



## Removal of Zinc Ions from Aqueous Solutions and Groundwater Using Activated Carbon as Ion Exchange Resin

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### Abstract

In this study, converting exhausted resin with no commercial value into a promising activated carbon as adsorbent with the aid of mineral acids H<sub>2</sub>SO<sub>4</sub> (S-AC) and H<sub>3</sub>PO<sub>4</sub> (P-AC), and base NaOH (OH-AC). This is achieved by mixing the exhausted resin with concentrated sulphuric acid, phosphoric acid and powdered sodium hydroxide separately. The properties of prepared activated carbon were characterized using SEM and FT-IR techniques. The adsorption parameters, including contact time, adsorbent dosage, initial concentration and solution pH as well as solution temperature were investigated. Adsorption models, kinetic and thermodynamic studies were performed to explore and predict the adsorption of Zn(II) onto the activated carbons from aqueous solutions and groundwater. Participation of OH<sup>-</sup>, COO<sup>-</sup> and SO<sub>3</sub><sup>-</sup> groups in the adsorption of zinc ions was confirmed by FT-IR analysis. Also, SEM images showed that morphological surface changes happened after the adsorption processes occurred. The data obtained show that, increasing the carbonization temperature to 900°C reduced the removal percentage of Zn<sup>2+</sup> significantly by S-AC but showed surprisingly little effect on the selectivity of P-AC and OH-AC adsorbent. pHPZC value for S-AC, P-AC and OH-AC at 450°C was 4.3, 5.5 and 7.1, respectively. Consequently, S-AC (450°C) has excellent adsorption properties than the other carbons. The optimum contact time was 300min using S-AC (450°C), the best dosage, initial concentration and pH are 0.4g, 50mg/l and 4, respectively. This study indicates the potential of S-AC to be applied as an economically viable and efficient adsorbent for the removal of Zn(II) from groundwater by batch technique. The Elovich model with a higher correlation coefficient value, R<sup>2</sup> = 0.9864 proves a better choice in the adsorption process of Zn(II) ions from polluted solutions and groundwater. The adsorption obeys Freundlich isotherm model and the Zn(II) adsorption reaction process is considered as chemisorption process due to electrostatic interaction.

### 1. Introduction

Environmental pollution is a major problem of the today's society, which attracts the researcher attention to its severe long-term consequences. Heavy metals are important environmental pollutants, and their toxicity is causing serious threats to fresh water sources, public health and all living organisms through air, soil and water pollution. Heavy metal ions and their species have the ability to persist in natural ecosystems for long times and to accumulate gradually in living tissues and food chains, and prolonged exposure to high levels of heavy metals causes numerous illnesses and disorders [1].

Evidently, the choice of the carbon precursor for

carbonization is crucial. It is known that micro porous carbons can be obtained by means of carbonization and subsequent activation, from poly (4-ethylstyrene-co-divinylbenzene [2] or waste polymers [3]. Generally, the synthesis of activated porous carbons involves two steps. The first one is the carbonization of the selected precursor in the temperature range from 300 to 900°C, giving rise to the removal of the most non-carbon hetero-elements. The second one is the activation step, which aims to develop the porosity and the surface area of the final carbon structure [4].

For the synthesis of carbons with high surface area, among the chemical activators, many reactants can be used, from mineral acids such as H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub> [5],

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strong bases (KOH or NaOH) [6]. Sulphuric acid ( $\text{H}_2\text{SO}_4$ ) serves as a super oxidizing agent that is frequently used as a low-cost chemical activator for the preparation of carbonaceous adsorbents from various ligno-cellulosic materials such as coconut leaves [7].

In this scenario, the present work aims to introduce a new, inexpensive, and renewable adsorbent for zinc removal by converting exhausted resin with no commercial value into a promising adsorbent with the aid of mineral acids ( $\text{H}_2\text{SO}_4$  (S-AC) and  $\text{H}_3\text{PO}_4$  (P-AC) and base NaOH (OH-AC) activation. The use of exhausted resin as renewable precursor for producing carbonaceous adsorbent materials in adsorption of  $\text{Zn}^{2+}$  from aqueous solutions and groundwater in the batch-model process will diminish the large amount of exhausted resin, reduce environmental complications and produce value-added products.

The effects of zinc concentration (zinc excess and zinc deficiency) in groundwater on human health were discussed as in figure 1 based on Plum et al., 2010 [8], that said that higher concentrations of zinc than permissible levels, causing health effects include skin, stomach cramps, kidney damage, diarrhea, nausea, vomiting, respiratory disorders, and mental fever. Noteworthy to mention that, the permissible limit of Zn(II) is 0.05mg/l according to World Health Organization (WHO, 2011) [9].

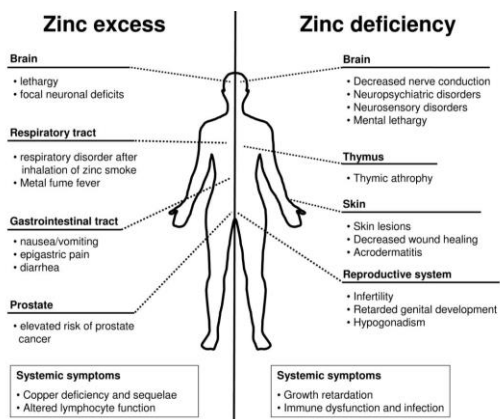


Figure 1. Comparison of the effects of zinc intoxication versus deficiency(After Plum et al., 2010)

## Experiments

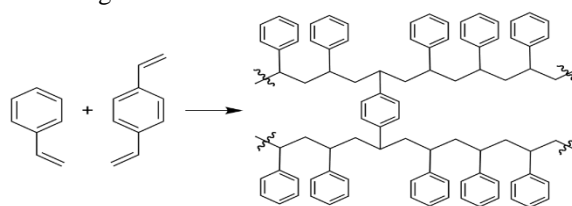
### Reagents

Sulfuric acid ( $\text{H}_2\text{SO}_4$ ), Phosphoric acid ( $\text{H}_3\text{PO}_4$ ), sodium hydroxide (NaOH), hydrochloric acid (HCl) and zinc chloride ( $\text{ZnCl}_2$ ) were purchased from Sigma-

Aldrich (St. Louis, MO, USA). Waste polystyrene as cation exchange resin (Amberjet 1500) was supplied by Beihua Chemical Building Materials Co., Ltd. (Hebei, China).

### Preparation of the carbon composites

Polystyrene divinylbenzene obtained by polymerization of (styrene and divinylbenzene), [Sketch 1]. The styrene ( $\text{C}_8\text{H}_8$ ) is polymerized with itself and with divinylbenzene ( $\text{C}_{10}\text{H}_{10}$ ) as the following structure.



Styrene Divinylbenzene Polystyrene divinylbenzene

Sketch 1. The polymerization process of styrene with divinylbenzene

Prior to its use, the resin waste was successively rinsed with ethanol, 5% HCl solution, 5% NaOH solution, and distilled water until the eluate had a neutral pH to remove impurities then dried  $60^\circ\text{C}$  for 12hrs. The carbonization was conducted in a horizontal cylindrical furnace ( $450^\circ\text{C}$  or  $900^\circ\text{C}$ ) for 3hrs (Qianqian et al., 2014) [10], after cooling the obtained carbon was activated by mixing with concentrated sulfuric acid, phosphoric acid and powdered sodium hydroxide separately at a mass ratio of 1:3. Subsequently, after cooling the obtained activated carbons (S-AC, P-AC and OH-AC) was crushed and washed with distilled water until the eluate had neutral pH, dried under vacuum.

### Batch adsorption experiments

Batch adsorption experiments were performed by shaking a mixture of a fixed amount of S-AC, P-AC and OH-AC separately with 25ml of zinc solution of a known concentration in a series of 100ml plastic bottles in a constant temperature shaker (Stuart CB302) for a known period of time. The suspensions were taken out at predetermined time intervals and centrifuged and analyzed using atomic absorption spectroscopy (SHIMADZU AA700). Several experiments were carried out with a variety of contact time, adsorbent dosage, initial concentration and solution pH as well as solution temperature, respectively. The amount of adsorbate that adsorbed

onto the carbon at time  $t$ ,  $q_t$  (mg/g) and removal% from aqueous solution or groundwater are calculated from Eqs.1 and 2, respectively.

$$q_e = \frac{(C_0 - C_e)V}{W \times 1000} \quad \text{-----} \quad 1$$

$$\text{The removal percentage yield (R \%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad 2$$

Where,  $C_0$  is the initial Zn(II) ion concentration (mg/l) at equilibrium,  $C_e$  is the concentration of Zn(II) at any time  $t$ ,  $V$  is the volume of the Zn(II) solution and  $w$  is the weight of carbon in (g). All experimental measurements were within  $\pm 0.1\%$  accuracy.

