $C$  is the value of intercept which gives an idea about the boundary layer thickness, that is, the larger intercept; the greater is the boundary layer effect.

$$\text{Elovich kinetics model: } q_t = \frac{1}{b} \ln ab + \frac{1}{b} \ln t \quad (15)$$

Where  $a$  and  $b$  parameter related to equation.

### Adsorption thermodynamics

Based on fundamental thermodynamic concepts, it is assumed that in an isolated system, energy cannot be gained or lost and the entropy change is the only driving force. The apparent equilibrium constant for the process has been shown to be [26]:

$$\Delta G^0 = -RT \ln K_c \quad (16)$$

$$K_c = \frac{C_o - C_{eq}}{C_{eq}} \quad (17)$$

Also, enthalpy changes ( $\Delta H^0$ ) and entropy changes ( $\Delta S^0$ ) can be estimated by the following equation:

$$\Delta G^0 = \Delta H^0 - \Delta S^0 T \quad (18)$$

where  $\Delta G^0$  is standard Gibbs free energy change in kJ/mol;  $\Delta H^0$  is change in enthalpy (heat of adsorption, kJ/mole),  $\Delta S^0$  is change in entropy in kJ/mol,  $R$  is the universal gas constant ( $=0.8314$  kJ/mol.K) and  $T$  is the temperature in K.

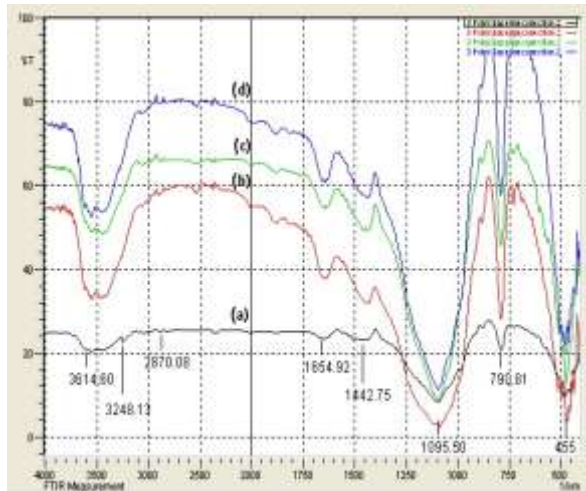


## Results and Discussion

### Characterization of the adsorbent

In order to find out which functions are responsible for  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Cd^{2+}$  adsorption, FTIR analysis of PC was carried out. Figure 1 show the spectra of raw and treated PC samples. The sharp bands near 455 define the Si-OH stretches. The peak at 790.81  $cm^{-1}$  is associated with the PH group. The band at 1095.50  $cm^{-1}$  is Si-O-Si and those at 1442.75 and 1654.92 are C=O groups. The sharp peaks at 2870.08, 3248.13 and 3614.60 are the O-H stretch [27]. Peak displacement decreasing define the change in the structure with  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Cd^{2+}$  imply the related functional groups to be responsible for the adsorption process. From these findings, it can be concluded that lead adsorbed more strongly than copper and cadmium respectively. Table 2 shows the main functional groups before and after PC was loaded with  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Cd^{2+}$  ions. The results show that the bands of hydroxyl and carbonyl groups shifted to higher transmission (peaks of adsorption) and therefore it plays the major role in adsorption of these ions. The bands of functional groups shifted to higher transmission with a total amount of 266.5, 201, and 108.5% for PC loaded with  $Pb^{2+}$ ,  $Cu^{2+}$ , and  $Cd^{2+}$ , respectively. Therefore, the order of adsorption of heavy metals removed by on the surface of PC is the following:  $Pb^{2+} > Cu^{2+} > Cd^{2+}$ .

**Figure 1:** FTIR analysis (a) raw PC (b)  $Cd^{2+}$  loaded PC (c)  $Cu^{2+}$  loaded PC (d)  $Pb^{2+}$  loaded PC



**Table 2:** Functional groups before and after PC was loaded with  $Pb^{2+}$ ,  $Cu^{2+}$ , and  $Cd^{2+}$  ions in the single system

