



Adsorption Characteristics of Heavy Metals on to Recycled Vehicular Tire Activated Carbon as Potential Adsorbent with Phosphoric Acid

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Abstract

Heavy metals considered poisonousness to plants and microorganisms in the earth and environmentally friendly contamination. The objective of the work is to transform vehicular tires, a greatly existing unwanted substance by treating with H_3PO_4 with and without treatment at $900^\circ C$ as a chemical agent into profitable adsorbent for the expulsion of Cu^{+2} , Zn^{+2} and Pb^{+2} ions. In this work, removal of Cu^{+2} , Zn^{+2} and Pb^{+2} ions by utilizing VTAC and the influence of different factors such as contact time, pH, adsorbent quantity, metal concentration and temperature on the adsorption have been calculated where the maximum adsorption of Cu^{+2} , Zn^{+2} and Pb^{+2} was 99.994, 99.5667 and 96.3974, respectively for ACs which was treated with H_3PO_4 with treatment at $900^\circ C$ and the equilibrium time was 72 hours and temperature of $30^\circ C$, PH 3, adsorbent dosage 5 mg/L and initial concentration 30 mg/L. The isotherm models that studied Langmuir and Freundlich and present Freundlich more suitable due to have high value correlation coefficient (R^2) and pseudo-first order and pseudo-second order kinetics also studied where pseudo-first order more suitable to describe the adsorption properties of VTAC as applied mechanism of Intraparticle diffusion model that appeared desirable results.

Keywords: *Activated carbon, Vehicular tire, Adsorption, Heavy metal ions.*

Introduction

Heavy metals can be defined as metallic elements that have (63.5 to 200.6 g/mol) atomic weights ranges and densities exceeding 5 g/cm^3 . Most heavy metals are toxic even at low concentrations. The source of trace metals in aquatic environment could be from anthropogenic or normal source. Normal source may include volcanic activity, continental weathering and forest fires, while anthropogenic sources may include industrial effluents, urban storm, water runoff, leaching of metals from garbage and solid dump, metal input from rural area [1, 2].

Heavy metals can be distinguished from other toxic contaminants by two features, the first is the tendency to accumulate in global ecological circle, in which natural water work as the main pathway and the other is non-biodegradability [3]. Copper (Cu), zinc (Zn), lead (Pb), nickel (Ni), cadmium (Cd), arsenic (As), chromium (Cr), mercury (Hg) and so on are the heavy metals that are regularly connected with poisonousness to plants and

microorganisms in the earth and environmentally friendly pollution [4] in association with the air and water, the earth atmospheres has a greatly lesser capacity to recoup from poisonous effluences for that reason contamination prompted by heavy metals and semimetals in is a danger environmentally friendly issue. Also, what happens in earth from biological and chemical responses for example (precipitation, oxidation, surface complexation, reduction, sorption and solution) that can result by some of follow elements that have possibly poisonous to living organisms and plants [5].

Some researchers have also identified heavy metals as "famous transition metals" that can be cause environmentally friendly contamination from a various sources involving (filtering of metal particles from the earth into rivers and lakes by acid rain, lead in petrol and manufacturing effluents) from these important metals are (zinc, lead

and copper) [6]. Heavy metals accumulate in several body parts including blood, liver, kidney, bones, feathers, hairs and eggs in a variety of taxa and are associated with many altered biological processes [7]. Adsorption as well as (oxidation, ion exchange, reduction, precipitation and membrane filtration) considered from the important old ways for heavy metal expulsion from wastewater and water. Among every one of the techniques adsorption is greatly actual and cost-effective. Activated carbon is one of the most popular adsorbents for the removal of metal ions from aqueous solutions the great price of ACs constrains its utilization as an adsorbent in modern countries despite the fact that the utilization of trade ACs a notable adsorbent for the expulsion of heavy metals from wastewater and water.

Subsequently, it is a developing need to get the ACs from inexpensive and usually obtainable unwanted substances. Various least cost adsorbents that create from agribusiness remains for example, (rice husk, coconut coir pith, banana pith, sawdust, apple wastes, peanut hull carbon, cottonseed hulls and sugarcane bagasse pith) that studied by different scientists for many adsorption purposes [8]. Now a day's rubber tire is one of the highly presented and simply acquirable unwanted materials and its safe disposal is an issue.

The rubber tires do not decompose simply due to their cross-linked structure and existence of additives and stabilizers. Therefore, it was planned to develop an efficient activated carbon from vehicular tire for the adsorption of heavy metals [9]. Activated carbon were utilized owing to its (large internal surface area, little raw material costs and its safe material considered) [10]. (Specific surface area and kind of surfactant useful gatherings, etc). From the characteristics which effect on adsorptions abilities of metallic ion on ACs.

Wholly chemical and physics characteristics affected by activation ways and the primary materials of activated carbon [11]. Surface morphology and pore structure of ACs depend on the precursors and chosen activation agents. In this work, H_3PO_4 is selected as the activating agent to produce AC from VT due to excellent dehydrating characteristics and capacity to improve and control the number of micropores with a very

similar pore size distribution. Also, the preparation temperatures to activate the carbon were also relatively low, hence creating the chemical activation process to be selected over physical activation and also chemical AC seems to be clearer and smoother associated to physical AC because of the removal of volatile compounds and contaminations through the activation process [12, 13]. The objectives of this study include the preparation, characterization and evaluation of adsorption properties of using VT based AC to remove Cu^{+2} , Zn^{+2} and Pb^{+2} ions.

Experimental

Materials and Methods

An adsorbate solution that utilized in this study was heavy metals Cu^{+2} , Zn^{+2} and Pb^{+2} ions that have purity 99.7%, 99.6 % and 99 %, respectively. HNO_3 and HCl were utilized as dissolute solutions where was dissolve 1g of Cu in 50 cm^3 of 5M HNO_3 , 1g of Zn in 30 cm^3 of 5M HCl , 1g of Pb in 50 cm^3 of 2M HNO_3 and all these solutions dilute to 1 Liter in a volumetric flask with deionized water then Store in a polythene bottle, separately. Also, measured pH was by utilizing a digital pH meter and thermostat with a working range of -20 to $+90^\circ\text{C}$ was utilized for temperature measurements, waste vehicular tire was obtained from an automobile workshop.

Adsorbent Preparation

The VT prepared from rubber vehicular tire that present in waste disposal places was cut into very small parts and repeatedly washed to remove impurities and ashes that were collected together. Then the wetted VT parts dried at 150°C for 4 h in an oven to remove any remaining water. The dried VT is then crushed utilized a mill and sieved to a preferred particle size ($75\text{ }\mu\text{m}$). The obtained material will be carbonized at 500°C for 5 h in a tubular furnace under a continuous Ar flow ($160\text{ cm}^3\text{ min}^{-1}$) at temperature rate of $10^\circ\text{C min}^{-1}$.

Ten grams of the obtained material will be mixed with forty grams of activating agent H_3PO_4 at percentage 1:4, separately where the mixed materials remain for 24 hours to ensure the reagents are fully curing the raw materials. The mixture is then filtered and repeatedly washed with distilled water until pH of the filtrate was in the range of 6.68 to

7.0. Then, the curing materials will be kept at 900°C in a silica crucible for 5 h in a tube furnace.

The collected AC is cooled at room temperature before being washed with distilled water to remove any remaining of activating agent H₃PO₄ then the solution was filtered by centrifugal and dried at 105°C. The dried product obtained is referred as vehicular tire activated carbon (VTAC). The activated carbon with and without heat treatment at 900°C will be evaluated for adsorption of metals [14, 9].

Characterization of Adsorbent

Fourier transform infrared (FTIR) spectroscopy will be carried out with FTIR spectrometer and scanning electron microscopy (SEM) utilized to discover the surface and morphologies of the VTACs where the samples will be shown by SEM images before and after adsorption of Cu⁺², Zn⁺² and Pb⁺² ions. It has also been energy dispersive spectroscopy utilized to determine

chemical composition of VTAC. Also, Powder X-ray diffraction patterns of VTAC were obtained using a Bruker AXS D8 powder diffractometer employing Cu K α radiation (40 kV, 45 mA, $\lambda = 1.5418 \text{ \AA}$), and 2°/min goniometer speed was employed for the analysis.

Adsorbent Studies

The adsorption tests of Cu⁺², Zn⁺² and Pb⁺² ions on VTAC were carried out at room temperature 30°C where 20 mL of the desired Cu⁺², Zn⁺² and Pb⁺² ions (30 mg L⁻¹) solution and 5 mg VTAC putting in a conical flask and remained mixing for 1 hr. After that the samples were filtered using filter paper and residual concentration of Cu⁺², Zn⁺² and Pb⁺² ions in the filtrate was estimated by utilizing atomic absorption spectroscopy. The quantity of Cu⁺², Zn⁺² and Pb⁺² adsorbed per unit gram of adsorbent (q_e) will be calculated from the mass balance equation [15]:

$$q_e \left(\frac{\text{mg}}{\text{g}} \right) = \frac{V(C_o - C_e)}{W} \quad (1)$$

Where V: the volume of the solution (L), W: the mass of the adsorbent used in a test (g), C_o: the initial concentration of the adsorbate solution (mg L⁻¹), C_e: the concentration of the adsorbate in the bulk phase at a given time (mg L⁻¹). And the adsorption percentage of each Cu⁺², Zn⁺² and Pb⁺² ions is calculated as follows[16]:

$$\text{Adsorption \%} = \frac{C_o - C_f}{C_o} \quad (2)$$

C_o: initial metal ion concentration
C_f: final metal ion concentration

For designate the adsorption isotherms of Cu⁺², Zn⁺² and Pb⁺² Langmuir and Freundlich isotherm models were utilized "The Langmuir isotherm" suppose a surface with uniform

limiting locations corresponding sorption energies, and no interface among adsorbed samples. Its numerical shape is composed as:

$$1/q_e = (1/Q_b) * (1/C_e) + (1/Q) \quad (3)$$

Where:

- C_e: is the balance concentration of the metallic ion (mg L⁻¹)
- Q_e: is the quantity adsorbed at balance and measured by (mg g⁻¹)
- B: constant is identified with the energy of adsorption (Lmg⁻¹)
- Q: is the Langmuir monolayer adsorption ability (mg g⁻¹).