## Results and discussion

### Characterization of the synthesized activated carbons

#### Functional groups determination by FT-IR

To better understand the differences among modified activated carbons produced by different modifiers, some analysis as FT-IR analysis was performed to identify surface functional groups on the carbon surfaces before and after the removal of zinc(II) from polluted groundwater. The characterization of the activated carbons before modification at  $450^\circ\text{C}$  by FT-IR analysis was shown in Fig.(2). In this figure, it noticed that; the relatively sharp band at  $3749.62 \text{ cm}^{-1}$  is characterized for non-hydrogen-bonded hydroxyl group, often satirically hindered the OH group. The broad band centered at  $3441 \text{ cm}^{-1}$  indicates the O-H stretching vibrations of surface functional groups and chemisorbed water associated with H-bonds and carboxylic groups. This band suggests the presence of strong H-bonds between the functional groups and the adsorbed water molecules. Weak absorption band at about  $3047.53 \text{ cm}^{-1}$  is ascribed to aromatic C-H stretching vibrations. The thermal activated carbon obtained at  $450^\circ\text{C}$  shows a small peak at  $1697.36 \text{ cm}^{-1}$  that characteristic of the C=O stretching vibration. The small intensity of this peak suggests a relatively low content of carboxylic groups as compared to other oxygen groups of carbon adsorbents [11]. The spectra show a relatively strong band at  $1573.91 \text{ cm}^{-1}$  due to combined stretching vibrations of conjugated C=O group and aromatic rings [12]. The existence of phenols is supported by O-H bending at  $1427.32 \text{ cm}^{-1}$  and C-O stretching at  $1165 \text{ cm}^{-1}$  vibrations of phenols [13]. The spectra that show bands at the main fingerprint between  $1327.03$  and  $1000 \text{ cm}^{-1}$ , usually found in oxidized carbons and have been assigned to

C-O stretching in acids, alcohols, phenols, ethers and esters. The existence of bands in the region between  $1000$  and  $624 \text{ cm}^{-1}$  is characterized for C-H bending of benzene derivatives.

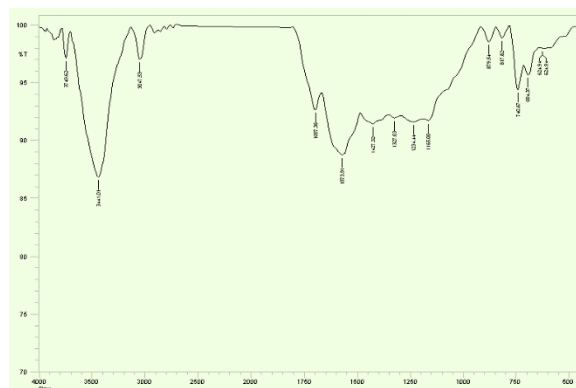


Figure 2. FT-IR spectrum of activated carbon at  $450^\circ\text{C}$

To clarify the characterization of the modified activated carbon S-AC, FT-IR spectra were done (Figs. 3a and 3b). As in (Fig.3a), the FTIR spectrum of the S-AC shows bands at  $3903.92$ ,  $3741.9$  and  $3433.29 \text{ cm}^{-1}$  assigned to  $\text{OH}^-$  stretching vibration. It noticed that, the band with intensity  $3433.29 \text{ cm}^{-1}$  in the concerned spectrum is lower than that appeared at the spectrum of the non-activated carbon (AC)  $3441.01 \text{ cm}^{-1}$  (Fig.2), this may be due to the fact that  $\text{H}_2\text{SO}_4$  initiated bond cleavage, leading to dehydration and elimination reactions that release volatile products such as water, acid, alcohol and other chemical substances. This is followed by partial aromaticity and re-combination of species to form a stronger cross-linked solid. In other words,  $\text{H}_2\text{SO}_4$  breaks many bonds in aliphatic and aromatic species present in the precursor material leading to liberation and the elimination of many lights and volatile substances causing partial amortization and thus carbonization. The appearance of bands at  $2916.37$  and  $2846.93 \text{ cm}^{-1}$  show C-H stretching of aldehyde compounds and indicates the effect of  $\text{H}_2\text{SO}_4$  on the activated carbon AC. Also, the appearance of bands at  $1697.93$ ,  $1635.64$  and  $1465.9 \text{ cm}^{-1}$  indicates to C-H bending of aromatic compound. However, the bands at  $\sim 1327.03 \text{ cm}^{-1}$  -  $1010.7 \text{ cm}^{-1}$  ( $\nu$ -C-O-C and/or C-O) is stretching in phenols, alcohols and  $\text{H}_2\text{SO}_4$  acid ( $-\text{SO}_3$  groups). In addition, if the spectrum of the modified activated carbon-  $\text{H}_2\text{SO}_4$  (S-AC) is compared with non-modified activated carbon by means of sulfur related absorption bands, it is seen that  $1165 \text{ cm}^{-1}$  and new absorption bands appeared in the spectrum of the

sample at around  $1072.42\text{--}1010.7\text{cm}^{-1}$  assigned to asymmetric and symmetric stretching vibration of  $\text{SO}_2$ , respectively, this confirmed the presence of surface  $\text{SO}_2$  complexes [7,14].

On the other hand, the FT-IR spectrum of the S-AC (Fig.3b) shows bands at  $3734.19$  to  $3433.29\text{cm}^{-1}$  assigned to  $\text{OH}^-$  stretching vibration, while the band appeared at  $3055.24\text{cm}^{-1}$  is assigned to C-H stretching. The appearance of bands at  $1681.93$  and  $1072.42\text{cm}^{-1}$  are assigned to C=O stretching and S=O stretching respectively, also the spectrum show bands around  $1072.42\text{--}1018.41\text{cm}^{-1}$  assigned to asymmetric and symmetric stretching vibration of  $\text{SO}_2$ , respectively. Also, this confirmed the presence of surface  $\text{SO}_2$  complexes. Noteworthy, the existence of bands at the region between  $1000$  and  $586.36\text{cm}^{-1}$  is characterized for C-H bending of benzene derivatives.

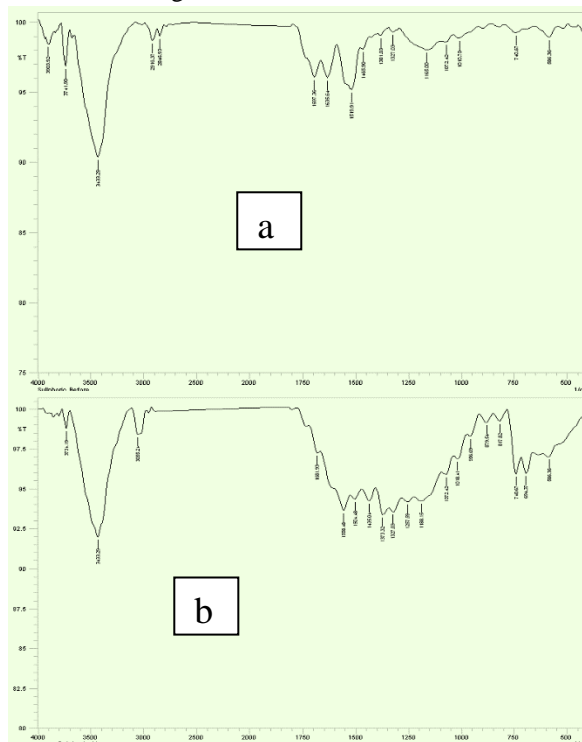


Fig.3: FT-IR Spectrum of the modified activated carbon (S-AC) before adsorption of Zinc (II) (a) and after adsorption of Zinc(II) (b)

Noteworthy to mention that, the surface chemistry of P-AC before and after zinc adsorption was analyzed. The spectra of P-AC activated carbon (Figs. 4a and 4b) show bands at  $3441.01$ ,  $3055.24$  and  $2499.75\text{cm}^{-1}$  indicates the O-H stretching. Also, the appeared bands at  $1705.07$ ,  $1697.36$  and  $1651.07\text{cm}^{-1}$  indicate the C-H bending of aromatic compound.

While, the appeared bands at  $1597.05$ ,  $1543.05$  and  $1519.91$  could be assigned to a C=O group and aromatic rings. However, the peak at  $1165\text{cm}^{-1}$  can be assigned to the stretching vibration of hydrogen-bonded P-O groups from phosphates or polyphosphates and the O-C stretching vibration in the P-O-C<sub>(aromatic)</sub> linkage. Therefore, oxygen and phosphorus enriched carbon were observed [15]. Noteworthy, the bands at  $1126.43$  and  $1118.71\text{cm}^{-1}$  indicate stretching vibrations of C-O-C in esters. The observation of those extra peaks suggests that the activated carbon surface was well modified in situ with the carbonization process, and the as-obtained carbon was significantly enhanced by covering functional groups and mineral precipitants, and then greatly strengthens the adsorption performance [16]. The existence of bands at the region between  $1000$  and  $493.78\text{cm}^{-1}$  is characterized for C-H bending of benzene derivatives.

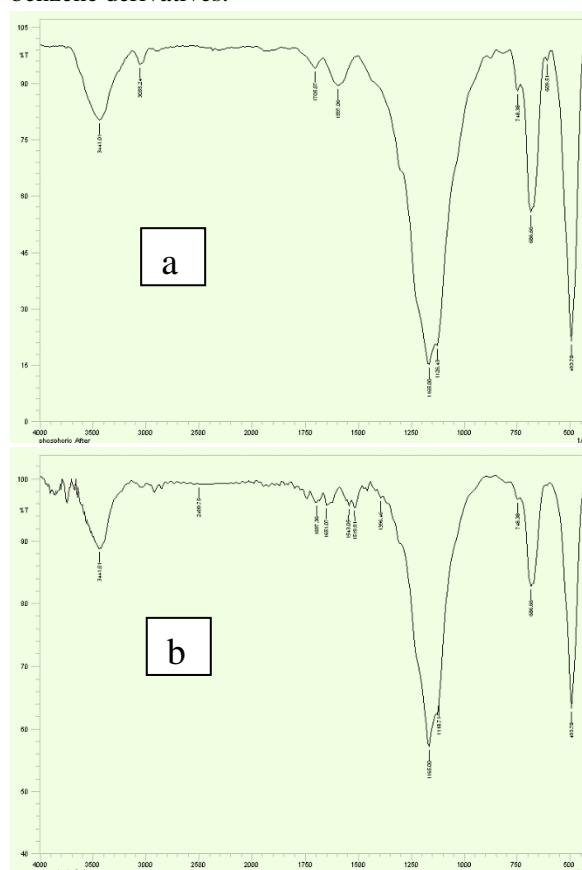


Fig.4: FT-IR spectrum of the modified activated carbon P-AC before adsorption of Zn(II) (a) and after adsorption of Zn(II) (b)