Wave Number, $cm^{-1}$	Type of bond	Functional group	Difference in peaks adsorption(%)		
			$Pb^{2+}$	$Cu^{2+}$	$Cd^{2+}$
3614.60	-OH	Hydroxyl group	33	29.5	14
3248.13	-OH	Hydroxyl group	43	35	21
2870.08	-OH	Hydroxyl group	56.5	38.6	33.6
1654.92	C=O	carbonyl groups	37.5	31	14
1442.75	C=O	carbonyl groups	35.5	25.5	8.5
1095.5	Si-O-Si	Siloxane groups	9	6	6
790.81	-PH	Phosphine groups	36	24	6
455	Si-OH	Silanol groups	16	7	5
Sum of differences in peaks adsorption %, after-before adsorption =			266.5 %	201 %	108.5 %

### Effect of pH

The influence of pH on the removal efficiency for the different metals is shown in Figure 2. Experiments concerning the effect of pH on the adsorption were carried out in the range of pH not influenced by the metal precipitation as metal hydroxide which is occurs at pH above 6 [28]. At very low pH (1-3), metal uptake was less and this is due to the fact that adsorbent surface protonate and the adsorbent surface become positively charge and access of metal ions to adsorbent surface would be restricted as a result of repulsive forces. Metal uptake increased with pH around 4. At this pH, functional groups onto adsorbent surface deprotonate and the adsorbent surface becomes negatively charged (i.e., increasing of  $OH^-$  groups), so in this region of pH metal ions can favorably be attracted onto the adsorbent [29]. Further, increasing the pH causes decreasing of negatively sites and thus reduce removal efficiency [30].

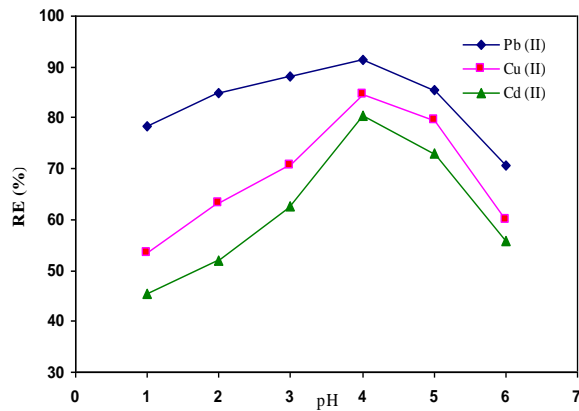


Figure 2: Effect of pH on the adsorption of metal ions onto PC at  $C_o=50\text{ mg/L}$ , agitation speed=200 rpm, contact time = 4 h, adsorbent dose=0.5 g/100mL and temperature= 30 °C

**Effect of agitation speed**

The effect of the agitation speed on the removal efficiency of all the metal ions using PC is shown in Figure 3. The efficiency values increase from: 56.866 to 93.453% for Lead, 38.706 to 90.152% for Copper and 34.472 to 83.136 for Cadmium respectively. It can be clearly seen that mixing speed increases the removal efficiency until it reaches a certain value and further increase is then of no benefit (i.e., above 250 rpm). The increase in efficiency is due to the increase in turbulence and as a consequence, the decrease in the external mass transfer resistance thickness around the adsorbent particles with increase in mixing speed [31]. Moreover these results clearly indicate that a mixing speed of 250 rpm is sufficient to obtain maximum removal efficiency by reducing the boundary layer thickness to a minimum value.

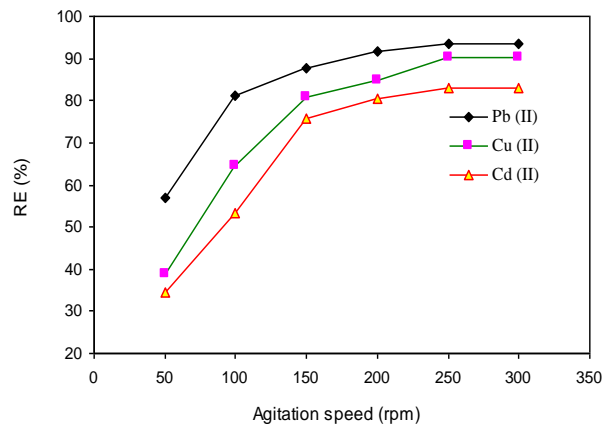


Figure 3: Effect of agitation speed on the adsorption of heavy

metal onto PC at  $C_o=50\text{ mg/L}$ , pH= 4, contact time = 4 h, adsorbent dose=0.5 g/100mL and temperature= 30 °C.