"A dimensionless separation" factor (R_L) term is referred to the vital features of the Langmuir equation [11]:

$$R_L = 1 / (1 + b C_o) \quad (4)$$

C_o: is the highest initial solute concentration
b: is Langmuir adsorption constant (L/mg)

Freundlich adsorption isotherm is an empirical equation that is used to describe adsorption in heterogeneous systems. Freundlich adsorption is based on the

distribution of adsorbate molecules between an adsorbent and the aqueous phases at equilibrium. The following equation describe Freundlich adsorption isotherm:

$$q_e = K_f C_e \quad (5)$$

The famous linear formula of the Freundlich's isotherm is known by Equ.

$$\text{Log } q_e = \text{log } K_f + \left(\frac{1}{n}\right) \text{log } C_e \quad (6)$$

Where:

n and K_f are the Freundlich coefficients.

A straight line is obtained as a result of plot between $\text{log } q_e$ and $\text{log } C_e$ with a slope and intercept of $1/n$ and K_f , respectively [16, 17].

Also, in this study utilized adsorption kinetics such as the pseudo-first order rate expression, popularly known as the

Lagergren equation, is generally described by the following equation:

$$\frac{dq}{dt} = k_1 (q_e - q_t) \quad (7)$$

Where:

q_e : is the quantity adsorbed at balance and measured by (mg g⁻¹), q_t : is the quantity of the metallic ions adsorbed at any time (mg/g), k_1 : is the rate constant (min⁻¹). Pseudo first-order model equation may be integrating for taking the formula [18]:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (8)$$

The pseudo-second-order kinetic model can be represented by the following equation [19]:

$$\frac{dq}{dt} = k_2 (q_e - q_t)^2 \quad (9)$$

k_2 = second order reaction rate constant for adsorption (g/mg.h). After integrating Eq. (9) and rearranging the solution, a linear form is obtained and expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

(Weber and Morris discovered Intra-particle diffusion model) that utilized for fitting the tests data where this model supposed that the motion of sorbate atoms in the inner of

adsorbent particles is the main rate-deciding advance in the adsorption procedure. The subsequent formula is a common represent of the kinetics [9].

$$Q_t = k_i t^{0.5} + C \quad (11)$$

Where:

k_i : is the rate constant for intra-particle diffusion

C : is the measure of boundary thickness.

Results and Discussion

Characterization of Adsorbent

The FE-SEM images depicting the morphological structure of the raw VT and the selected AC prepared at activating agent H₃PO₄ without and with treatment at 900°C, respectively and morphology after adsorption of Cu⁺², Zn⁺² and Pb⁺². The surface of raw VT as shown in Fig. 1 (A) poor porous and having no cavities while in (a) found that many new large pores were clearly observed on the

surface of the AC which was activated with H₃PO₄ without treatment at 900°C. But(b) by activation at 900°C with H₃PO₄ resulted in the creation of more pores and a substantial removal of volatiles matter where in depending on the activation temperatures, the porosity of the external surfaces of the activated carbons were developed [20]. Also studied in FE-SEM image in Fig. 1(a₁, a₂, a₃) of VTAC after adsorption of (Cu, Zn and Pb) that showed an aggregated irregular surface with a large number of micro pores of various

sizes at the surface where the dissimilar surface after adsorption may be due to the

adsorption of (Cu, Zn and Pb) in the pores of the adsorbent.

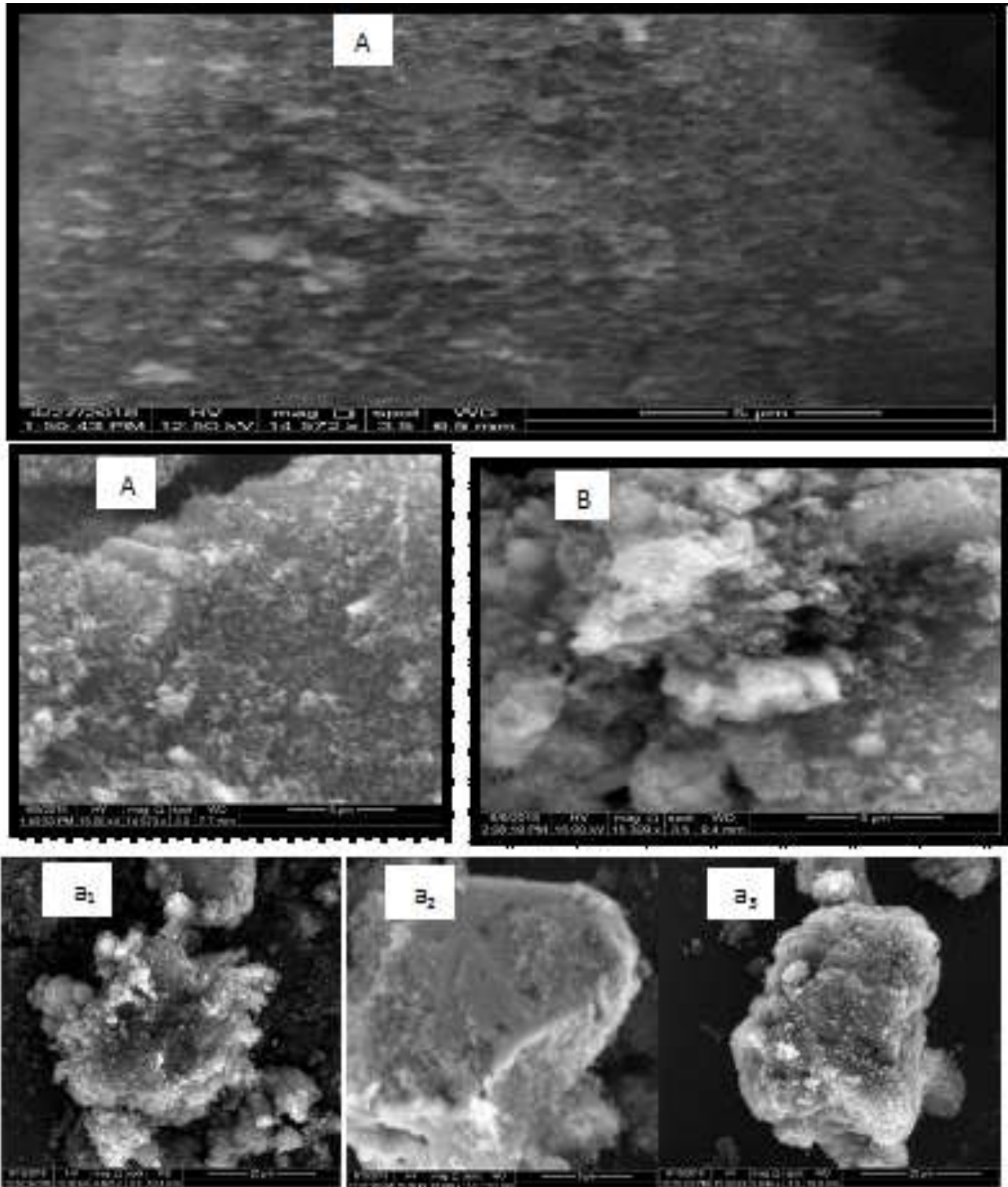


Fig. 1: Scanning electron micrographs of (A) pure VTAC (a,b) VTAC treated with H₃PO₄ without and with treatment at 9000, respectively (a₁) Cu adsorbed by VTAC treated with H₃PO₄ with treatment at 9000 C (a₂) Zn adsorbed by VTAC treated with H₃PO₄ with treatment at 9000 C (a₃) Pb adsorbed by VTAC treated with H₃PO₄ with treatment at 9000 C, respectively

Energy Dispersive Spectroscopy Analysis (EDS) showed that the elemental composition of pureVT specimen and VTACs, it's clear that the carbon is the predominant component with present other elements (O, N and S) besides that present other elements at small quantities (H, P and Si) .

where VTACs have greater carbon percentage than pure vehicular tire which creates them more carbonaceous substance [14].