The modification of AC to OH-AC was characterized also by using FT-IR spectroscopy (Figs.5a and 5b). Overall no obvious change of any

peak could be observed. Several main peaks were detected such as the broad peaks in the region between  $3433.29 - 3749.62\text{cm}^{-1}$  and  $3047 - 3855\text{cm}^{-1}$  in Figs. 5a and 5b, respectively, these peaks assigned to the O-H stretching. Also, the appearance of low peaks at  $2916.37, 2854.65$  and  $1836.23\text{cm}^{-1}$  in Figs. 4a and 4b, respectively, indicate C-H stretching of aromatic compound. The appearance of shoulder peaks at  $1743.65, 1705.07$  &  $1697.35\text{cm}^{-1}$  and  $1635.64, 1612.49$  &  $1573.91\text{cm}^{-1}$  corresponds to the functional group of C=O stretching. While, the existence of peaks in the region between  $1041, 1165$  &  $1157\text{cm}^{-1}$  indicates to the functional group C=C stretching. Also, the being of peaks in the region between  $516-902\text{cm}^{-1}$  refers to the functional group of C-H bending. These findings revealed that the OH-AC has OH, CO and COOH as their functional groups. The introduction of NaOH onto AC may increase the amount of the functional groups on OH-AC, and NaOH have OH groups. The presence of these functional groups will make the surface of the adsorbents to be more hydrophilic and thus could enhance the absorption of positive metal ions [17 and 18]. After adsorption processes, several different and new peaks were represented. The new peaks could be attributed to C-adsorbate bond of the modified activated carbons [19]. A new peak appearing at  $445\text{cm}^{-1}$  is responsible for the zinc oxygen bond [20].

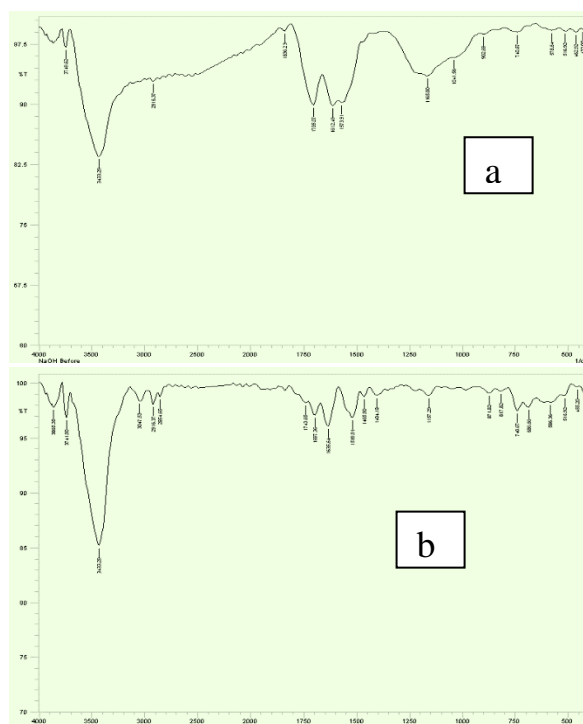


Fig.5: FT-IR spectrum of the modified activated

carbon OH-AC before adsorption of Zn(II) (a) and after adsorption of Zn(II) (b)

#### Scanning electron microscope

This characteristic was done for the S-AC activated carbon (as an example) to show the microstructure of the modified activated carbon (S-AC) before and after adsorption of zinc ions was investigated using scanning electron microscope technology (Figs. 6a and 6b). As in Fig. 6a, it can be observed that the surface of the S-AC has cracked and is slightly damaged, while in Fig. 6b, the activated carbon surface shows numerous and is significantly damaged, as a result of the dehydrating action of the agent. This is confirmed by Marzbali et al., 2016 [21] who stated that these cavities created further active sites, which led to more adsorption processes.

Clearly, it can be observed that the surface of the activated carbon after the adsorption process became smooth where the cracks were disappeared and also few cavities was shown as a result of zinc adsorption (Fig. 6b).

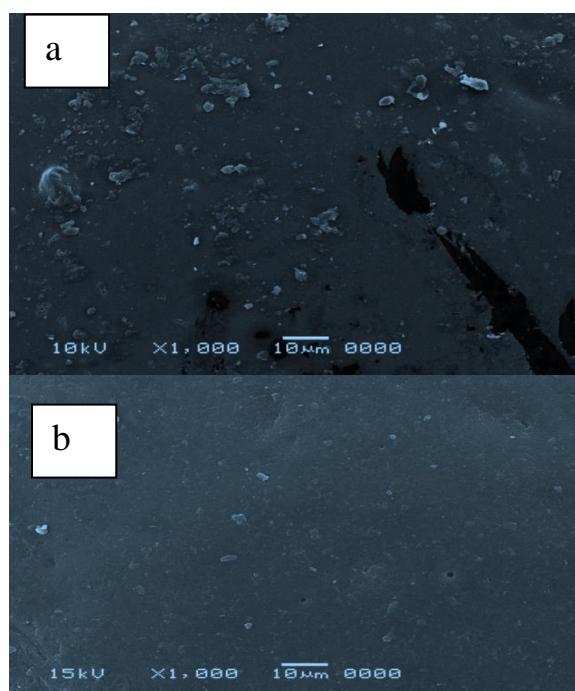


Fig.6: SEM image of modified activated carbon S-AC before adsorption process of Zn(II) (a) and after the adsorption process of Zn(II)

#### Surface charge analysis

The point of Zero charge is the pH for which the net surface charge of the adsorbent is equal to zero. The surface charge of the prepared activated carbons was determined by  $\text{pH}_{\text{PZC}}$  analysis, where  $\text{pH}_{\text{PZC}}$  values for

S-AC, P-AC and OH-AC carbonized at 450°C are 4.3, 5.5 and 7.1 while at 900°C  $pH_{PZC}$  values are 5.2, 4.1 and 8.7, respectively, Figs.(7a and 7b). This is further reconfirming the availability of the acidic functional groups on the carbon's surface. Generally, oxygen-containing functional groups can strengthen the interactions between adsorbents and adsorbate by forming surface complexes, cation- $\pi$  bonding, electrostatic attraction and/or ion exchange, resulting in a faster adsorption rate and a higher adsorption ability [22]. Figs.(7a and 7b) show that the difference between isoelectric points,  $pH_{PZC}$  (i.e. Their acidity) values is proportional to the oxygen content of the prepared modified activated carbons. This is due to the trends of the presence of oxygenated groups on the carbon surface to increase the strength of the electrostatic interaction (increase of adsorption uptake via the increase of the surface charge by shifting the  $pH_{PZC}$  to acidic values of S-AC). A negative surface charge of the carbon's surface can be obtained at pH environment above the  $pH_{PZC}$ , preferring the adsorption of zinc cation species. Generally, the adsorption of zinc cation species can be attributed to the presence of OH,  $COO^-$ , and  $SO_3^-$  groups on the surface of the carbons. As the  $pH_{PZC}$  of S-AC is lower than that of both P-AC and OH-AC, so, S-AC has excellent adsorption properties for the removal of  $Zn^{2+}$  from aqueous solution and groundwater [7].

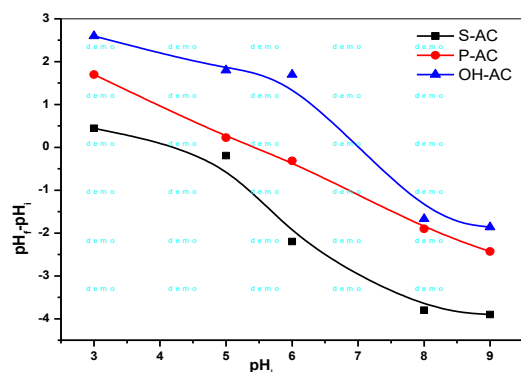


Fig.7a. Point of zero charge of different activated carbons (carbonized at 450°C)

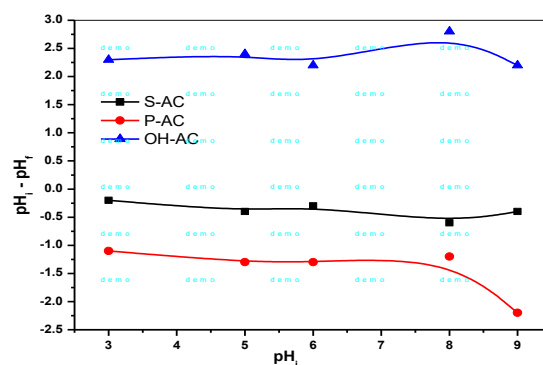


Fig.7b. Point of zero charge of different carbons (carbonized at 900°C)

### Effects of various factors on the zinc adsorption process using S-AC 450°C

To obtain the optimization of the adsorption conditions in aqueous solutions, there are different important parameters were studied.

#### Effect of contact time on the adsorption process

The investigation of this parameter can save money and energy in the case of industrial-scale adsorption processes. The zinc ions adsorption process at different contact times was studied by adding 0.1g of S-AC, P-AC and OH-AC adsorbents individually in 25 ml of zinc ions solution of concentration 5mg/l without adjusting pH. As shown in Fig.8, the removal percentage of zinc ions swiftly increase at the first 60min of contact time until reaching to the equilibrium at about 300min using S-AC (450°C) and maximum removal percentage of 82%. After that, no significant change was observed in the removal percentage by increasing the contact time. However, the maximum removal percentage of 28% was achieved at the same equilibrium time of 300min using S-AC (900°C). On the other hand, maximum removal percentages of 38% and 16% was observed at 300min and 180min for both P-AC (450°C and 900°C, respectively), while 240min and 180min was sufficient to achieve the maximum removal percentages of 48% and 36% of  $Zn^{2+}$  from aqueous solutions using both OH-AC (450°C) and OH-AC (900°C), respectively.