**Effect of adsorbent Mass**

The effect of varying the adsorbent dose (mass) on the adsorption of various metal ions is shown in Figure 4. It is clearly seen that the removal efficiency increases as the PC mass increases. As the PC mass increases the number of binding sites for the ions also increases. After some point, adsorption capacity was steady due to a screen effect between adsorbent, this produced a block of the adsorbent active sites by an increase of adsorbate (heavy metal ions) in the system [32]. Similar observations were also made by other investigators [20] [33]. Removal efficiency increases for Lead from: 66 to 97%, 42.222 to 95.514% for Copper and 32 to 90.758% for Cadmium. Thus in next experiments, the optimum dosage was fixed at 0.7, 1.2 and 1.3 for  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Cd^{2+}$  respectively.

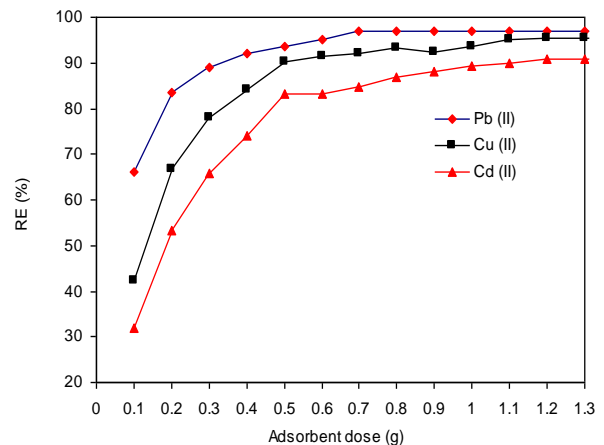


Figure 4: Effect of adsorbent dose on the adsorption of heavy metals onto PC at  $C_o=50\text{ mg/L}$ , pH= 4, contact time = 4 h, agitation speed=250 rpm and temperature = 30 °C.

**Effect of contact time and adsorption kinetics**

Contact time plays an important role in the efficient removal of heavy metals using PC. Therefore, the adsorption of  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Cd^{2+}$  at constant temperature, initial concentration, optimum agitation speed, optimum adsorbent dose and optimum pH was studied as a function of contact time to determine the equilibrium time. The influence of contact time on the adsorption capacity for different metal ions is shown in Figure 5. Removal efficiency increases for lead from 0 to 98.347%, for copper from 0 to 96.333% and cadmium from 0 to 94.374% as the contact time increases from 0 to 360 min. The results clearly revealed that rate of

adsorption is higher at the beginning and this is due to availability of a large number of active sites on the adsorbent. As these sites are exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles [34]. Maximum removals were attained within the first 240 min of stirring time. There must not be seemed to be much benefit after 300 min. Therefore the equilibrium time was set to be 300min in further experiments.

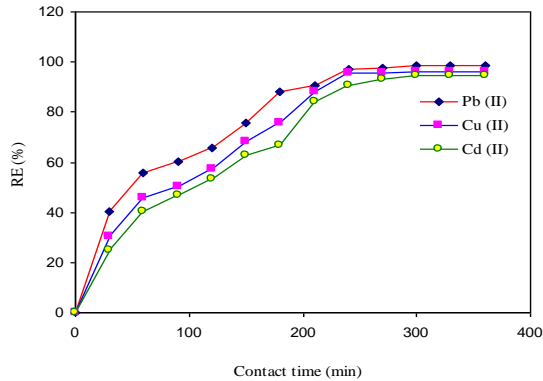


Figure 5: Effect of contact time on the adsorption of heavy metals onto PC at  $C_0= 50 \text{ mg/L}$ ,  $\text{pH}= 4$ , optimum adsorbent dose, agitation speed=250 rpm and temperature= 30 °C

The effect of contact time on adsorption kinetics had been studied with initial concentration of 50 mg/L at 303K, pH 4, adsorbent mass 0.5 g. Adsorption kinetics was modeled by the pseudo first-order Lagergren, pseudo second-order rate equation, intraparticle diffusion equations, and elovich model. Table 3 demonstrates the results of these models. The rate of adsorption on PC observed to follow the second-order rate law derived by Lagergren Eq. (13). Fig. 6 shows the Lagergren plot of  $t/q_t$  vs. time (min) for the three metal ions. The calculated values of  $k_s$  for each solute were found to be 0.003, 0.005, and 0.004 (g/mg.min) for  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Cd}^{2+}$  ions, respectively. This indicates that the rate of mass transfer of  $\text{Cu}^{2+}$  is higher than the other components. In other words,  $\text{Cu}^{2+}$  is adsorbed by the PC at a higher rate than others. However, the value of constant (C) in the intraparticle diffusion model is not equal to zero, suggesting that adsorption proceeds from boundary layers mass transfer across the interfaces to the intraparticle diffusion within the pores of adsorbent. This indicates the mechanisms of  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  adsorption are complex and both the surface adsorption and intraparticle diffusion contribute to the rate-determining step [35].