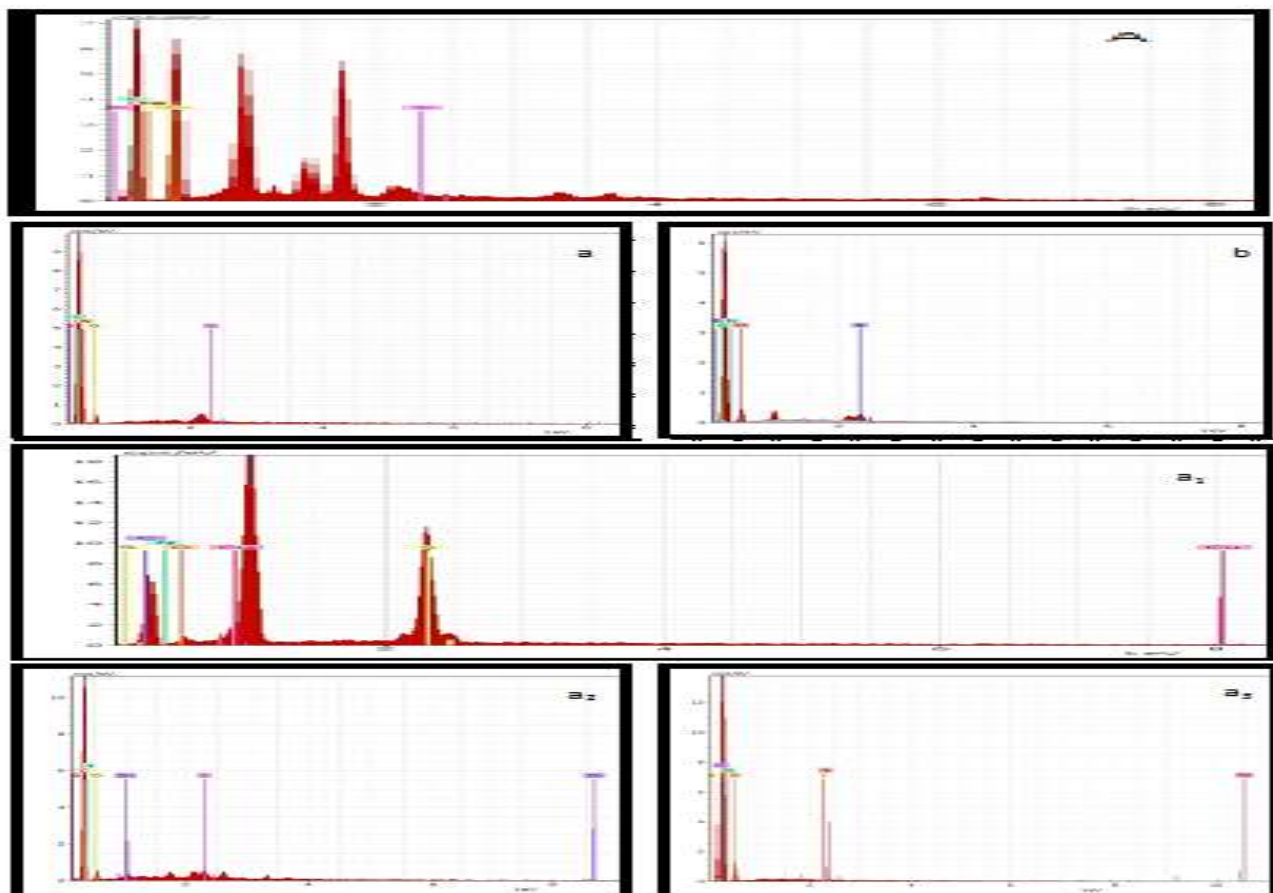


Fig .2 energy dispersive spectroscopy of (A) pure VTAC (a,b) VTAC treated with H₃PO₄ without and with treatment at 9000, respectively (a1) Cu adsorbed by VTAC treated with H₃PO₄ with treatment at 9000 C (a2) Zn adsorbed by VTAC treated with H₃PO₄ with treatment at 9000 C (a3) Pb adsorbed by VTAC treated with H₃PO₄ with treatment at 9000 C, respectively

And Fourier infrared transform in Fig. 3 in general, because the same raw substance utilized all the spectra almost presented the functional group and comparable form. Appearance of chief peaks nearly at 3715 cm⁻¹ show the existence of hydroxyl groups (OH) by the AC which was treated with H₃PO₄ without treatment at 900°C [21]. While other peaks appeared at 2668.69 cm⁻¹ that's referred for carboxylic groups (C=O) [19] and peaks at 2348 cm⁻¹ referred to P-H groups [14] and

Silane (Si-H) groups in the raw substance as well as produced ACs were established by the peak at about 2111.21 cm⁻¹ [22]. Also, the bands of aromatic C=C bonds was observed at wave numbers of 1523.31 cm⁻¹ [23,21,22]. And the peak at 938.21 cm⁻¹ attributed to the phosphorus-involving groups (P=O) where the activated carbons displayed numerous bands which appear between 900 and 1200 cm⁻¹ at low temperature (500-600°C) [24].

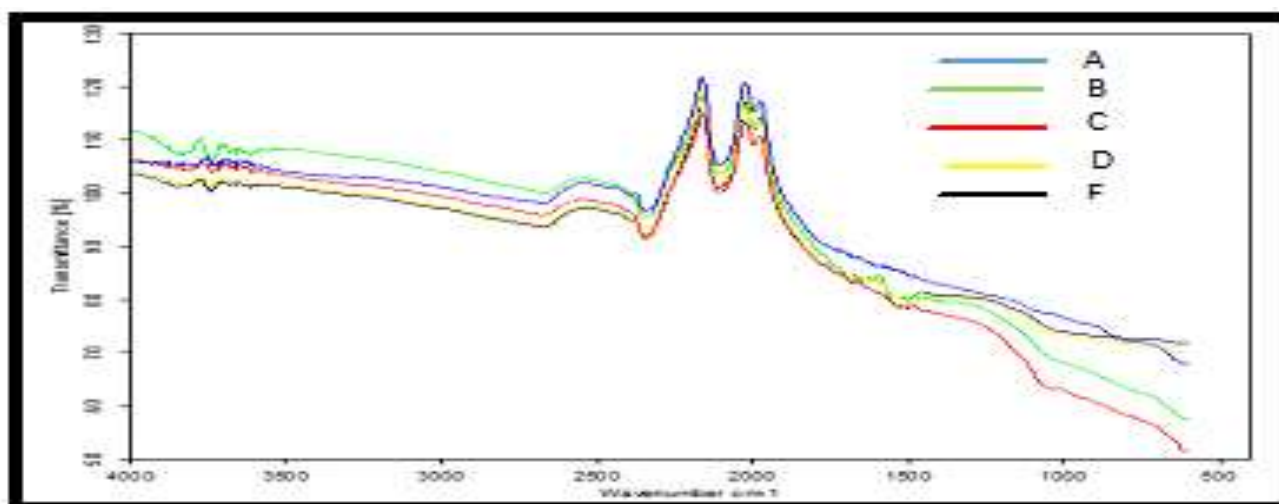


Fig. 3 FTIR spectra of (a) pure VT (b) VTAC which was treated with H₃PO₄ without treatment at 9000C before adsorption (c, d, e) VTAC which was treated with H₃PO₄ without treatment at 9000C after adsorption of Cu²⁺, Zn²⁺ and Pb²⁺, respectively

Fig. 4 refer for the peaks that appeared of (a) pure VT and (b) VTAC which was treated with H₃PO₄ with treatment at 900°C before adsorption and (c,d,e) VTAC which was treated with H₃PO₄ with treatment at 900°C after adsorption of Cu⁺², Zn⁺² and Pb⁺², respectively. Where peaks shifted to greater quantities (3781.45, 2677, 2359, 2116.44 and

1525.67 cm⁻¹) of OH, C=C, P-H, Si-H and C=C, respectively and appearance new peaks 1215, 1053, 956, 763 and 698 which referred to C-O, C=C, P=O vibrations, C-H and O-H, respectively. In general, appeared new peaks and shifted it to higher quantities after adsorption due to adsorption metals on the surface of AC [9, 21].

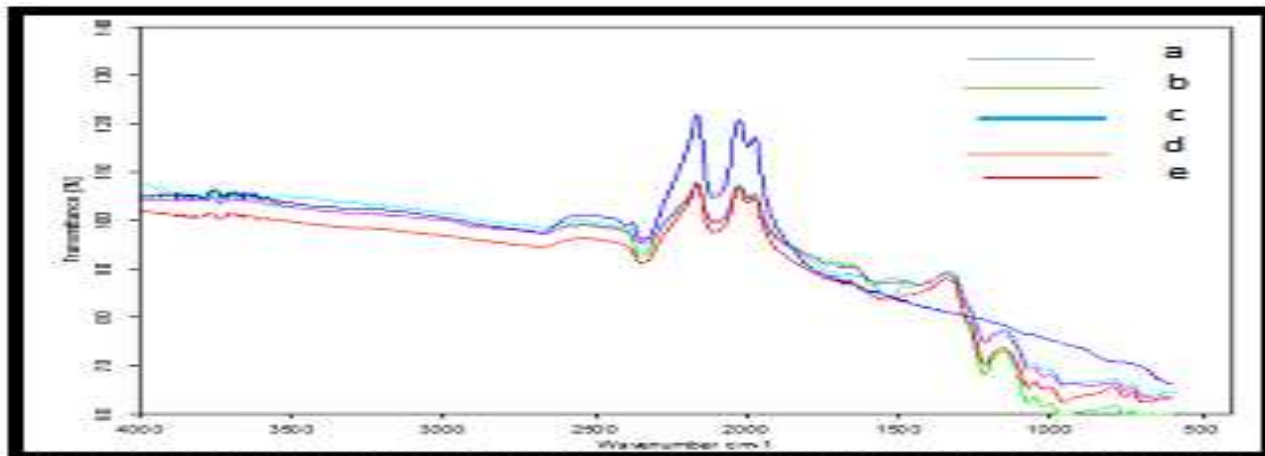


Fig. 4: FTIR spectra of (a) pure VT (b) VTAC which was treated with H₃PO₄ with treatment at 900°C before adsorption (c, d, e) VTAC which was treated with H₃PO₄ with treatment at 900°C after adsorption of Cu⁺², Zn⁺² and Pb⁺², respectively

Fig. 5 shows the XRD patterns of the raw vehicular tire substance and the activated carbon produced at activating agent H₃PO₄ with and without treatment at 900°C, respectively. Where sample A₁ referred to pure VT that appearance broad peaks around 2θ 24° and 44° that indicate to the amorphous structure [9, 25].

crystanillity [14]. But with regard by A₃ sample that denoted to VTAC which was treated with H₃PO₄ with treatment at 900°C which appeared sharp peaks at 2θ 23.19, 34.72 and 37.2 appearance these peaks in sample this indicates that carbon have a tendency to crystallize at a higher temperature [26].

While A₂ sample referred to VTAC which was treated with H₃PO₄ without treatment at 900°C that appeared small peaks at 2θ 28.48, 47 and 56 this indicates that AC near to micro crystalline structure due to activating agent H₃PO₄ when reacted with raw vehicular tire substance causing little of

Finally A₄ sample that referred to VTAC which was treated with H₃PO₄ with treatment at 900°C after adsorption which alike the structure of AC (H₃PO₄) with treatment at 900°C before adsorption because same the starting material that utilized.