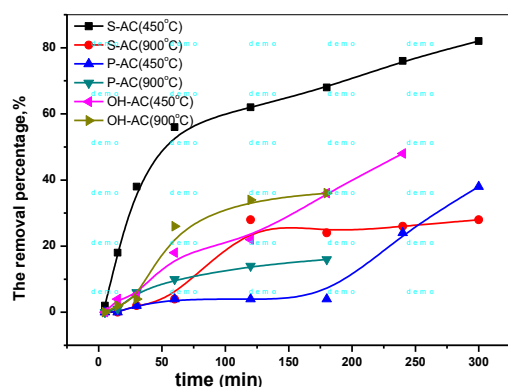


Fig.8 Effect of contact time on the removal percentage of Zn (II)

It is worth noting that, Fig.8 shows that, increasing the carbonization temperature to 900°C reduced the removal percentage of  $Zn^{2+}$  significantly by S-AC but shows surprisingly little effect on the selectivity of P-AC and OH-AC adsorbent [23]. In other word, further increase of the carbonization temperature to 900 °C resulted in a decrease of the surface area, that may be due to a collapse of the structure of the prepared activated carbon. Based on the above, it was decided to not further examine the activated carbon sample of AC 900°C [24].

According to the above results, it could be shown a higher removal percentage, happened at temperatures lower than 900°C (AC 900°C). Consequently, choosing optimum carbonization temperature as 450°C (AC 450°C) was suitable to maximize of zinc ions removal.

#### Effect of sorbent dosage on the adsorption process

The amount of adsorbent has an another important role in the adsorption process as it determines the adsorption capacity. The influence of adsorbent dosage on the adsorption process of  $Zn^{2+}$  ions was examined with S-AC, P-AC and OH-AC ranges individually from 0.1g(100mg) to 0.4g (400mg), while the initial metal ion concentration of 50mg/l and the temperature of 23°C during the contact time of 300min (Fig.9). The adsorption efficiency was sharply increased from 40 to 92%, from 40 to 72% and from 39.6 to 94% for S-AC, P-AC and OH-AC respectively, with carbon loading increases, respectively. These results can be explained by the fact that for the optimum adsorption, extra sites must be available for the adsorption reaction, whereas by increasing the carbon dosages, the number of sites available for adsorption increases, then the adsorption capacity  $q_t$  (mg/g) was decreased. This is confirmed by Kyzas et

al., 2016 [24] who said that with the increase of the amount of carbon, the decrease of  $q_t$  is due to the unsaturation of the sites during the adsorption reaction. From the Fig.9, it was shown that the best dosage is 0.4g.

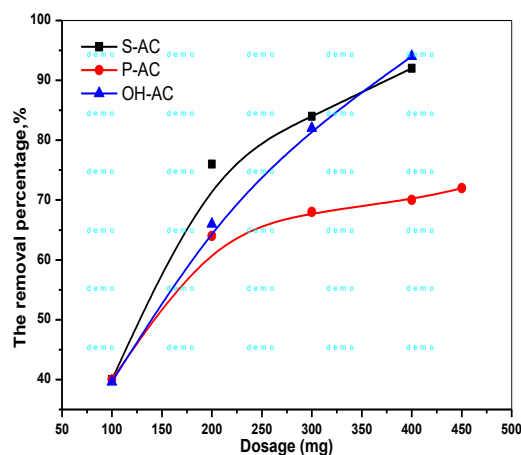


Fig.9. Effect of different carbon dosage on the removal percentage of Zn(II)

#### Effect of initial concentration on the adsorption process

The effect of initial  $Zn^{2+}$  concentrations on their removal (%) onto the prepared different carbons, S-AC, P-AC and OH-AC was examined with initial zinc ion concentration from 50 to 150mg/l, at temperature of 23°C, adsorbent dosage of 0.4g(400mg) in 25 ml of zinc ions solution and contact time 300min. Fig.10 displays that the removal efficiency of zinc ion declines from 40% to 34.6%, from 40 to 26.6% and from 39.6 to 33.33%, while the uptake capacity increases from 5 to 13mg/l, from 5 to 10mg/l and from 4.95 to 12.5mg/l using S-AC, P-AC and OH-AC, respectively. The higher adsorption of zinc ions at low concentration can be related to the increase of available active sites on the adsorbent surface for lesser number of zinc ions, while the reduction in the adsorption of zinc ions at the high initial concentration can be related to the diminution of available active sites. Consequently, the best initial concentration is 50mg/l.

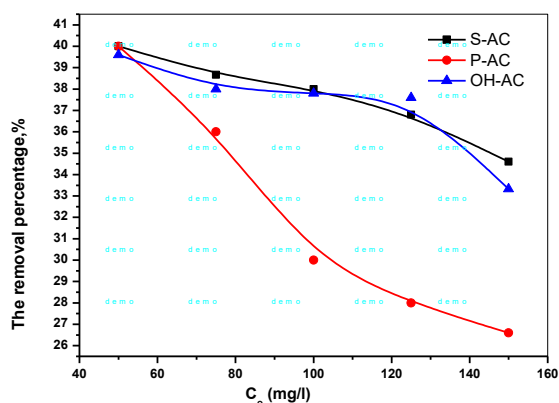


Fig.10. Effect of Initial concentrations on the removal percentage of Zn(II)

### Effect of aqueous solution pH on the adsorption process

The influence of solution pH on the sorption capacity of different prepared carbons namely; S-AC, P-AC and OH-AC was studied at varying pH values, contact time 300min, dosage 0.4g and initial concentration 50mg/l (Fig.11). The solution pH was found to severely affect the metal uptake capacity of the carbon, where at pH values about 4.0 a maximum removal percentage (78%) was reached and then decreased at higher pH using S-AC. On the other hand, the maximum removal percentage of Zn(II) shows a gradual increase with the increase of the solution pH to reach 24% at pH 4 using P-AC. Although, the maximum removal percentage of Zn(II) reached to 72% at low pH 2 using OH-AC. This is due to the surface functional groups are found to play an important role in metal binding at different pH conditions [25]. Where, at lower pH values, the functional groups are protonated with  $H^+$ , or other light metal ions which imply that the majority of the binding sites were occupied. As the pH increases, the concentration of  $H^+$  ions decreases and negatively charged biomass surface can interact with the positively charged metal ions. In other words, the pH also influences the chemical speciation of metal in the solution. For instance, Zn(II) is present mainly as  $Zn^{2+}$  at  $pH < 7$ ; and at  $pH 8-9$ , it exists mainly as  $Zn^{2+}$  and  $Zn(OH)_2$ , and in small quantities as  $Zn(OH)^+$ . The precipitation occurs in pH values higher than 8 (pH 10) for Zn(II) ions in solution [26].

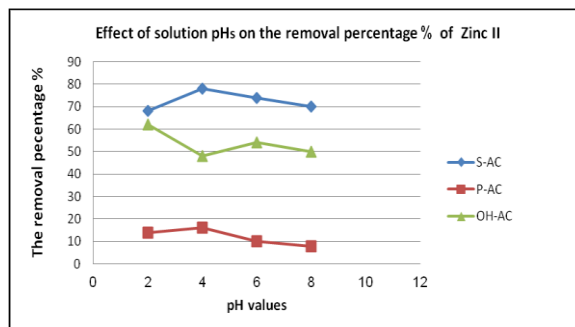


Fig.11. Effect of solution pHs on the removal percentage of Zinc (II)

### Effect of aqueous solution temperature on the adsorption process

Temperature is an important factor influencing adsorption process. The effect of solution temperature on metal ion adsorption performance was studied at four different temperatures, pH 4, contact time 300min, dosage 0.4g and initial concentration 50mg/l, and the results are shown in Fig.12.

It was shown from Fig.12 that, the adsorption increases as the temperature increase until the temperature was raised beyond 33 and 43°C for P-AC and S-AC carbons, respectively, the metal ion adsorption decreased. This could be attributed to the degrading stability of adsorption sites with increasing temperature. High agglomeration rates at elevated temperature drastically reduced its adsorption efficiency.

Also, the Fig. 12 clearly shows that higher adsorption is achieved at the lowest temperature 23°C for OH-AC carbon and hence the performance reduce at higher temperature. This is supported by Nagireddi, 2016 [27] who stated that, the observations are in good agreement with the theoretical insight that higher temperatures are not favorable for adsorption process. In other words, adsorption of zinc ions on the OH-AC carbon is an exothermic process so it should give better performance at lower temperature. But with the increase in temperature, the diffusivity of solute increases resulting in lowering of pore diffusion resistance. These two counter effects make adsorption thermodynamics as a process specific parameter, having its own operating window [28].