Table 3 Kinetic models parameters for  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  ions adsorption onto PC.

Model	Parameters	$\text{Pb}^{2+}$	$\text{Cu}^{2+}$	$\text{Cd}^{2+}$
Pseudo-first-order	$q_{eq}$ (mg/g)	33.014	20.869	29.635
	$K_L$ (L/min)	0.030	0.030	0.033
	$R^2$	0.826	0.816	0.739
Pseudo-second-order	$q_{eq}$ (mg/g)	7.758	4.484	4.151
	$K_s$ (g/mg.min)	0.003	0.005	0.004
	$R^2$	0.986	0.978	0.973
Intraparticle diffusion	C	1.864	0.511	0.194
	$K_{id}$ (mg/g.min <sup>0.5</sup> )	0.358	0.208	0.194
	$R^2$	0.934	0.949	0.969
Elovich	A (mg/g.min)	0.88	0.458	0.047
	$b$ (g/mg)	0.784	1.363	1.502
	$R^2$	0.972	0.959	0.935

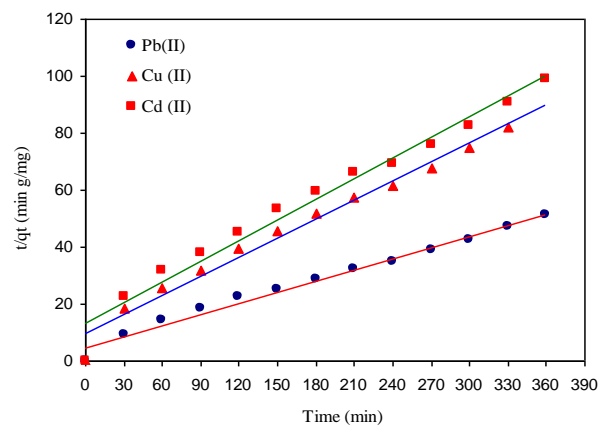
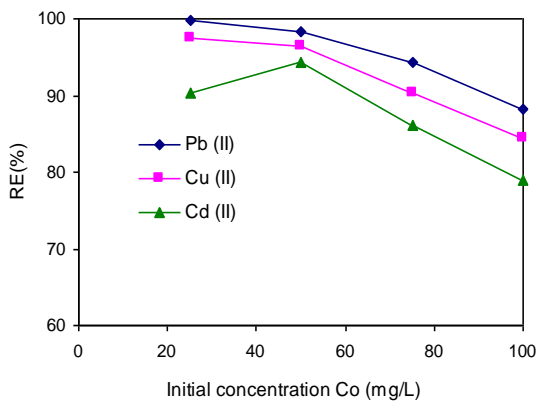


Figure 6: Pseudo-second order model for adsorption of metal ions onto PC.

**Effect of initial metal ion concentration**

The experiment was performed at distinct initial  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  concentrations ranging from 25 to 100 mg/L. As shown in Figure 7, the efficiency values decreases from: 99.8 to 88.236%

for lead, 97.576 to 84.457% for copper and 90.276 to 79.013% for cadmium respectively as the initial concentration increased from 25 to 100 mg/L. This is due to the lack of binding sites in the PC sample for the adsorption of metal ions at higher concentrations. The effect of initial metal concentration could be explained as follow: at low metal ion/adsorbent ratio, metal ion adsorption involves higher energy binding sites. As the metal ion/adsorbent ratio increase (i.e., at higher initial concentration), the higher energy binding sites are saturated and adsorption begins on lower energy binding sites, resulting in decrease in the adsorption efficiency [32].