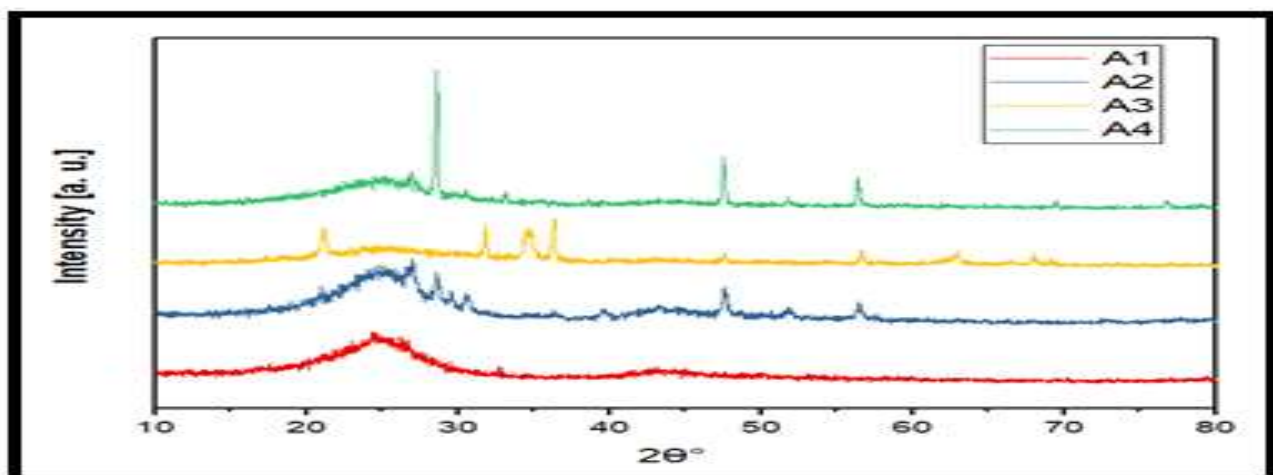


Fig. 5: X-Ray Diffraction Patterns of (A1) pure VTAC (A2) VTAC which was treated with H₃PO₄ without treatment at 900°C (A3) VTAC which was treated with H₃PO₄ with treatment at 900°C (A4) Cu adsorbed by VTAC treated with H₃PO₄ with treatment at 900 C, respectively

Effect of Different Parameters on Adsorption of Heavy Metals (Cu, Zn and Pb) by Modified ACs

Effect of Contact Time

The results shown in Fig. 6 (a and b) shows the percentage of adsorbed ions Cu^{+2} , Zn^{+2} and Pb^{+2} on to ACs which was treated with H_3PO_4 with and without treatment at 900°C surfaces as a function of contact time, respectively. It is noted that the adsorption of Cu^{+2} , Zn^{+2} and Pb^{+2} increases rapidly with time and then reaches equilibrium.

Two region can be observed on the curve of contact time, first region in which the metal's adsorption (Cu^{+2} , Zn^{+2} and Pb^{+2}) takes place rapidly within a short time and the second region was equilibrium. At equilibrium time there is no active site on the ACs. Where the quick adsorption at the primary stage might be because of available of the exposed surfactant region and the activating locations on the adsorbent and the highest driving

forces which creating quick exchange of metal ions to the surfactant of adsorbent particles. Also the further slow in amount of ion adsorbed with time may be due to aggregation of metal ions around the adsorbent particles. This aggregation may hinder the migration of the adsorb ate, as the adsorption sites become saturated, and resistance to diffusion of metal ions in the adsorbents increases [14].

All experiments showed the highest removal Cu^{+2} followed by Zn^{+2} and Pb^{+2} , respectively. The perfect results were obtained for (Cu, Zn and Pb) metal ions for ACs which was treated with H_3PO_4 with treatment at 900°C and the equilibrium time was 72 hours and temperature of 30°C which adsorption percentage was 99.994, 99.5667 and 96.3974, respectively. These test results are in great concurrence with the results acquired by [12, 11], who found that the adsorption percentage increases with increasing the contact time.

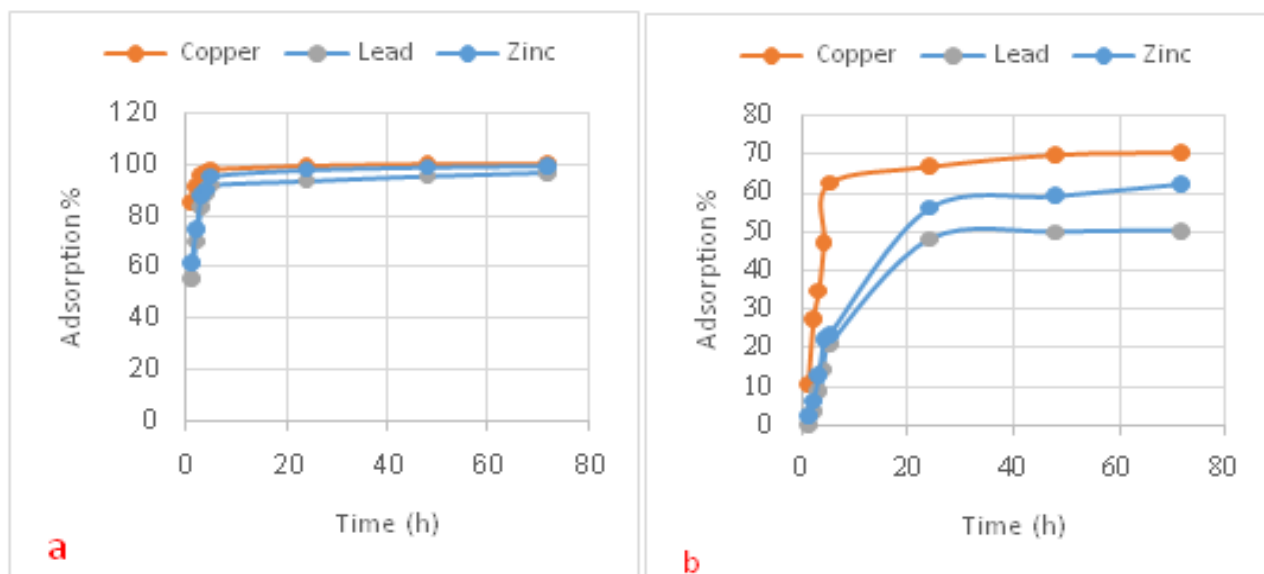


Fig. 6 :The effect of contact time on percentage removal of Cu^{+2} , Zn^{+2} and Pb^{+2} Initial concentration of metal ion is 30 mg/L, temperature 30°C , $\text{pH}=3$, and ACs =5 mg. (a, b) AC treated with H_3PO_4 with and without treatment at 9000°C , respectively

Effect of pH on Ions Adsorption

Fig. 7 (a and b) show the effect of pH on the adsorption of Cu^{+2} , Zn^{+2} and Pb^{+2} on to ACs which was treated with H_3PO_4 with and without treatment at 900°C , respectively. As can be seen, the pH of the solution plays an important role in affecting the adsorption features of Cu^{+2} , Zn^{+2} and Pb^{+2} onto ACs. The adsorption of Cu^{+2} , Zn^{+2} and Pb^{+2} onto ACs increases with the increase in pH range of 3–8. It found from tests at strong acidic medium the adsorption capacity was little. When pH 3, adsorption capacity rise rapidly up to pH 8

since most metallic binding locations may appear and conveyed negative charges, with following attraction of metal ions with positive charge and adsorption onto the adsorbent surface. Where the increase in adsorption capacity at $\text{pH}=8$ could be due to the adsorption of ions onto the surface of adsorbents and precipitation. These test results are in great concurrence with the results acquired by [27]. Generally, because of presence competition between metal ions and hydrogen ions for the same adsorption locations a reduction in ions adsorption at

acidic pH occurs. On the other hand, increasing in pH values up to alkaline medium improve metallic adsorption's percentage moreover variations in surfactant charge and the precipitating of the suitable salts happens of the dominating existence of

hydrated species of heavy metals, Thusly the rise in metallic expulsion as pH rises can be described based on a reduction in competitions among metal species and hydronium ions for the surfactant locations [11, 28].

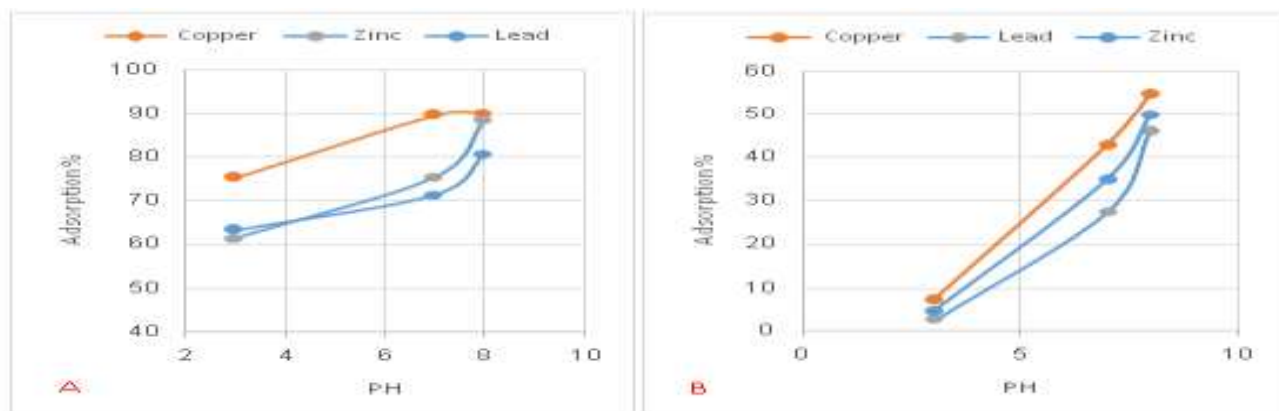


Fig. 7 The effect of pH on the percentage of adsorption of Cu²⁺, Zn²⁺ and Pb²⁺ Initial concentration of metal ion is 30 mg/L, temperature 300 C, contact time 1hr. and AC dosage 5 mg. (a, b) AC treated with H₃PO₄ with and without treatment at 9000C, respectively

Effect of Metal Concentration

Different concentrations of (Cu, Zn and Pb) solutions of 30, 40,50,60,70 and 80 ppm were utilized to study their influence on the percentage removal of (Cu, Zn and Pb) ions keeping the other factors constant. Fig. 8 (a and b) show the percentage removal of Cu, Zn and Pb ions at different concentrations. It is clearly shown that the percentage removal of Cu²⁺ and Zn²⁺ decreases by increasing the concentration by utilizing the same dosage of ACs.