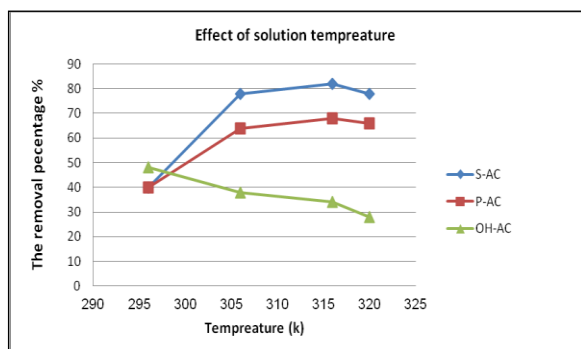


Fig.12. Effect of solution temperature on the removal percentage of zinc II

### Thermodynamic Study

Thermodynamic study is much more useful as it provides effective information on carrying out the adsorption process. To find out the thermodynamic parameters of zinc adsorption onto prepared carbons, a study was carried out at four different temperatures (296, 306, 316 and 320K). This helpful study was done to find out the consequence of temperature on the zinc adsorption process onto S-AC, P-AC and OH-AC. The thermodynamic parameters related to adsorption method, such as free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) were determined by using the following equations:

$$\Delta G^\circ = -RT \ln K_d \quad \text{-----} \quad (3)$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad \text{-----} \quad (4)$$

Where  $K_d$  is the adsorption equilibrium constant ( $q_e/C_e$ ),  $R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and  $T$  is the temperature in Kelvin. The values of  $\Delta S^\circ$  and  $\Delta H^\circ$  can be determined from the intercept and slope of a linear plot of  $\ln K_d$  against  $1/T$  (Fig.13). The calculated values of  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  are shown in Table 1. The negative value of  $\Delta G^\circ$  indicates the feasibility and spontaneous nature of the adsorption process of  $\text{Zn}^{2+}$  on S-AC, P-AC and OH-AC, and more negative value indicates that the adsorption process becomes more spontaneous with rise in temperature to 320K, which favors the adsorption process. The negative value of  $\Delta H^\circ$  for OH-AC represents an exothermic adsorption process and negative value of  $\Delta S^\circ$  for OH-AC indicates the decrease in randomness at the solid-solution interface during the adsorption process.

**Table 1. Thermodynamic parameters for Zn(II) adsorption onto the carbons in aqueous solution.**

Carbon	Temp.	$\Delta G^\circ$ KJ/mol	$\Delta H^\circ$ KJ/mol	$\Delta S^\circ$ J/mol K	$R^2$
--------	-------	----------------------------	----------------------------	-----------------------------	-------

S-AC	296	4.417	53.28	169.82	0.6516
	306	0.308			
	316	-0.341			
	320	-0.801			
P-AC	296	4.417	37.75	115.26	0.7962
	306	2.063			
	316	1.660			
	320	-0.907			
OH-AC	296	4.417	-20.34	-83.30	0.8027
	306	0.401			
	316	5.400			
	320	-6.787			

On the other hand, the  $\Delta H^\circ$  parameter has positive values of 53.28 and 37.75 kJ/mol for the adsorption of Zn(II) ions on both S-AC and P-AC adsorbents, respectively, indicating the endothermic nature of the adsorption process of zinc ions onto the S-AC and P-AC carbons in the temperature range of 296 to 320K. The  $\Delta S^\circ$  parameter was found to be 169.82 and 115.26 J/mol K for the adsorption of Zn(II) on S-AC and P-AC, respectively. The positive values of  $\Delta S^\circ$  show the affinity of the adsorbent and the increasing randomness at the solid-solution interface during the adsorption of Zn(II) on S-AC and P-AC. However, the positive values of  $\Delta G^\circ$  indicate the infeasibility and nonspontaneous nature of the adsorption process of  $\text{Zn}^{2+}$  on S-AC, P-AC and OH-AC at 296, 306 and 316K, respectively.

So, based on the previous results, the S-AC was selected for the treatment of different groundwater samples in the northwest coast (Egypt).

### Adsorption kinetics studies

Adsorption kinetics studies help in assessing the adsorption mechanisms in terms of order and rate constants, and provides useful information on possible rate control steps. Four kinetic models, pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion models were used to study the kinetics of the adsorption process of zinc by two groups of activated carbons, first group includes S-AC 450°C, P-AC 450°C and OH-AC 450°C and the second group includes S-AC 900°C, P-AC 900°C and OH-AC 900°C.

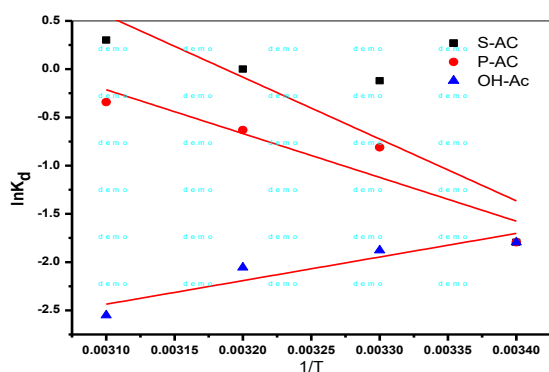


Fig.13. Van't Hoff plots of zinc ions adsorption on various carbons

### The pseudo-first order model (Lagergren, 1898)

Lagergren [29] suggested a pseudo-first-order equation for sorption of liquid, solid system based on solid capacity. It assumes that the rate of change of sorbate uptake with time is directly proportional to the difference in the saturation concentration and the amount of solid uptake with time. The Lagergren equation is the most widely used rate equation in liquid phase sorption. The general equation of the pseudo-first order model is generally expressed as follows;

$$\frac{dq}{dt} = k_1(q_e - q_t) \text{-----} 5$$

Where  $q_e$  and  $q_t$  are the amount of metal sorbed per unit weight of sorbent at equilibrium and at any time  $t$  (mg/g), respectively, and  $k_1$  is the rate constant of pseudo-first order sorption ( $\text{min}^{-1}$ ). After integration and applying boundary conditions, for  $t = 0$  and  $q = 0$ , the integrate form of Eq.(5) became;

$$\ln(q_e - q_t) = \ln q_{e,1} - k_1 t / 2.303 \text{-----} 6$$

The values of rate constant ( $k_1$ ) and equilibrium capacity ( $q_{e,1,cal}$ ) can be obtained from the slope and intercept of plotting  $\log(q_e - q_t)$  against time.

A plot of  $\ln(q_e - q_t)$  versus  $t$  (Fig.14) gave a linear curve, and the data obtained from the adsorption experiments of Zn(II) onto the first and second groups of activated carbons were summarized in table (2).

It is evident that the high correlation coefficient ( $R^2$ ) values obtained by pseudo-first order model suggests that this model is appropriate for Zn(II) adsorption.

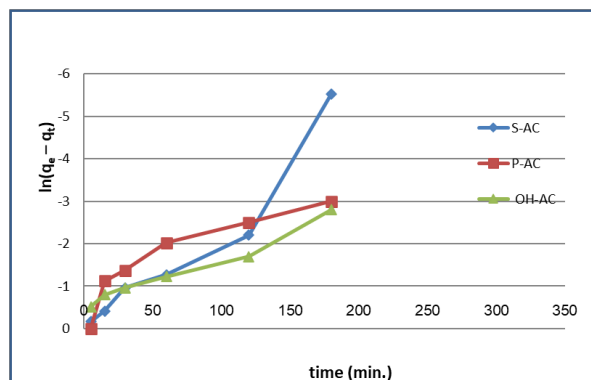


Fig.14. Pseudo-first order plot of zinc(II) adsorption process

### The pseudo-second order model (Ho et al., 2000)

Ho et al., 2000 [30] developed a pseudo-second-order model which is based on the assumption of chemisorption of the adsorbate on an adsorbent, i.e., the amount of sorbed sorbate on the sorbent. Also, this model is based on the assumption that the rate limiting step may be a chemical sorption involving valence forces through the sharing or exchange of electrons between the adsorbent and the adsorbate [31].

If the rate of sorption is a second order mechanism, the pseudo-second order chemisorption kinetic rate equation is expressed as;

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \text{-----} 7$$

Where  $k_2$  is the rate constant of pseudo-second order sorption [ $\text{g}/(\text{mg min})$ ],  $q_e$  is the amount of solute sorbet at equilibrium (mg/g) and  $q_t$  is the amount of solute sorbet on the surface of the adsorbent at any time  $t$ (mg/g).

Integrating the equation 7 for the boundary conditions for  $t = 0, q = 0$  gives

$$\frac{t}{q} = \frac{1}{k_2 q_{e,2}^2} + \frac{1}{q_{e,2}} t \text{-----} 8 \text{ and}$$

$$h = k_2 q_{e,2}^2 \text{-----} 9$$

Where  $h$  [ $\text{mg}/(\text{g min})$ ] means the initial adsorption rate, and the constants can be determined experimentally by plotting of  $t/q$  against  $t$ .

The values of the obtained  $R^2$  from the pseudo-second order model indicate the suitability of this model for predicting the adsorption of Zn(II) onto the first group includes S-AC 450°C, P-AC 450°C and OH-AC 450°C. Also, the values of the obtained  $R^2$  from the pseudo-second order model indicate the unsuitability of this model for predicting the adsorption of Zn(II) onto the second group includes S-

AC 900°C, P-AC 900°C and OH-AC 900°C.

The pseudo-second order model describes the adsorption equilibrium capacity as well as the chemisorptive behavior of the adsorption process. A plot of  $t/q_t$  versus  $t$  (Fig.15) gave a linear curve. These results implied that the pseudo-second order is fitting for the adsorption of Zn(II) onto the first group of carbon (450°C) only. So, this suggests that the rate-limiting step of the adsorption process is chemical adsorption.

The lower correlation coefficient values suggest that the pseudo-second order model is not appropriate for Zn(II) adsorption.