**Figure 7: Effect of initial concentration on the adsorption of heavy metals onto PC at pH= 4, agitation speed=250 rpm, optimum adsorbent dose, contact time = 5h and temperature= 30 °C**

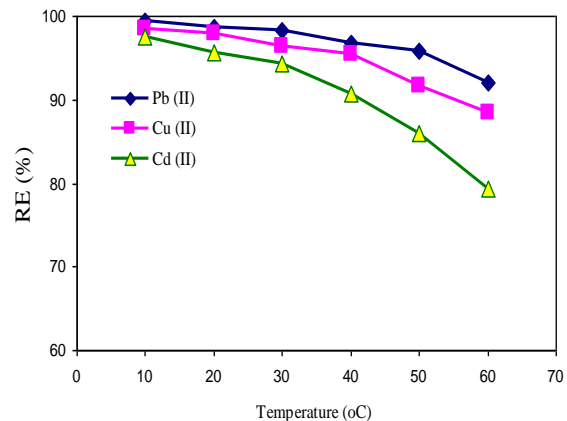
### Effect of temperature and adsorption thermodynamics

The temperature has two major effects on the adsorption process. Increasing the temperature will increase the rate of adsorbate diffusion across the external boundary layer and in the internal pores of the adsorbent particles because liquid viscosity decreases as temperature increases. In addition, temperature affects the equilibrium capacity of the adsorbent depending on whether the interaction between the adsorbent and the adsorbate is exothermic or endothermic [31]. Figure 8 shows the adsorption efficiency of  $Pb^{2+}$ ,  $Cu^{+2}$  and  $Cd^{+2}$  ions onto PC at six different temperatures of 10, 20, 30, 40, 50 and 60 °C. It can be seen that as the temperature increases, the adsorption capacity of Lead, copper and Cadmium all decrease drastically. For instance, for an initial concentration is 50 mg/L the adsorption efficiency of the adsorbent decreases from 99.338 to 92.968 %, 98.49 to 88.398% and from 97.536 to 79.316% for Lead, Copper and cadmium ions

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respectively as the temperature increase from 10 to 60 °C. As a whole, it is clearly seen that as the temperature increases the loading capacity for the same initial adsorbate concentration decreases. This means that the rate of desorption was more significant than the rate of adsorption, which implies that adsorption is an exothermic reaction, a well-known scientific fact [36].

Table 4 shows the thermodynamic constants of adsorption for  $Pb^{2+}$ ,  $Cu^{+2}$  and  $Cd^{+2}$  onto PC. The value of enthalpy  $\Delta H^\circ$  was  $-38.844$ ,  $-34.768$ , and  $-36.131$  kJ/mol for  $Pb^{2+}$ ,  $Cu^{+2}$  and  $Cd^{+2}$  ions, respectively, suggested the physisorption and exothermic nature of adsorption. This is also supported by the decrease in the values of uptake capacity of adsorbent with the rise in temperature [37]. The values of entropy  $\Delta S^\circ$ ,  $-0.0954$ ,  $-0.0872$ , and  $-0.0968$  /mol K, reflect the affinity of  $Pb^{2+}$ ,  $Cu^{+2}$  and  $Cd^{+2}$  ions to be adsorbed onto PC. The negative values of  $\Delta G^\circ$  confirm the feasibility of the process and the spontaneous nature of adsorption [38].



**Figure 8: Effect of temperature on the adsorption of heavy metals onto PC at  $C_0= 50$  mg/L, pH= 4, agitation speed=250 rpm, optimum adsorbent dose, contact time = 5h**



Table 4 Thermodynamic parameters for the adsorption of  $Pb^{2+}$ ,  $Cu^{+2}$  and  $Cd^{+2}$  onto PC.

Metal	Temperature (K)	$-\Delta G^\circ$ (kJ.mol <sup>-1</sup> )	$-\Delta H^\circ$ (kJ.mol <sup>-1</sup> )	$-\Delta S^\circ$ (J.mol <sup>-1</sup> K <sup>-1</sup> )	R <sup>2</sup>
$Pb^{2+}$	383	11.790	38.844	0.0954	0.974
	393	10.652			
	303	10.293			
	313	8.928			
	323	8.379			
$Cu^{2+}$	383	9.828	34.768	0.0872	0.975
	393	9.485			
	303	8.234			
	313	7.875			
	323	6.447			
$Cd^{2+}$	383	8.655	36.131	0.0968	0.989
	393	7.549			
	303	7.104			
	313	5.911			
	323	4.869			
	333	3.721			

Adsorption isotherm models

Adsorption isotherms constants for single component systems

The parameters for each model for single component system were estimated by nonlinear regression using STATISTICA version-6 software. All parameters with the square of the correlation coefficient (R<sup>2</sup>) are summarized in Tables 5. The adsorption isotherms for single component system of  $Pb^{2+}$ ,  $Cu^{+2}$  and  $Cd^{+2}$  onto PC are shown in Figure 9, 10, 11.