Where the adsorption percentage of Cu²⁺ and Zn²⁺ ions was the maximum at little concentrations and reduced with the rise in metal's concentration. The reason behind this is attributable to the Cu and Zn ions are no longer near to the surfactant of the adsorbent since the adsorbent (AC) have reached their

limited surfactant for adsorbing the metal ions.

More increasing in metallic concentration carried no rise in adsorption, which resulting from overlying of adsorption locations because of great crowding of adsorbent particles [12]. While with regard to Pb²⁺ions, the adsorption abilities raised as the Pb concentration raised. The higher concentrations can supply the drive force enough for overcoming the resistance of the mass transfer of Pb (II) between solid and liquid phases. The Pb concentration was greater, and then the driving force was greater, and therefore the adsorption ability would be greater. In other words the adsorption goes down in case of low initial metal ion concentration. These test results are in great concurrence with the results acquired by [11, 29].

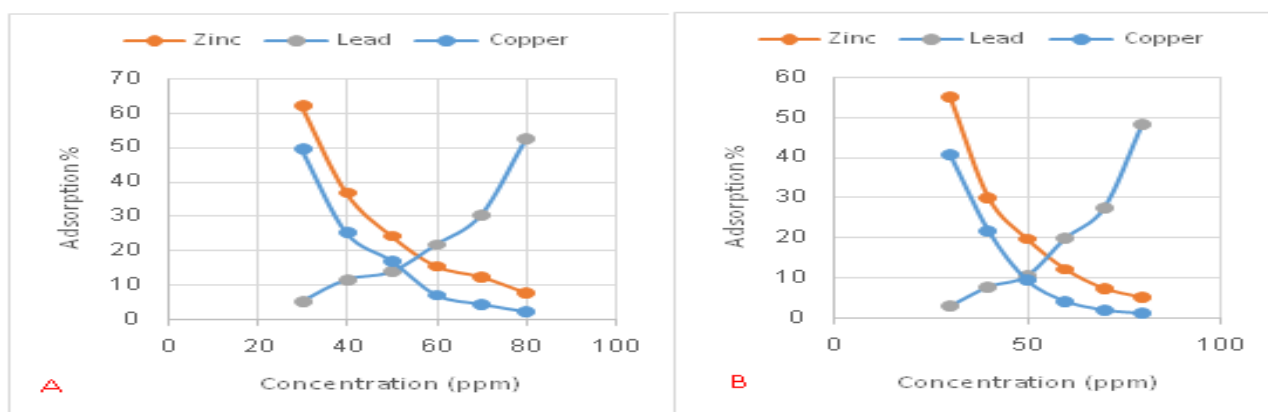


Fig. 8 The percentage removal of Cu²⁺, Zn²⁺ and Pb²⁺ at various concentrations (ppm), contact time=1 hr., pH=3, temperature 30 0C and ACs dosage=5 mg.(a, b) AC treated with H₃PO₄ with and without treatment at 9000C, respectively

Effect of ACs Dosage

The batch adsorption experiments were carried out by utilizing different amounts of ACs of (5-30) mg/L. The results shown in Fig. 9 (a, b) indicate that the adsorption capability increases with increases in ACs dosage. Where the quantity of adsorption for (Cu, Zn and Pb) ions increases with increases adsorbent dose. Increase in adsorption with adsorbent dosage can be attributed to

availability of more adsorption sites and increased adsorbent surface area. Where the higher adsorption capacity observed from all experiments were 99.5743, 96.7833 and 91.5931 for Zn²⁺, Cu²⁺ and Pb²⁺ions, respectively for ACs which was treated with H₃PO₄ with treatment at 900°C. These test results are in great concurrence with the results acquired by [11], who found that the adsorption ratio increases with increasing the quantity of ACs.

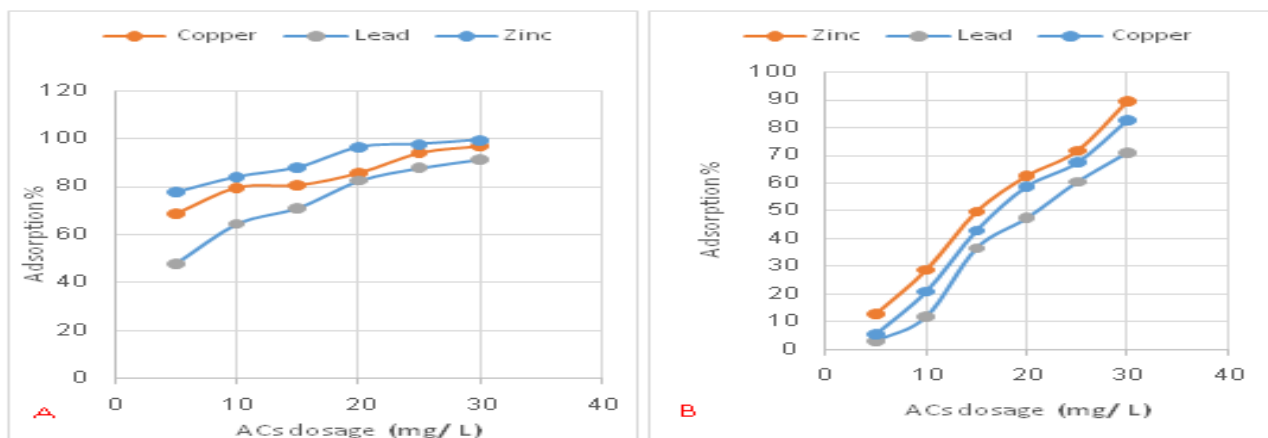


Fig. 9 The effect of ACs dosage on percentage of adsorption of Cu²⁺, Zn²⁺ and Pb²⁺ initial concentration of metal ion is 30 mg/L, temperature 30o C, pH =3 and contact time 1hr. (a,b) AC treated with H₃PO₄ with and without treatment at 9000C, respectively

Effect of Temperature on Adsorption

The influence of solution's temperature on (Cu, Zn and Pb) ions removal was studied at four various temperatures 30, 40, 50 and 60°C. Where the results in Fig. 10 (a, b) showed that increasing the temperature considerably influenced the amount of Cu²⁺, Zn²⁺ and Pb²⁺ adsorbed from solution by various adsorbents. The improvement in the adsorption's ability may owe to the chemical interaction among adsorbent and adsorbate locations or the raised percentage of intra particle diffusion of (Cu, Zn and Pb) particles into the pores of the adsorbents due to

decrease solution's viscosity at high temperatures. Where the higher adsorption capacity observed from all experiments were 89.9233, 83.2767 and 76.9933 for Cu²⁺, Zn²⁺ and Pb²⁺ions, respectively for ACs which was treated with H₃PO₄ with treatment at 900° C. Where the activator, H₃PO₄ utilized raised the negative charge of phosphate groups on VTAC surface; thus adsorption capacity for Cu²⁺, Zn²⁺, Pb²⁺ions increased [30]. These test results are in great concurrence with the results acquired by [11], who found that the adsorption ratio increases with increasing the quantity of ACs.

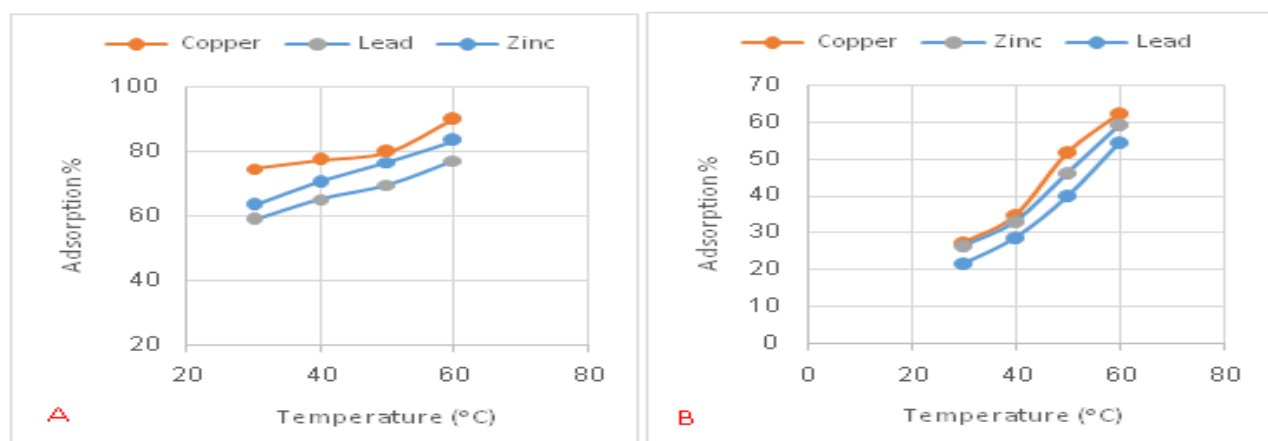


Fig. 10: The effect of solution temperature on percentage of adsorption of Cu²⁺, Zn²⁺ and Pb²⁺ Initial concentration of metal ion is 30 mg/L, ACs dosage=5 mg, pH =3 and contact time 1hr. (a,b)AC treated with H₃PO₄ with and without treatment at 9000C, respectively

Adsorption Isotherms

Langmuir and Freundlich isotherm models were used to describe the adsorption isotherms of (Cu, Zn and Pb) ions on to ACs which was treated with H₃PO₄ with and without treatment at 900°C, respectively. Where the distribution of ACs particles between adsorbent is a measure of the position of equilibrium in an adsorption process and can be investigated through

$$RL = \frac{1}{(1 + b C_0)}$$

Where adsorption process is desirable when R_L quantities greater than zero and less than one but it is undesirable when R_L greater than one while if R_L equal to 1 and 0 the adsorption process is linear and irreversible, respectively. Where present that quantities R_L lie between zero and one for all experiments, it is seen that the adsorption's ability of metal ions (Cu, Zn and Pb) is

these models. Langmuir model assumes that adsorption occurs at specific homogeneous adsorption sites within the adsorbent and intermolecular forces decrease rapidly with the distance from the adsorption surface while heterogeneous surface energies are considered in Freundlich isotherm model [31]. The vital characteristics of Langmuir's isotherm may be described by equilibrium constant (R_L) or a separation factor, which is defined as:

desirable. But in all types of ACs the linear plot of log q_e versus log C_e in the Freundlich isotherm along with a high value correlation coefficient (R²) greater than Langmuir isotherm, indicating that the Freundlich isotherm provides a better fit with the equilibrium data from Langmuir isotherm [32].