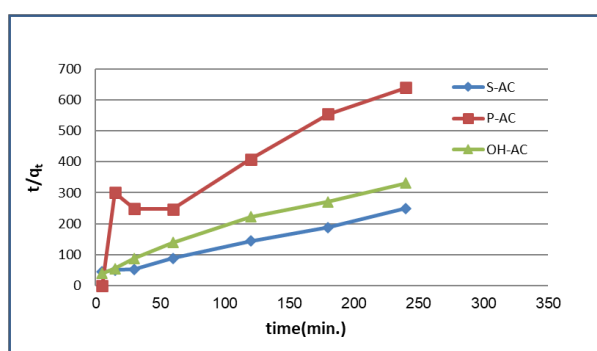


Fig.15. Pseudo-second order plot of zinc(II) adsorption process

### Elovich kinetic model

The Elovich [32] equation has general application to chemisorption kinetics. This equation has been applied satisfactorily to some conception data, and has been found to cover a large range of slow adsorption [33]. The Elvis equation is often valid for a system in which the adsorbing surface is heterogeneous.

The equation is formulated as;

$$dq_t/dt = a \exp(-bq_t) \text{-----} 10$$

or integrated form as;

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} (\ln t t_0) \text{-----} 11$$

Taylor et al. [34] studied the kinetics of zinc ion sorption by soils and concluded that the Elovich equation is the best fitting equation.

Elovich model can be used to interpret the sorption of zinc onto activated carbon. This can be done by plotting  $q_t$  against  $\ln(t)$ .

The parameters  $a$  and  $b$  are calculated from the intercept and the slope of lines according to the Elovich equation,  $q = 0$  at  $t = 0$ , therefore, the time constant  $t_0$  can be calculated from this equation  $t_0 = 1/ab$ .

From the Fig.(16), it was shown that when the mass of sorbent is fixed, the increase in concentration caused the constant a to increase but the constant b decrease when the concentration was fixed, the effect of increasing the mass sorbent increased the constant a and b.

In general; (i) enhanced initial uptake due to certain particularly active surface sites at small t, quickly becoming dependent on the main kinetics (or diffusion) controlling process [35]. (ii) An initial rate retardation due to a boundary layer film resistance before the controlling kinetic (diffusion) mechanism stabilizes for most of the adsorption process [36 & 37].

The Elovich kinetic model equation is generally expressed as follows;

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} (\ln t_0 t) \text{-----} 11$$

Where  $\alpha$  is the initial adsorption rate in mg/(g.min) and  $\beta$  (g/mg) is the desorption constant related to the extent of the surface coverage and activation energy for chemisorption. Both the Elovich coefficients (kinetic constants)  $\alpha$  and  $\beta$  will be estimated from the slope and intercept of the linear plot of  $q_t$  versus  $\ln(t)$ .

If the adsorption process of Zn(II) was carrying out using S-AC 450°C, P-AC 450°C, P-AC 900°C and OH-AC 450°C carbons, it will fits the Elovich model and a plot of  $q_t$  versus  $\ln(t)$  should yield a linear relationship with a slope of  $(1/\beta)$  and an intercept of  $1/\beta \ln(\alpha\beta)$  [38].

As in table 2, the correlation coefficients obtained by Elovich model showed good linearity with both S-AC 450°C ( $R^2 = 0.9864$ ), P-AC 450°C ( $R^2 = 0.9720$ ), P-AC 900°C ( $R^2 = 0.9517$ ) and OH-AC 450°C ( $R^2 = 0.9741$ ) which means that this model is a good model for adsorption of Zn(II) onto this carbons.

On the other hand, it can also be observed that Elovich model gave an account of the occurrence of desorption process, while this model was poor fits for S-AC 900°C ( $R^2=0.8370$ ) and OH-AC 900°C ( $R^2=0.8654$ ), It is clear that the correlation coefficients obtained were almost linear which indicated that Elovich model fitted well for adsorption. The model gave a good correlation for adsorption on highly heterogeneous surface carbon. Besides, it is also shown that along with surface adsorption, chemisorptions was also a dominant phenomenon taking place [39].

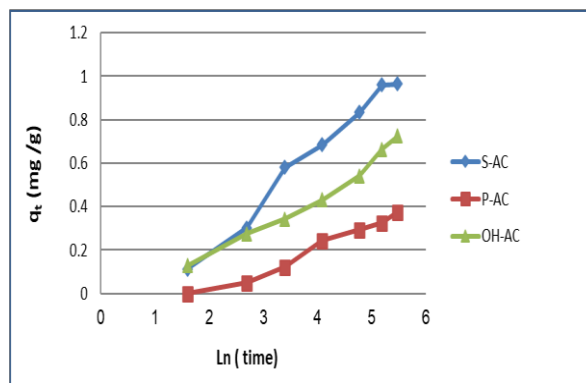


Fig.16. Elovich plot of Zn(II) adsorption process Intra-particle diffusion equation (Weber and Morris, 1963)

The initial rate of the intraparticle diffusion according to Weber and Morris, 1963 [40] is the following;

$$q_t = K_{int} t^{0.5} + C \text{-----} 12$$

Where  $K_{int}$  is the intraparticle diffusion rate coefficient ( $\text{mg g}^{-1} \text{min}^{1/2}$ ) and  $C$  ( $\text{mg g}^{-1}$ ) provides an idea about the thickness of the boundary layer. The  $K_{int}$  and  $C$  can be obtained from the slope and intercept of a straight line plot of  $q_t$  versus  $t^{0.5}$  (Fig.17).

The kinetic results were analyzed by the intra-particle diffusion model in order to elucidate the diffusion mechanism.

The obtained correlation coefficients ( $R^2$ ) of the intra-particle diffusion are 0.9139, 0.8840 and 0.8832 suggesting that two or more steps are involved in Zn(II) adsorption onto the OH-AC 450°C, P-AC 900°C and S-AC 900°C, respectively. Higher values of the obtained  $R^2$  from intra-particle diffusion model indicate that this model fitted well for adsorption of Zn(II) by OH-AC 450°C, P-AC 900°C and S-AC 900°C, respectively, while the lower value indicates the unsuitability of this model for predicting the adsorption of Zn(II) onto the other adsorbents of this model.

Weber and Morris's intra-particle diffusion model helps to identify the diffusion mechanism and the rate-limiting step. The boundary layer thickness ( $C$ ) and intra-particle diffusion rate constant ( $K_{int}$ ) can be deduced from the intercept and slope of the plot of  $q_t$  versus the square root of time ( $t^{1/2}$ ), respectively. It was observed from the plot that, the adsorption process takes place in two phases. The first phase depicts the

rapid adsorption of zinc ions over a certain period of time, whereas the adsorption rate became slower in the second phase. This could be due to the chemisorptive interactions during the first stages of the adsorption process followed by intra-particle diffusion in the second stage. From Fig.17, the lines failed to pass through the origin, which suggests that intra-particle diffusion cannot be considered the rate-limiting step.

As in table 2, the obtained correlation coefficients by intra-particle diffusion model was 0.9139, and 0.8840 0.8832 for OH-AC 450°C, P-AC 900°C and S-AC 900°C, respectively, which means that the intra-particle diffusion model was fitted for adsorption of Zn(II) onto OH-AC 450°C, P-AC 900°C and S-AC 900°C, while it was poor fitted for adsorption of Zn(II) onto the other adsorbents.

The previous results were shown that the activation temperature (450°C) is the best temperature for activation of adsorbent carbons. The pseudo-first order model is appropriate for predicting the adsorption process of Zn(II) onto (S-AC 450°C, P-AC 900°C, OH-AC 450°C and OH-AC 900°C), while the pseudo-second order model is fitted for predicting the adsorption process of Zn(II) only onto S-AC 450°C and OH-450°C. Also, Elovich model is appropriate for predicting the adsorption process of Zn(II) onto S-AC 450°C, P-AC 450°C, P-AC 900°C and OH-AC 450°C carbons. Finally, the intra-particle diffusion model is appropriate for predicting the adsorption process of Zn

(II) only onto the OH-AC 450°C. So, the Elovich model is the best model for adsorption of Zn(II) onto these activated carbons.

### Adsorption isotherm modeling of the ions

Isotherms are the equilibrium relations between the concentration of adsorbate on the solid phase and its concentration in the liquid phase. From the isotherms, the maximum adsorption capacity can be obtained. These data provide information on the capacity of the sorbent or the amount required to remove a unit mass of pollutants under the system conditions. The data in table (3) has been subjected to different adsorption isotherms. Langmuir, Freundlich, Temkin and D-R are the most common isotherms describing solid-liquid adsorption system.

Adsorption isotherm experiments were also performed by agitating an amount of the activated carbons (S-AC, P-AC and OH-AC) with a 25ml aqueous solution at varying metal ion concentrations and interval times. The contents were continually agitated in a temperature controlled flask shaker. At the end of the pre-determined time intervals, the amount adsorbed was determined from the difference in the initial and residual concentrations of the metal ion in the liquid phase. The data were fitted into table 3.