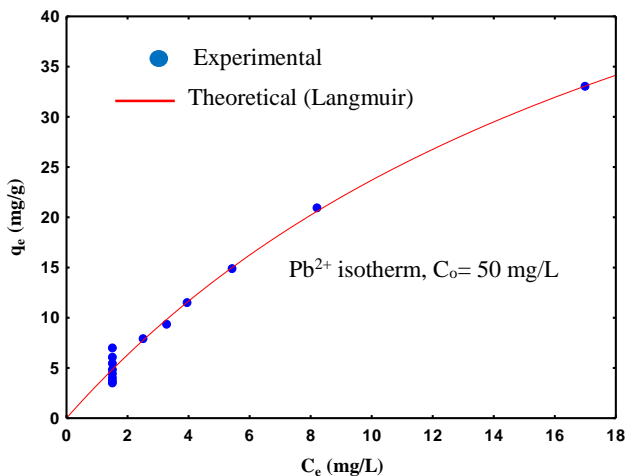


Figure 9: Adsorption isotherm for lead onto PC

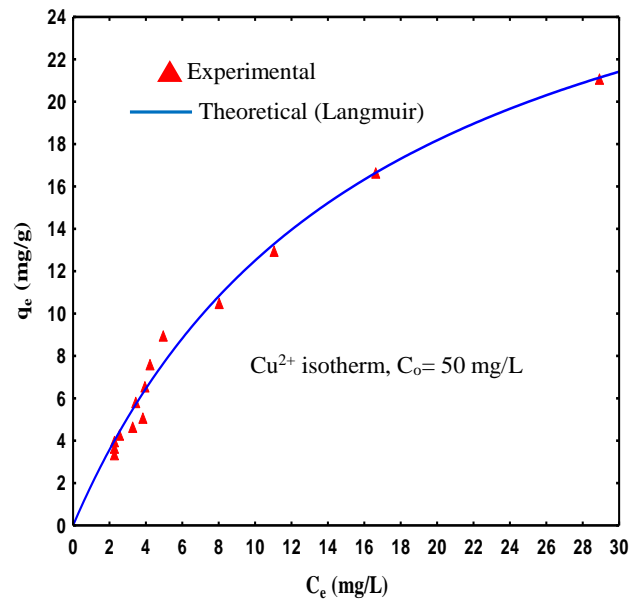


Figure 10: Adsorption isotherm for copper onto PC

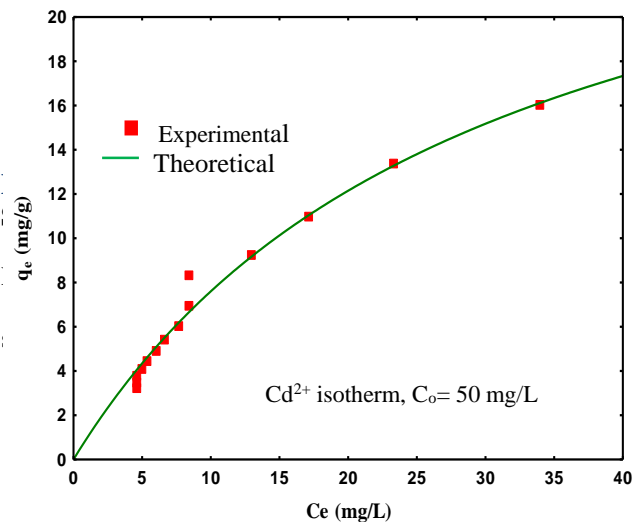


Figure 11: Adsorption isotherm for cadmium onto PC

**Table 5 Parameters of single solute isotherm for metal ions onto PC**

Model	Parameters	Pb <sup>2+</sup>	Cu <sup>2+</sup>	Cd <sup>2+</sup>
Freundlich	K <sub>f</sub> (mg/g)(L/mg) <sup>(1/n)</sup>	3.851	2.729	1.511
	n	1.304	1.604	1.464
	R <sup>2</sup>	0.991	0.985	0.982
Langmuir	q <sub>m</sub> (mg/g)	76.104	33.288	30.254
	b(L/mg)	0.045	0.060	0.034
	R <sup>2</sup>	0.994	0.993	0.992
	R <sub>L</sub>	0.307	0.249	0.373
Redlich–Peterson	K <sub>RP</sub> (mg/g L/mg)	0.098	1.962	0.029
	a <sub>RP</sub> (L/mg) <sup>mR</sup>	-0.976	0.052	-0.989
	β	-0.009	1.037	-0.014
	R <sup>2</sup>	0.989	0.990	0.975
Combination of Langmuir-Freundlich	q <sub>m</sub> (mg/g)	75.026	30.996	21.498
	b (L/mg) <sup>1/n</sup>	0.046	0.061	0.030
	n	0.995	0.951	0.7852
	R <sup>2</sup>	0.993	0.991	0.990
Khan	Q <sub>max</sub> (mg/g)	40.285	31.790	28.921
	b <sub>k</sub> (L/mg)	0.088	0.063	0.035
	a <sub>k</sub>	0.653	0.973	0.969
	R <sup>2</sup>	0.993	0.992	0.989

From Figure 9, 10, 11 and Table 5 for single component systems, the following conclusions can be drawn:

1. The Langmuir model gives the best fit for the experimental data for single, binary and ternary component adsorption system for lead, copper and cadmium ions recognized by the highest values of (R<sup>2</sup>). This indicates that the adsorption process occurs as a mono layer.
2. The equilibrium isotherm for each component is of favorable type (i.e., 0 < R<sub>L</sub> < 1). R<sub>LPb<sup>2+</sup></sub> = 0.307, R<sub>LCu<sup>2+</sup></sub> = 0.249 and R<sub>LCd<sup>2+</sup></sub> = 0.373.