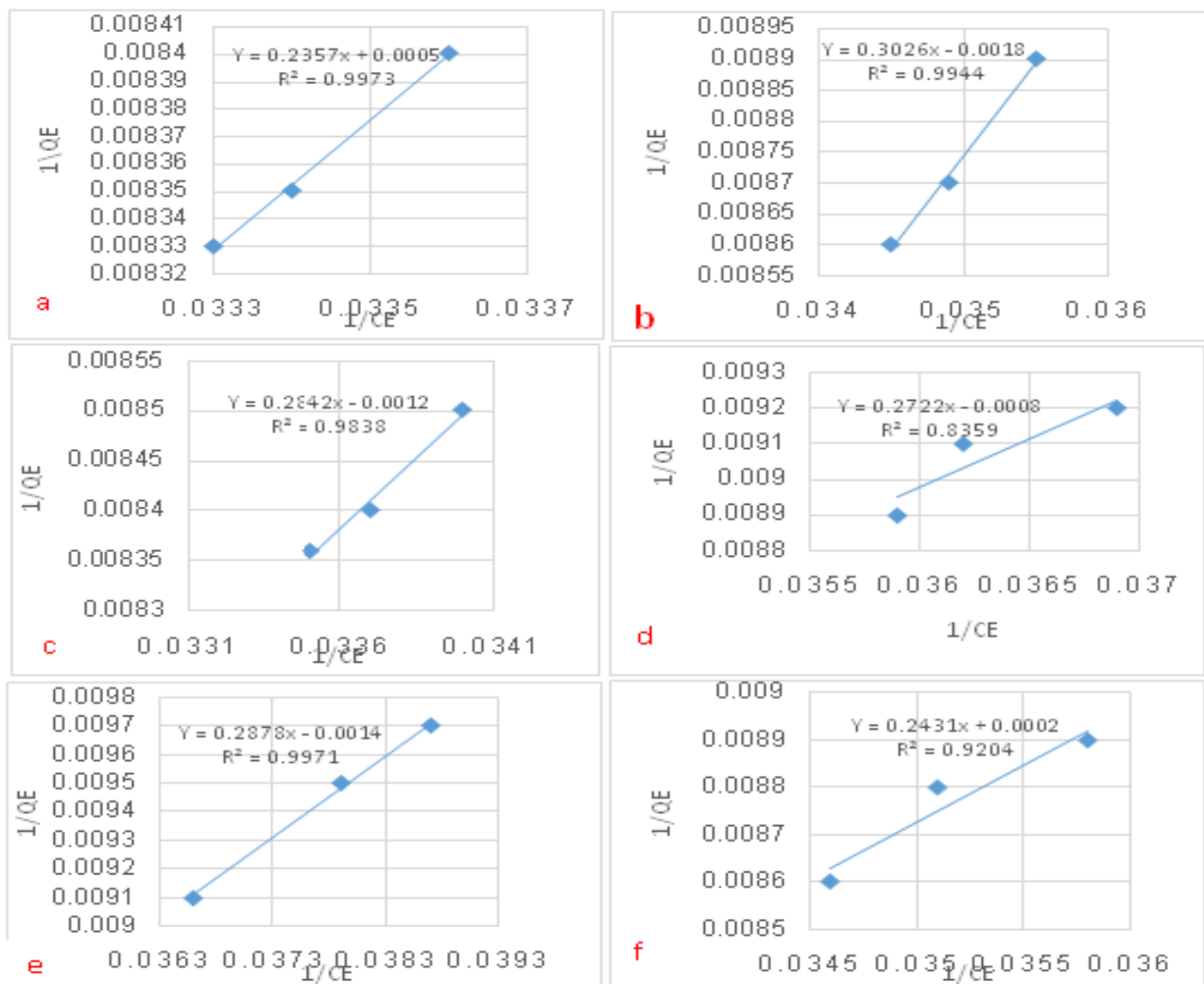


Fig. 11 : Adsorption isotherm Langmuir model for (a, b) Cu+2 on to ACs which was treated with H₃PO₄ with and without treatment at 900°C, respectively (c,d) Zn+2 on to ACs which was treated with H₃PO₄ with and without treatment at 900°C, respectively (e,f) Pb+2 on to ACs which was treated with H₃PO₄ with and without treatment at 900°C, respectively

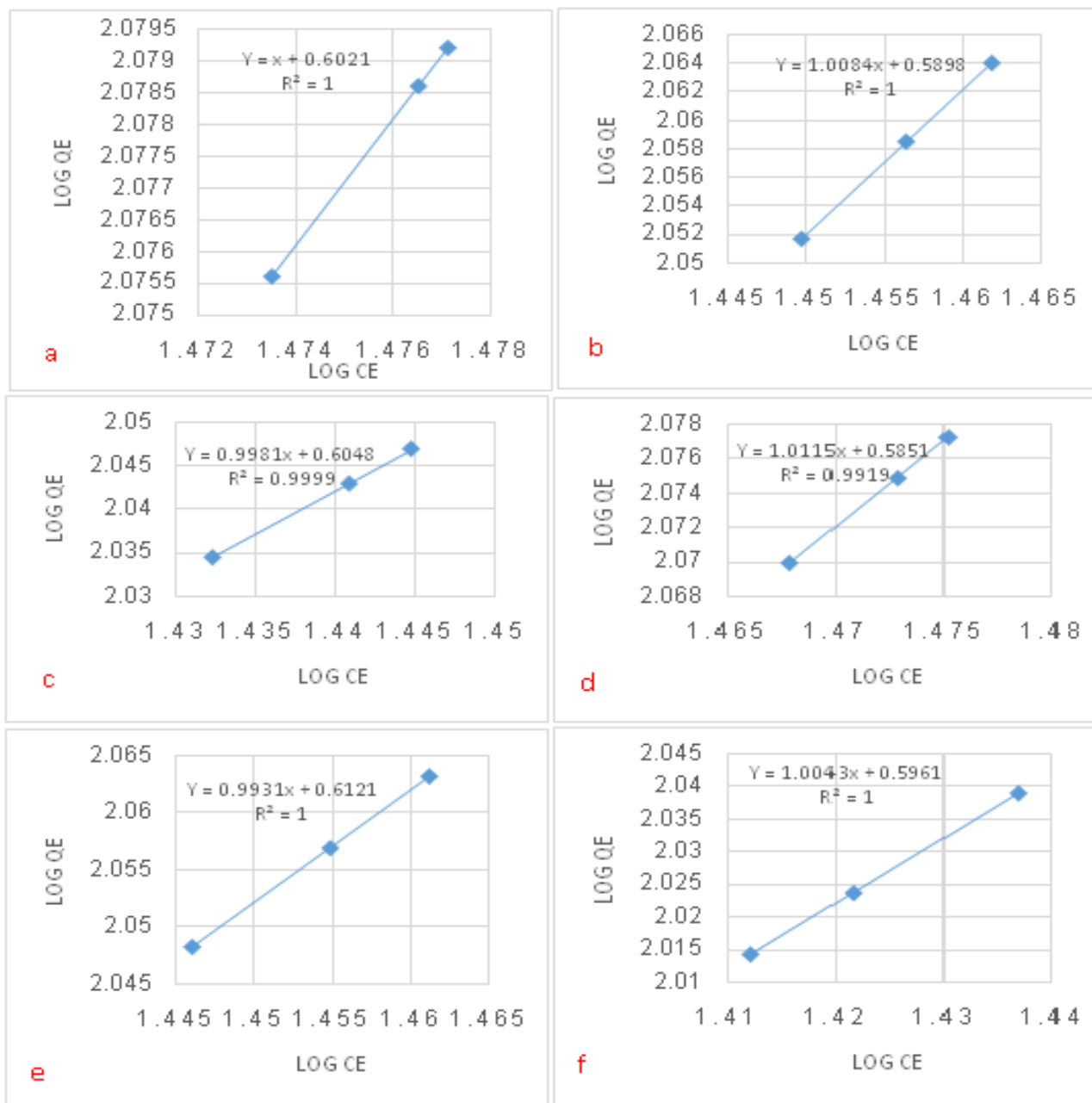


Fig. 12: Adsorption isotherm Freundlich model for (a, b) Cu+2 on to ACs which was treated with H3PO4 with and without treatment at 9000C, respectively (c,d) Zn+2 on to ACs which was treated with H3PO4 with and without treatment at 9000C, respectively (e,f) Pb+2 on to ACs which was treated with H3PO4 with and without treatment at 9000C, respectively

Kinetic Study

Two kinetics models were utilized to calculate the percentage of the adsorption process. These kinetic models are pseudo-first order and pseudo-second order. This kinetics was utilized to study of adsorption of (Cu, Zn and Pb) onto the surface of ACs which was treated with H₃PO₄ with and without treatment at 900°C, respectively under the following conditions: Initial concentration of metal ion is 30 mg/L, temperature 30°C, and pH=3, and ACs =5 mg.

Applicability of a particular type of rate equation is selected based on the value of coefficient R². Both the values of R² for the

"pseudo first order" and "pseudo second order" rate models were nearly closer but pseudo-first-order model described very well because R² values the closet to one for three metals adsorbed over VTAC [14].

And also applied Intra particle diffusion model to study adsorption of (Cu, Zn and Pb) ions onto the surface of ACs which was treated with H₃PO₄ with and without treatment at 900°C, respectively in this model the relationship between t^{0.5} versus q_t would be linearly if "intra particle diffusion" is associated with the adsorption's process where the high values of the R² suggest that the adsorption of (Cu, Zn and Pb) ions occur due to intra-particle diffusion [9].