Table 2. The kinetic parameters of Zn<sup>2+</sup> adsorption in aqueous solutions using different carbons

Kinetic model	S-AC (450°C)	S-AC (900°C)	P- AC (450°C)	P-AC (900°C)	OH- AC (450°C)	OH-AC (900°C)
PFO						
q <sub>e,1</sub> ,cal	1.146	1.0224	0.4976	0.3338	0.5903	0.6075
k <sub>1</sub>	0.0277	0.0159	0.0142	0.0227	0.0118	0.0273
R <sup>2</sup>	0.9184	0.8640	0.8264	0.9089	0.970	0.9484
PSO						
q <sub>e, 2</sub> ,cal	1.1461	0.7745	0.4583	0.4474	0.8046	8.7873
k <sub>2</sub>	0.0127	0.0013	0.0227	0.00243	0.0129	0.0001
h	0.0292	0.0020	0.0208	0.0022	0.0207	0.0028
R <sup>2</sup>	0.9954	0.0106	0.8457	0.1349	0.9808	0.0011
Elovich						
β	4.3421	10.050	9.8912	16.556	6.6800	6.8870
α	0.0736	0.0085	0.0151	0.0081	0.0592	0.0166
R <sup>2</sup>	0.9864	0.8370	0.9720	0.9517	0.9741	0.8654
Intraparticle diffusion						
K <sub>int</sub>	0.0032	0.0013	0.0021	0.0011	0.0023	0.0028
C	0.3744	0.0057	0.0641	0.0201	0.2335	0.0192
R <sup>2</sup>	0.7747	0.8832	0.8454	0.8840	0.9139	0.8495

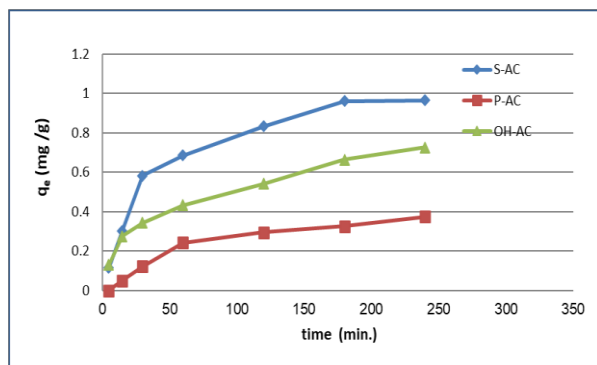


Fig.17. Intra-particle diffusion model plot of Zn (II) adsorption process

### Langmuir isotherm [41]

Langmuir isotherm [41] is often used to describe adsorption of solute from liquid solutions on the adsorbent and this model assumes monolayer adsorption onto a homogeneous surface with a finite number of identified sites. In order to know the feasibility of the isotherm, the essential features of the Langmuir model can be expressed in terms of separation factor or equilibrium parameter  $R_L$ .

The Langmuir equation is represented in the linear form as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_{max}} + \frac{C_e}{Q_{max}} \quad \text{-----} \quad 13$$

Where  $C_e$  is the equilibrium concentration of adsorbate (mg/l),  $q_e$  is the amount of solute sorbate at equilibrium (mg/g),  $K_L$  is the Langmuir adsorption constant ( $L \text{ mmol}^{-1}$ ) which is related to the affinity of the binding sites and?  $Q_{max}$  is the theoretical maximum adsorption capacity (mg/g).

Langmuir plots ( $\frac{C_e}{q_e}$  vs.  $C_e$ ) for adsorption of metal ions onto the treated carbon at different concentrations (Fig.18).

For the Langmuir isotherm model, a dimensionless constant ( $R_L$ ), commonly known as separation factor or equilibrium parameter can be used to describe the favorability of adsorption on the polymer surface by;

$$R_L = \frac{1}{(1+K_L C_0)} \quad \text{-----} \quad 14$$

Where,  $C_0$  is the initial metal ions concentration and  $K_L$  is the Langmuir equilibrium constant.

The values of  $R_L$  indicate that the shapes of isotherms to be either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ). The  $R_L$  values for Zn ions were calculated and plotted

against the initial metal ion concentration (Fig.19).

Also, it is observed from Fig.18 that, the sorption of Zn ions on the activated carbons (S-AC, P-AC and OH-AC) increases as the initial metal ion concentration increase, indicating that this adsorption is even favorable for Zn ions concentrations that have been investigated [42]. It is noticed that  $R_L$  values in this study are in the order ( $0 < R_L < 1$ ), indicated that the activated carbons (S-AC, P-AC and OH-AC) are favorable for adsorption of Zn(II) ions from aqueous solutions.

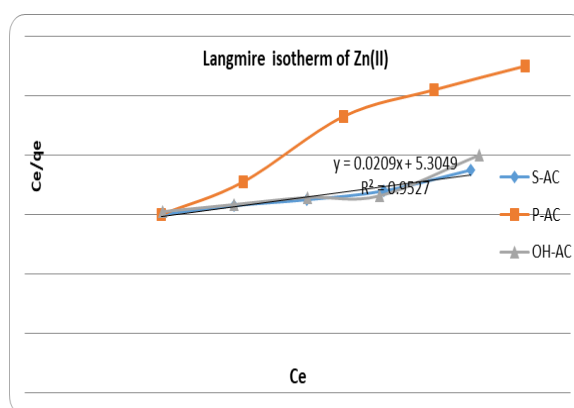


Fig.18 Langmuir isotherm of zinc (II)

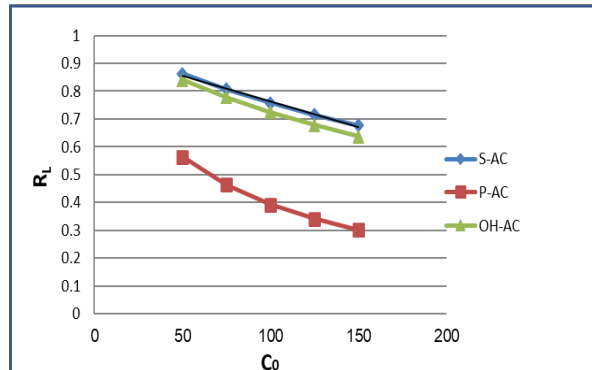


Fig.19 Effect of initial concentration on the separation factor

### Freundlich isotherm [43]

Freundlich isotherm [43] represents the relationship between the amounts of ionic species exchanged per unit mass of the activated carbon ( $q_e$ ) and the concentration of the ionic species at equilibrium ( $C_e$ ).

The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of sorption heat over the surface. It can be stated in the linear form as follows;

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad \text{-----} \quad 15$$

Where,  $K_F$  ( $\text{mg g}^{-1}$ ) and  $n$  are the isotherm constants that indicate the capacity and intensity of the adsorption, respectively.

The linear plot between  $\ln q_e$  versus  $\ln C_e$  gives a slope which is equal to the value of  $1/n$  and the intercept is  $\ln K_F$  (Fig.20). The magnitude of  $1/n < 1$  indicates the favorability of the adsorption process.

It obvious from (Fig.20) that, the uptake increases with the increase of the initial concentration and this may be due to that at lower concentration of the solute in the solution leads to low adsorption where at higher concentration of the solute, the adsorption process will increase due to the abundance of the zinc ions in the solution.

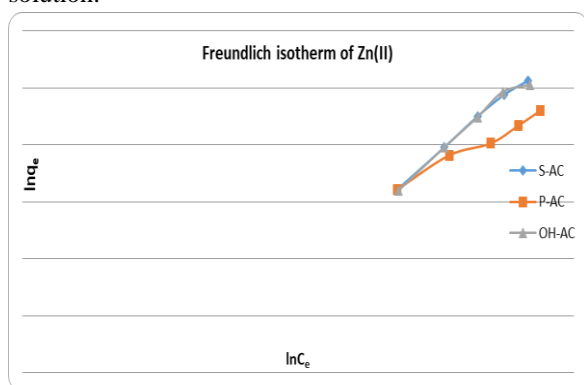


Fig.20 Freundlich isotherm of Zn(II)

### Temkin isotherm [44]

The Temkin isotherm model takes into account the effects of indirect adsorbate/adsorbent interactions on the adsorption process [45].

The Temkin isotherm has been used in the following form:

$$q_e = \left(\frac{RT}{b_T}\right) \ln A_T + \left(\frac{RT}{b_T}\right) \ln C_e \quad \text{-----} \quad 16$$

Where,  $B_T = \left(\frac{RT}{b_T}\right)$  is the Temkin constant (J/mol) which is related to the adsorption heat,  $T$  is the absolute temperature (K),  $R$  is the gas constant ( $8.314 \text{ J/mol K}$ ), and  $A_T$  is the Temkin isotherm constant (L/g). ( $B_T$ ) and ( $A_T$ ) can be calculated from the slope ( $b_T$ ) and intercept ( $b_T \ln A_T$ ) of the plot of  $q_e$  vs.  $\ln C_e$ .

Temkin isotherm assumed that (i) the heat of adsorption ( $\Delta H_{\text{ads}}$ ) of all molecules in the layer decreases linearly as a result of increase surface coverage and (ii) adsorption is characterized by a uniform distribution of binding energies up to some maximum binding. The Temkin isotherm is valid only for an intermediate range of ion concentrations [46]. A plot of  $q_e$  versus  $\ln C_e$  enables the determination of the

isotherm constants  $B_T$  and  $A_T$  from the slope and the intercept (Fig.21), respectively. Temkin isotherm parameters have also been listed in the table (3).

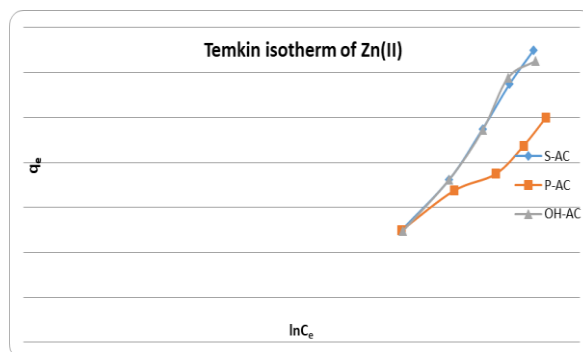


Fig.21 Temkin isotherm of zinc (II)

As in the table (3),  $A_T$  values of Zn (II) with respect to the activated carbon (S-AC, P-AC and OH-AC) are 0.0724, 0.1279 and 0.0743 respectively,

It is obvious from Fig.(21) that, the uptake increases as the initial concentration increase. This may be due to that, the lower concentration of the solute in the solution leads to low adsorption where, by increasing the solute concentration, the adsorption tends to increase due to the abundance of Zn(II) ions in the solution.