3. The adsorption capacity (q<sub>m</sub>) for lead is greater than copper and cadmium in single system, Pb<sup>2+</sup> (q<sub>m</sub>) 76.104 mg/g > Cu<sup>2+</sup> (q<sub>m</sub>) 33.288 mg/g > Cd<sup>2+</sup> (q<sub>m</sub>) 30.254 mg/g. This behavior may be attributed to several reasons from which the hydrated ionic radius Å. The ions with hydrated radius smaller than the pore size are able to move easily within the pores. The hydrated ionic

radius are as follow: Pb<sup>2+</sup> (4.01 Å) < Cu<sup>2+</sup> (4.19 Å) < Cd<sup>2+</sup> (4.26 Å). In addition, the molar mass is as follow: Pb(NO<sub>3</sub>)<sub>2</sub> 331.2 g·mol<sup>-1</sup> > CuSO<sub>4</sub>·5H<sub>2</sub>O 249.69 g·mol<sup>-1</sup> > Cd(NO<sub>3</sub>)<sub>2</sub> 236.42 g·mol<sup>-1</sup>.

A comparison of the maximum adsorption capacity (q<sub>max</sub>) of the PC sample with that of some other adsorbents reported in the literature is given in Table 6.

**Table 6 Adsorption capacities (q<sub>max</sub>, mg/g) for metal ions of various adsorbents**

Adsorbent	Pb <sup>2+</sup> q <sub>m</sub> (mg/g)	Cu <sup>2+</sup> q <sub>m</sub> (mg/g)	Cd <sup>2+</sup> q <sub>m</sub> (mg/g)	References
Kaolinite	1.14			[39]
Sand	0.169	0.144		[40]
Dried activated sludge		80.6	69.2	[32]
Crab shell		243.9		[41]
Natural zeolite			5.17	[42]
Rice husk	58.1		16.7	[43]
Activated carbon	52.21			[44]
modified diatomite		8.00	2.32	[45]
Phosphate rock		1.814		[46]
Cement Kiln Dust	2.445			[47]
PC	76.104	33.288	30.254	Present study

#### Adsorption isotherms constants for ternary component systems

The adsorption isotherms for ternary component systems of pb<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup> onto PC are shown in Figure 12, whereas Table 7 represents the parameters of each used model and the square of the correlation coefficient (R<sup>2</sup>) are also shown in this Table.