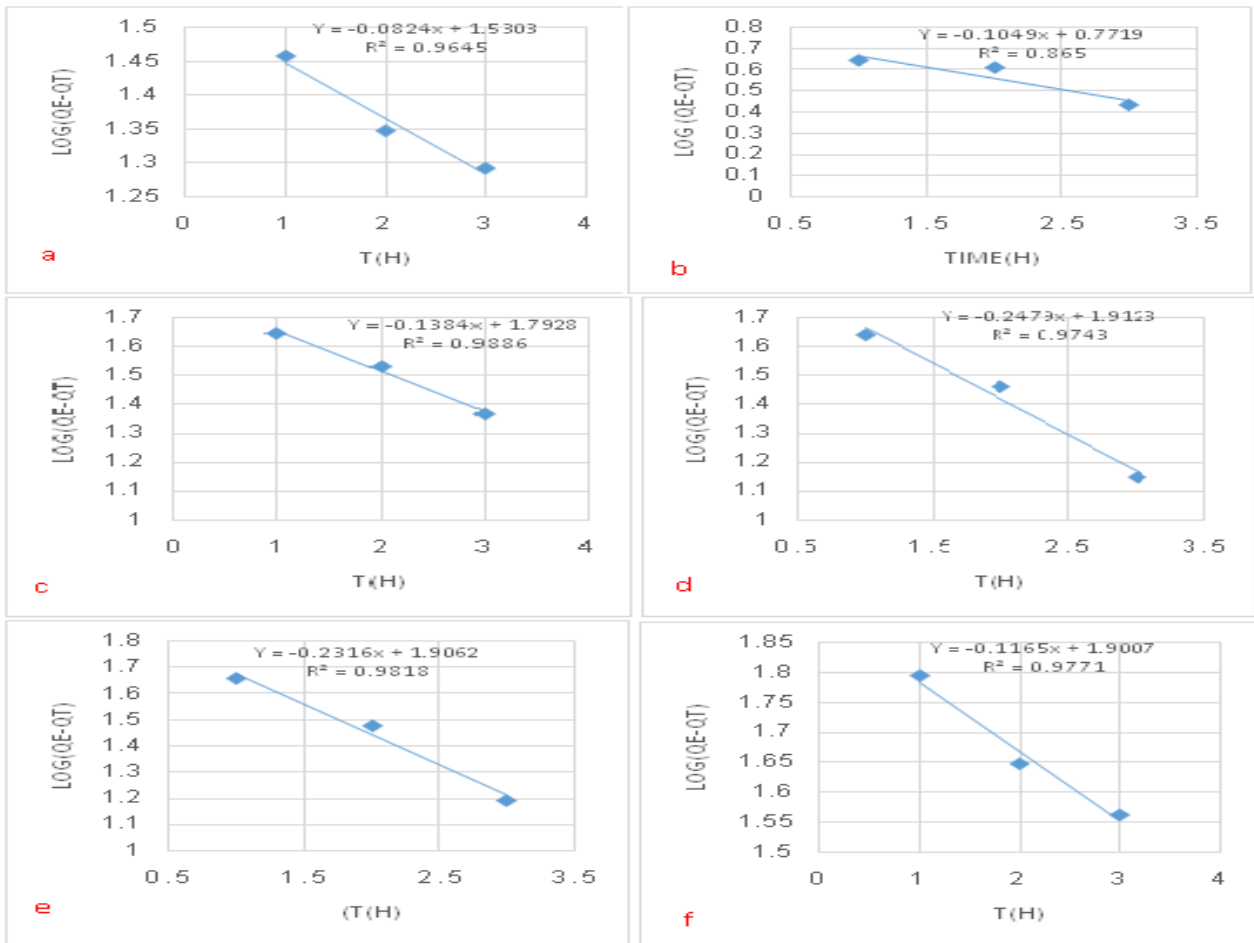


Fig. 13:Pseudo-first order for Adsorption (a, b) Cu²⁺ on to ACs which was treated with H₃PO₄ with and without treatment at 9000C, respectively (c,d) Zn²⁺ on to ACs which was treated with H₃PO₄ with and without treatment at 9000C, respectively (e,f) Pb²⁺ on to ACs which was treated with H₃PO₄ with and without treatment at 9000C, respectively

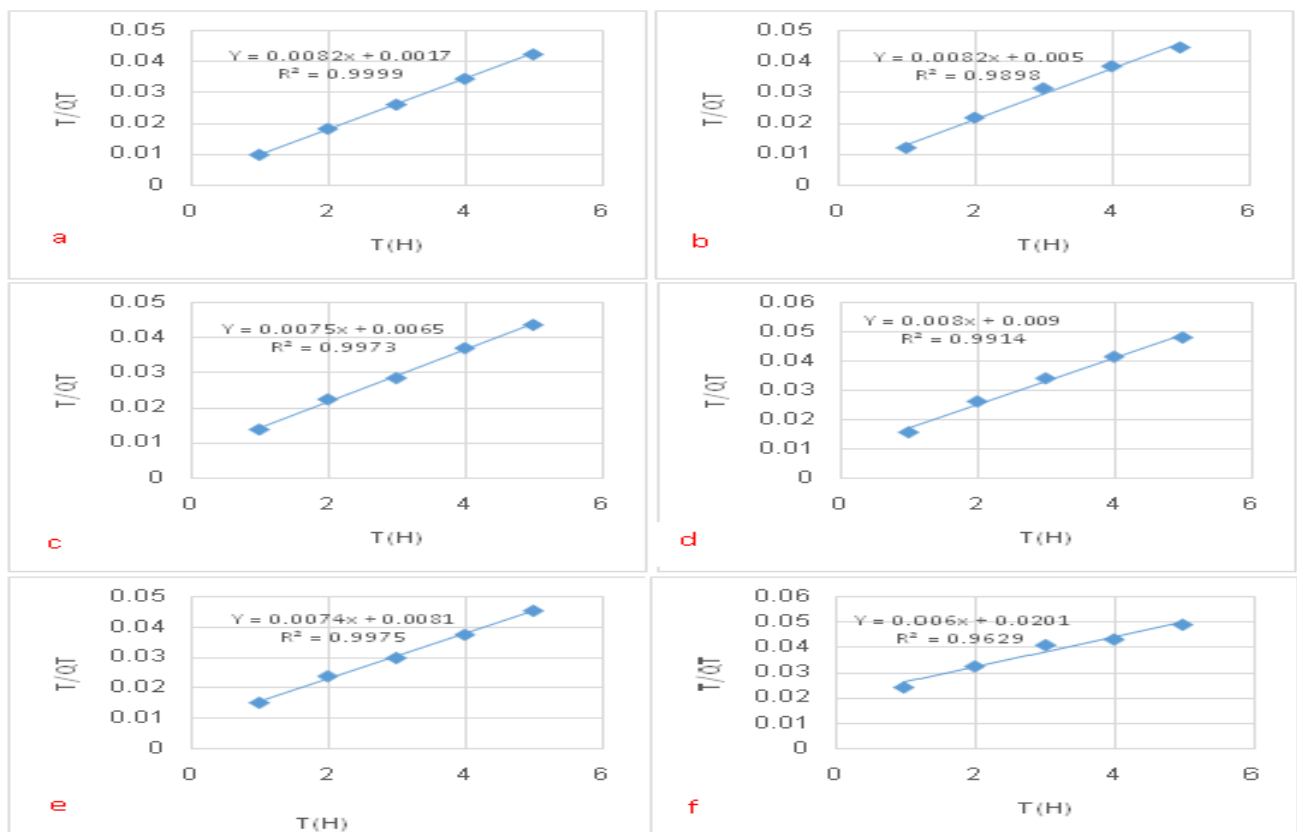


Fig. 14:Pseudo-second order for Adsorption (a, b) Cu²⁺ on to ACs which was treated with H₃PO₄ with and without treatment at 9000C, respectively (c,d) Zn²⁺ on to ACs which was treated with H₃PO₄ with and without treatment at 9000C, respectively (e,f) Pb²⁺ on to ACs which was treated with H₃PO₄ with and without treatment at 9000C, respectively

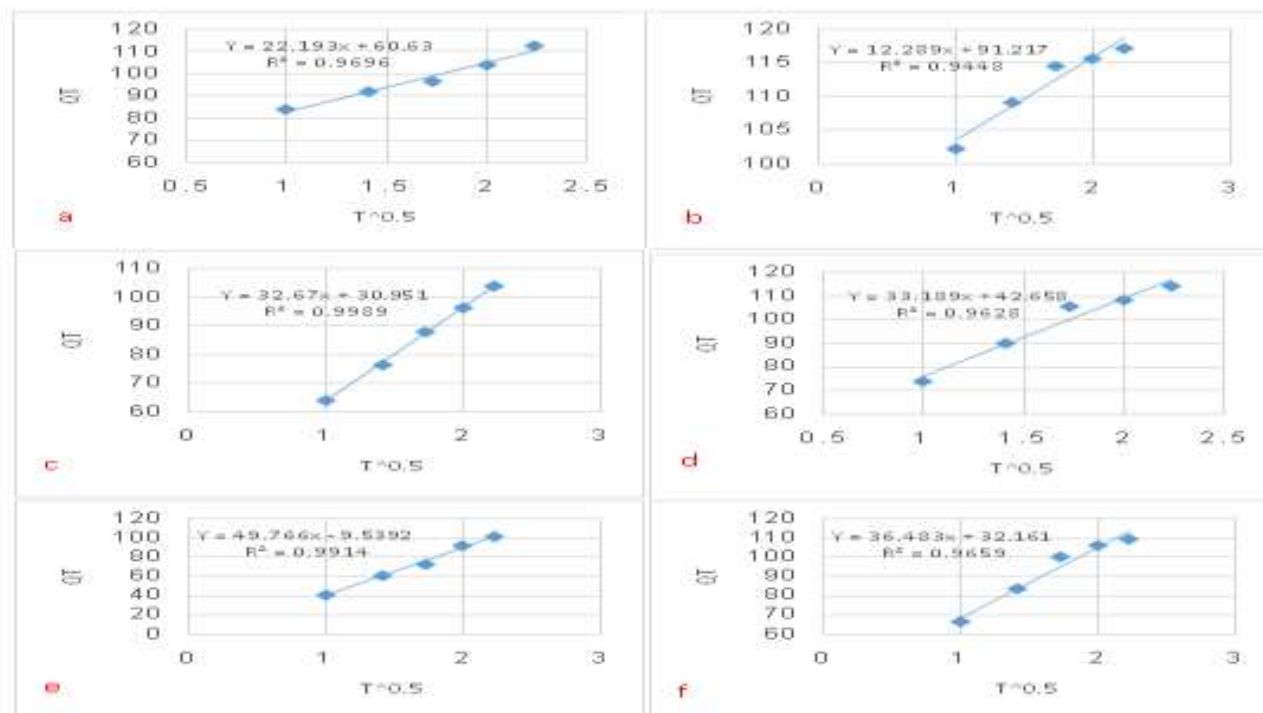


Fig. 15 Intra-particle diffusion mechanism for Adsorption (a, b) Cu+2 on to ACs which was treated with H3PO4 with and without treatment at 9000C, respectively (c,d) Zn+2 on to ACs which was treated with H3PO4 with and without treatment at 9000C, respectively (e,f) Pb+2 on to ACs which was treated with H3PO4 with and without treatment at 9000C, respectively