### Dubinin–Radushkevich isotherm model [47]

Dubinin–Radushkevich isotherm model (D-R) is an empirical adsorption model that is generally applied to express adsorption mechanism with Gaussian energy distribution onto a heterogeneous surface [48]. This isotherm is only suitable for an intermediate range of adsorbate concentration because it exhibits unrealistic asymptotic behavior and does not predict Henry's laws at lower pressure [49]. It is usually applied to differentiate between physical and chemical adsorption of metal ions [50].

The linear form of Dubinin and Radushkevich isotherm model equation can be expressed as;

$$\ln q_e = \ln(X_{D-R}) - \beta \varepsilon^2 \quad \text{-----} \quad 17$$

Where  $X_{D-R}$  is the theoretical monolayer saturation capacity ( $\text{mg g}^{-1}$ ),  $\beta$  is the Dubinin–Radushkevich model constant ( $\text{mol}^2 \text{ J}^{-2}$ ).  $\varepsilon$  is the polanyi potential and is equal to

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right) \quad \text{-----} \quad 18$$

Where  $R$ ,  $T$  and  $C_e$  represent the gas constant (8.314 J/mol K), absolute temperature (K) and adsorbate equilibrium concentration (mg/L), respectively.

The  $X_{D-R}$  and  $\beta$  can be calculated from the slopes ( $\beta$ ) and intercepts  $\ln(X_{D-R})$  of the plot of  $(\ln q_e)$  vs.  $(\varepsilon^2)$ , Fig.(22). Where, the value of  $E_{D-R}$  is related to the sorption mean free energy (KJ/mol).

The relationship is expressed as:

$$E_{D-R} = \frac{1}{\sqrt{2\beta}} \text{-----19}$$

The Dubinin–Radushkevick sorption isotherm is preferable than the Langmuir isotherm as its derivation is not based on the ideal assumption such as equipotency of the sorption sites, absence of stoic hindrance between sorbed and incoming particles and surface homogeneity on a microscopic level. Also the Dubinin–Radushkevick equation has been used to determine the mean free energy of sorption.

From table (3), the mean sorption energy ( $E_{D-R}$ ) was evaluated as 50, 70.71 and 50 (kJ/mol) for the sorption of Zn(II) on the activated carbons S-AC, P-AC and OH-AC, respectively.

According to Şahan et al., 2018 [51], the ( $E_{D-R}$ ) values range from 1.0 to 8.0 (kJ/mol) for physical adsorption and from 8.0 to 16 (kJ/mol) for a chemical ion exchange and higher than 16 (KJ/Mol) for chemical reaction. While the ( $E_{D-R}$ ) value for the adsorption of Zinc(II) on the activated carbon more than 16 (kJ/mol), So, the Zn(II) adsorption reaction process is considered as chemisorption process due to electrostatic interaction.

It is obvious from the table (3) that, the Freundlich isotherm model is the best therm imodel for Zn(II) adsorption from polluted solutions.

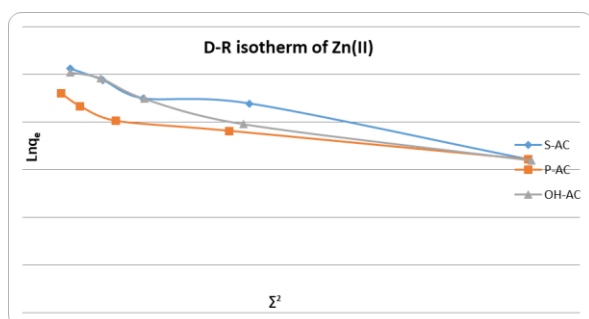


Fig.22 D-R isotherm of zinc (II)

### Groundwater treatment

In this study, some of groundwater samples were collected from the groundwater resources of Ras El

Hekma area at the Northwest coast area-Egypt (Fig.23), and transported to the Desert Research Center laboratories to analyze based on the international standard methods according to Fishman and Friedman, 1985 [52] to determine the trace elements in the collected water samples (Table 4). As shown in table 4, it was noticed that some groundwater samples are unsuitable for drinking purposes as they have  $Zn^{+2}$  concentration more than the safe limit (0.05mg/l; WHO, 2011), [9]. So, it must be using an adsorbent (as S-AC 450°C) to decrease the concentration of Zinc ions from this polluted groundwater and to achieve this aim, the removal process of  $Zn^{+2}$  from groundwater have been studied according to the best conditions of Zn(II) removal using S-AC 450°C carbon with dosage 0.4g, at pH 4 and contact time 300min and the obtained results were summarized in table 4.

Table 3. Isotherm parameters of Zn(II) adsorption on the S-AC, P-AC and OH-AC

Isotherm model	S-AC	P-AC	OH-AC
Langmuir			
$Q_{max}$ (mg/g)	15.38	15.394	40.584
$K_L$ (L/mg)	0.01548	0.015471	0.004765
$R_L$	0.455228-	0.36055-	0.446777-
$R^2$	0.386084	0.231448	0.368356
Freundlich			
$1/n$	0.8225	0.5682	0.8135
$K_f$ (mg/g)	0.3099	0.7352	0.3192
$R^2$	0.9954	0.9908	0.986
Temkin			
$A_T$ ( $Lg^{-1}$ )	0.0724	0.1279	0.0743
$B_T$	6.2087	3.6922	6.0574
$R^2$	0.9899	0.9907	0.9885
D-R			
$\beta$ ( $mol^2/kJ^2$ )	$2 \times 10^{-4}$	$1 \times 10^{-4}$	$2 \times 10^{-4}$
$X_{D-R}$ (mg/g)	13.389	9.673	9.673
$E$ (kJ/mol)	50.00	70.71	50.0
$R^2$	0.9674	0.9243	0.9464

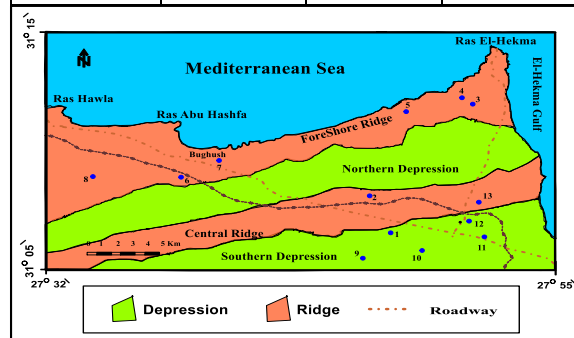


Fig.23 Location map of the collected groundwater samples



Table 4. The concentrations of Zn(II) in the collected groundwater samples in the study area

Sample No.	Concentration of Zinc ions (mg/l) before treatment process	Concentration of Zinc ions (mg/L) after treatment process	The removal percentage %
1	0.122		
2	1.870		
3	0.919	0.594	35.36
4	0.675	0.456	32.44
5	0.150		
6	0.256		
7	0.016		
8	0.457		
9	0.363		
10	0.011		
11	1.820	1.297	28.73
12	0.289	0.209	27.68
13	0.264		
14	0.363	0.255	29.75

The obtained results (Table 4) showed that the prepared S-AC 450°C carbon is more efficient for the removal of Zn(II) from groundwater in the study area and the removal percentage % ranges from 26 to 34% (Fig.24).

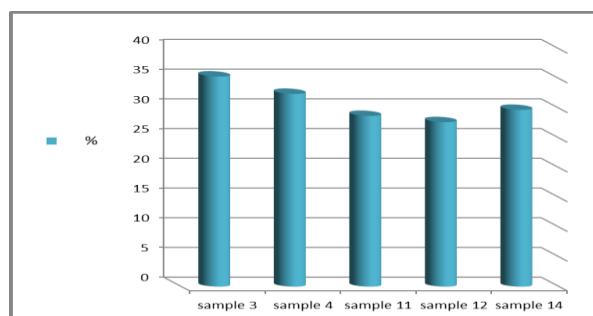


Fig.24 The removal percentage % of some collected groundwater samples

### Conclusion

In the present study, polystyrene divinyl benzene (Amberjet 1500 cation exchange resin) waste-derived carbon at 450°C and 900°C was prepared, characterized and applied as a cost-effective adsorbent for Zn(II) removal from the polluted groundwater after the modification with H<sub>2</sub>SO<sub>4</sub> (S-AC), H<sub>3</sub>PO<sub>4</sub> (P-AC) and NaOH (OH-AC). The effects of the functional parameters such as solution pH, contact time, temperature and initial concentration on the Zn(II) removal efficiency by the activated carbons were evaluated. The activated carbons exhibited greater

adsorption efficiency at 450°C than at 900°C, this may be due to its porosity and surface functionality. The maximum adsorption was achieved at pH values 4, 2 and 4, temperature 316, 316 and 296 K for both S-AC, P-AC and OH-AC, respectively, carbon dosage 0.4g, initial zinc concentration 50mg/kinetically, it was shown that the temperature 450°C is the best temperature for activation of adsorbent carbons. Thermodynamics calculations affirmed that Zn(II) adsorption processes onto S-AC and P-AC was endothermic processes while the adsorption processes onto OH-AC was exothermic process. the prepared S-AC, P-AC and OH-AC can be considered as an effective adsorbent for Zn(II) removal from aqueous solutions and polluted groundwater. While, the obtained results indicated that S-AC has high adsorption capacities for Zn<sup>2+</sup> compared with other adsorbents, such as P-AC and OH-AC. Therefore, S-AC 450°C can be used for groundwater treatment as it gives higher satisfactory removal efficiency.

### Recommendations

To increase the removal percentage of Zn<sup>2+</sup> ions from groundwater in the study area, the treatment processes must be repeated more than one time, i.e., two or three times (successive consecutive removal processes).

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