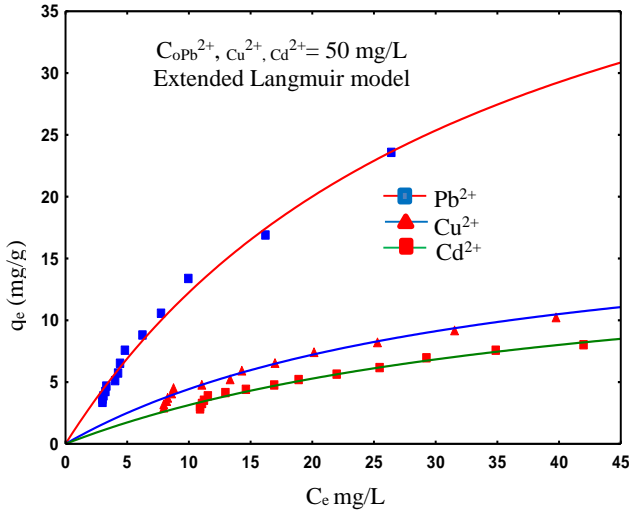


Figure 12: Adsorption isotherms of (Pb<sup>2+</sup> + Cu<sup>2+</sup> + Cd<sup>2+</sup>) in ternary system onto PC

Table 7: Parameters of ternary systems solutes isotherms for Pb<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup> ions onto PC.

Ternary system				
Model	Parameter s	Pb <sup>2+</sup>	Cu <sup>2+</sup>	Cd <sup>2+</sup>
Extended Langmuir	q <sub>m</sub> (mg/g)	54.519	19.300	16.583
	b (L/mg)	0.053	0.045	0.038
	R <sup>2</sup>	0.994	0.990	0.989
	R <sub>L</sub>	0.272	0.309	0.347
Extended Freundlich	K <sub>F</sub> , (mg/g)(L/mg) <sup>1/n</sup>	1.995	1.007	0.707
	n	1.308	1.551	1.508
	R <sup>2</sup>	0.988	0.984	0.984
Redlich-Peterson	k <sub>rp</sub> (mg/g)	120.122	47.709	24.598
	a <sub>rp</sub> (L/mg)	0.006	-0.010	0.007
	β	1.227	1.229	1.096
	R <sup>2</sup>	0.989	0.988	0.971
Combination of Langmuir-Freundlich	q <sub>m</sub> (mg/g)	34.431	14.5273	11.178
	b (L/mg)	0.0708	0.045	0.0272
	n	0.791	0.807	0.7389
	R <sup>2</sup>	0.993	0.989	0.983

For ternary system, Table 7 and Figure 12 show that, extended Langmuir model seems to give the best fitting for the experimental data for metal ions adsorption in combined system. There is a weak competition in ternary systems in the adsorption capacity of Lead, whereas the uptake of Copper and Cadmium is much reduced by the presence of Lead solute due to high affinity between Lead and PC as cleared from Figure 12.

### 7. Conclusions

In batch adsorption studies, data showed that Porcelinate rocks had considerable potential for the removal of lead, copper and cadmium from aqueous solution. Langmuir isotherm was fitted very well with experimental data. From the Langmuir isotherm, the maximum adsorption capacity of the PO sample was found as 76.104, 33.288 and 30.254 for Pb<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup> respectively for single system (Pb<sup>2+</sup>>Cu<sup>2+</sup>>Cd<sup>2+</sup>). However, for combined system the adsorption capacity decreased

Due to competitive between ions toward adsorbent surface. Optimum adsorption conditions for ions removal are as follows: pH 4, contact time 240 min, adsorbent mass= 0.7 ,1.2,1.3g for Pb<sup>2+</sup>,Cu<sup>2+</sup>+Cd<sup>2+</sup> respectively , mixing speed 250 rpm. The maximum adsorption capacity of the Porcelinate rock was found to decrease as the temperature increases. It was clear that the adsorption kinetics of metal ions to porcelinate rock obeyed pseudo-second order adsorption kinetics. The adsorption reaction was found to have negative values of both ΔH° and ΔS°. This suggests an exothermic reaction and an increase in randomness at the solid-liquid interface during the adsorption of metal ions onto the adsorbent. The interactions are thermodynamically favorable and are accompanied by increase in Gibbs energy. Thus, thermodynamic parameters showed that adsorption of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup> on porcelinate rock was spontaneous in nature and that the process is physisorption. The results obtained indicate that it is possible to design a continuous process for wastewater treatment by adsorbing the ions. This continuous process will be subjected of further investigations in our labs.

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