Conclusion

In this study, a low-cost activated carbon has been created from freely existing unwanted vehicular tires by utilizing H₃PO₄ as chemical agent. The created AC professionally to expulsion of Cu²⁺, Zn²⁺ and Pb²⁺ ions under influence different factors. In general, the adsorption Cu²⁺, Zn²⁺ and Pb²⁺ onto ACs increases with increasing contact time and maximum expulsion was at 72 hour and by increasing PH from 3-8 increases the rate of adsorption. Also, by increases temperature from (30-80°C) lead to increases the expulsion

rate of metals, expulsion rate increases with increasing adsorbent dosage from 5 ppm to 30 ppm for Cu²⁺, Zn²⁺ and Pb²⁺ and with regard to original concentration of metals that studied the expulsion rate of Cu²⁺ and Zn²⁺ increases with increasing concentration from 30 ppm to 80 ppm while with increasing original concentration of Pb²⁺ the rate of adsorption is reduced. Where concluded that the Freundlich, pseudo-first order model more suitable for adsorption Cu²⁺, Zn²⁺ and Pb²⁺. Also, applied mechanism of Intraparticle diffusion model and appeared desirable results.

References

- LI Simeonov, MV Kochubovski, BG Simeonova (2011) "Environmental heavy metal pollution and effects on child mental development", First edition, *Springer*.
- OA Aghoghovwia, OA Oyelese, EI Ohimain (2015) "Heavy metal levels in water and sediment of Warri River , Niger Delta , Nigeria," *International Journal of Geology, Agriculture and Environmental Sciences*, 3 (1): 20-24.
- PA Ekwumemgbo, NO Eddy, IK Omoniyi (2005) "Heavy metals concentrations of water and sediments in oil exploration zone of nigeria", 579-582.
- G Brunetto, PAA Ferreira, GW Melo, CA Ceretta, M Toselli (2016) "heavy metals in vineyards and orchard soils", *Revista Brasileira de Fruticultura.*, 39 (2):1-12.
- A Violante, PM Huang, GM Gadd (2008) "Biophysico-chemical processes of heavy metals and metalloids in soil environments", First edition, *John Wiley and Sons, Inc.*.
- ML Sanchez (2008) "Causes and effects of heavy metal pollution", First edition, *Nova Science Publishers, Inc.*.
- A Frantz, M Pottier, B Karimi, H Corbel, E Aubry, C Haussy, J Gasparini, M Castrec-Rouelle (2012) "Contrasting levels of heavy metals in the feathers of urban pigeons from close habitats suggest limited movements at a restricted scale," *Environmental Pollution*, 168: 23-28.

8. M Madhava Rao, A Ramesh, G Purna, Chandra Rao, K Seshaiyah (2006) "Removal of copper and cadmium from the aqueous solutions by activated carbon derived from Ceiba pentandra hulls," *Journal of Hazardous Materials*, 129 (1-3): 123-129.
9. H Gupta, B Gupta (2016) "Vehicular tire as potential adsorbent for the removal of polycyclic aromatic hydrocarbons", *Polycyclic Aromatic Compounds*, 1-15.
10. FB Aarden (2001) "Adsorption onto heterogeneous porous materials: equilibria and Kinetics", *Master Thesis*, Eindhoven University of Technology,.
11. El-Wakil AM, FS Awad (2014) "Removal of lead from aqueous solution on activated carbon and modified activated carbon prepared from dried water hyacinth plant", *Journal of Analytical and Bioanalytical. Techniques*, 5 (2):1-14.
12. A Borhan, NA Abdullah, NA Rashidi, MF Taha (2016) "Removal of Cu²⁺ and Zn²⁺ from single metal aqueous solution using rubber-seed shell based activated carbon", *Procedia Engineering*, 148: 694-701.
13. A Heidari, H Younesi, A Rashidi, A Ghoreyshi (2014) "Adsorptive removal of CO₂ on highly porous activated carbons prepared from Eucalyptus camaldulensis wood: Effect of chemical activation", *Journal of the Taiwan Institute of Chemical Engineers*, 45: 579-588.
14. VK Gupta, B Gupta, A Rastogi, S Agarwal, A Nayak (2011) "A comparative investigation on adsorption performances of mesoporous activated carbon prepared from waste rubber tire and activated carbon for a hazardous azo dye-Acid Blue 113", *Journal of Hazardous Materials*, 186 (1): 891-901.
15. MM Rahman, M Adil, AM Yusof, YB Kamaruzzaman, RH Ansary (2014) "Removal of heavy metal ions with acid activated carbons derived from oil palm and coconut shells", *Materials*, 7 (5):3634-3650.
16. S Pang, K Yung (2014) "Prerequisites for achieving gold adsorption by multiwalled carbon nanotubes in gold recovery", *Chemical Engineering Science*, 107: 58-65.
17. BJ Kadhim (2017) "Preparation and identification of carbon nanotubes and activated carbon from seeds of Iraqi dates kentar and spinel Co₃O₄-Ni₃O₄. Kinetic adsorption and photocatalytic activity studies", *Doctor Thesis*, University of Kufa, Department of chemistry,.
18. JC Moreno-Pirajan, L Giraldo (2012) "Heavy metal ions adsorption from wastewater using activated carbon from orange peel," *E-Journal of Chemistry*, 9 (2): 926-937.
19. ZZ Chowdhury (2013) "Preparation, characterization and adsorption studies of heavy metals onto activated adsorbent materials derived from agricultural residues," *Doctor Thesis*, University of Malaya, Department of Chemistry.
20. D Prahas, Y Kartika, N Indraswati, S Ismadji (2008) "Activated carbon from jackfruit peel waste by H₃PO₄ chemical activation: Pore structure and surface chemistry characterization," *Chemical Engineering Journal*, 140: 32-42.
21. SMA Collin, GJ Wan, M Ashri, B Wan, D Krishnaiah, HS Yee (2015) "Preparation and characterization of activated carbon from Typha orientalis leaves," *International Journal of Industrial Chemistry*, 6: 9-21.
22. R Gottipati (2012) "Preparation and Characterization of Microporous Activated Carbon from Biomass and its Application in the Removal of Chromium (VI) from Aqueous Phase", *Doctor Thesis*, National Institute of Technology, Department of Chemical Engineering,.
23. LM Grishchenko, VE Diyuk, OP Konoplitska, VV Lisnyak, RT Maryichuk (2017) "Modeling of copper ions adsorption onto oxidative-modified activated carbons," *Adsorption Science and Technology*, 35 (9-10): 884-900,.
24. MA Nahil, PT Williams (2012) "Pore characteristics of activated carbons from the phosphoric acid chemical activation of cotton stalks," *Biomass and Bioenergy*, 37: 142-149.
25. NK Hamadi, S Swaminathan, XD Chen (2004) "Adsorption of Paraquat dichloride from aqueous solution by activated carbon derived from used tires," *Journal of Hazardous Materials*, 112 (1-2) 133-141.
26. T Liou (2010) "Development of mesoporous structure and high adsorption capacity of biomass-based activated carbon by phosphoric acid and zinc chloride

- activation,” *Chemical Engineering Journal* , 158 (2): 129-142.
27. PU Shah, NP Raval, NK Shah (2015) “Adsorption of copper from an aqueous solution by chemically modified cassava starch,” *Journal of Materials and Environmental Science*, 6 (9): 2573-2582.
 28. T Bohli, I Villaescusa, A Ouederni (2013) “Comparative study of bivalent cationic metals adsorption Pb (II), Cd (II), Ni (II) and Cu (II) on olive stones chemically activated carbon,” *Journal of Chemical Engineering and Process Technology* , 4 (4): 1-7.
 29. AM Puziy, OI Poddubnaya, VN Zaitsev, OP Konoplitska (2004) “Modeling of heavy metal ion binding by phosphoric acid activated carbon,” *Applied Surface Science*, 221: 421-429.
 30. J Song, R Zhang, K Li, B Li, C Tang (2014) “Adsorption of copper and zinc on activated carbon prepared from typha iatifolia L . ”, *Clean Soil Air Water*, 9999 (42): 1-7.
 31. N Unlu, M Ersoz (2006) “Adsorption characteristics of heavy metal ions onto a low cost biopolymeric sorbent from aqueous solutions”, *Journal of Hazardous Materials*, 136: 272-280.
 32. A Vimalkumar, J Thilagan, K Rajasekaran, C Raja, MN Flora (2018) “Preparation of activated carbon from mixed peels of fruits with chemical activation (K 2 CO 3) -application in adsorptive removal of methylene blue from aqueous solution,” *International Journal of Environment and Waste Management*, 22(1-4): 260-271.