

## USE OF ENVIRONMENTALLY FRIENDLY MATERIALS TO REMOVE SOME POLLUTANTS FROM AQUEOUS SOLUTIONS

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**ABSTRACT :** During this work, the root of the *Gundelia* plant, which is one of the types of nuts, was used to prepare activated carbon with phosphoric acid ( $H_3PO_4$ ) and zinc chloride ( $ZnCl_2$ ) and used as an adsorbent surface to remove lead ions ( $Pb^{+2}$ ) and para-phenylene diamine (PPD) dye. It was prepared by using infrared spectroscopy (FT-IR) and showed that it contains many functional groups such as hydroxyl (OH) and carbonyl (C=O). The surface morphology was also diagnosed using scanning electron microscope (SEM) and it was shown that the rough surface contains many pores and gaps, ash content and moisture were measured, and the outer and inner surface area was determined using methylene blue indicator, iodine indicator, and pH at zero charge point (pH pzc) was determined. The effect of contact time, adsorbent dose, temperature, and initial concentration of the adsorbent materials on the percentage of adsorption was studied. The initial concentration of the adsorbents increases the amount of adsorption ( $Q_e$ ), but the percentage of adsorption decreases with the increase in the initial concentration. The adsorption isotherms (Langmuir and Freundlich) were applied. It was found that the adsorption process fully corresponds to Freundlich's equation and partially with the Langmuir equation. The adsorption kinetics were studied, and it was found that the adsorption follows the equation False second order. The thermodynamic functions ( $\Delta G$ ,  $\Delta S$  and  $\Delta H$ ) were calculated and it was found that the adsorption process is endothermic as the adsorption increases with increasing temperature and that the adsorption process is spontaneous and accompanied by an increase in randomness, meaning that it is less uniform on the adsorbent surface than it is in the solution and an analytical study was conducted. Preconcentration methods include Batch method and the column method to remove small concentrations of ions in large quantities of aqueous solutions.

**Key words :** Aqueous solutions, Langmuir equation, surface morphology, *Gundelia* plant.

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### INTRODUCTION

The term chemical pollutant refers to any anthropogenic compound that is spread or present in higher than normal amounts in the environment<sup>(1)</sup>. More than 100,000 chemicals manufactured for commercial purposes, and many of them enter the aquatic environment through the atmosphere, runoff or direct disposal into water<sup>(2)</sup>. The danger of chemical pollutants is not limited to their presence, but the possibility of them undergoing interactions with species and other chemicals and their interaction with light or even with living organisms<sup>(3)</sup>. For an optimal study of chemical pollutants, they are often divided based on their chemical structure into inorganic pollutants and organic pollutants<sup>(4)</sup>. Inorganic pollutants are pollutants that include heavy metals, various types of nutrients, and salts that occur naturally or resulting from human activity. It is usually a

difficult task to confront exposure to water inorganic pollutants. Heavy metals, for example, lead (Pb) have a variable behavior, these elements are not subject to decomposition as in many organic pollutants<sup>(5)</sup>. amounts above the maximum levels of inorganic pollutants can cause a range of harmful effects on the liver, kidneys, digestive system, and skin (depending on the level of exposure)<sup>(6)</sup>. The term organic pollutants refers to toxic chemicals that contain carbon in their composition, which negatively affect human health and the environment throughout the world because they are transmitted by water or wind and are not limited to the contaminated area. It maintains its permanence in the environment for a long time, and it can also accumulate in one species and be transmitted to another through the food chain<sup>(7)</sup>. The dyes show a high solubility in water, so they are difficult to remove by conventional methods. These dyes cause

damage to water bodies and prevent light from penetrating through the water, which leads to a decrease in the rate of photosynthesis and levels of dissolved oxygen affecting aquatic organisms as a whole<sup>(8)</sup>. Paraphenylene diamine (PPD) hair dye is used as a permanent hair dye, its danger is summarized by causing the oxidation process to produce several intermediate compounds that have the ability to cause strong allergic reactions, mutagenicity as well as being highly toxic<sup>(9)</sup>. Adsorption technology is considered the most effective technology due to its high efficiency and low cost. It uses many natural and synthetic adsorbents such as some agricultural waste represented by sugar cane, fruit peels, natural clay and others, and industrial waste such as gravel, fly ash, and activated carbon derived from biological sources. Nanomaterials based on minerals and other elements, zeolite-based adsorbents and inexpensive polymers for removing various pollutants from wastewater<sup>(10)</sup>.

## MATERIALS AND METHODS

**Preparation of the raw material :** 1 kg of the husks of the *Gundelia* root were collected and washed with distilled water several times and left to dry at room temperature for several days, after which it was ground and the powder dried in a drying oven at a temperature of 60°C within 24 hrs.

**Preparation of activated carbon :** Two types of activated carbon were prepared according to the substance in which it was activated.

**Activation with phosphoric acid :** 25 g of the prepared powder was placed in three glass cups and phosphoric acid was added to it in a ratio of (1:1), (1:2) and (1:3) and mixed well and then dried at (110°C). For 48 hrs, it was calcined in a furnace at (450°C) for three hours and the samples were washed with distilled water until the pH of the wash water became 6 to 7 to remove the effect of activation on the surface of the activated carbon. The resulting activated carbon was dried at (110°C) for a period of 48 hours. The three forms of activated carbon were named CHP<sub>1</sub>, CHP<sub>2</sub> and CHP<sub>3</sub>.

**Activation with zinc chloride :** 25 g of the powder was placed in three glass beakers and a solution of zinc chloride (100 mL) prepared from anhydrous zinc chloride in a ratio of (1:1), (1:2) and (1:3) was added. Then it was stirred. The mixtures were placed using a magnetic stirrer for an hour and then placed in a drying oven at 110°C for 48 hrs and calcined in the incineration oven at 450°C for three hours, then the three samples were washed with distilled water several times within 15 min. Then they were washed with a solution of 3M hydrochloric acid

repeatedly during half an hour and then the samples were washed again with distilled water until the pH of the wash water became about 6 to 7 and the samples were dried in the drying oven at 110°C for 48 hrs. Activated carbon forms with zinc chloride CZn<sub>1</sub>, CZn<sub>2</sub> and CZn<sub>3</sub>.

**Characterization of activated carbon and raw material :** The chemical surface functions of the different models of activated carbon and the raw material were determined using FT-IR spectroscopy, and the surface morphology was also diagnosed using scanning electron microscopy (SEM).

## Ash content and moisture

Ash content was measured by placing (0.5g) of dried activated carbon at (110°C) in an incubator for 2 hrs, then placing it in a crucible of known mass and entering the incinerator at 800°C for 3hrs. Then measuring the ash mass the percentage of ash is expressed by the following mathematical formula:

$$\% \text{ Ash} = \frac{m2}{0.5} \times 100$$

The moisture content was determined by placing (0.5g) of activated carbon in a crucible and the whole was weighed and then dried in the drying oven at (110°C) several times until the mass became stable. The percentage of moisture is expressed by the following mathematical formula<sup>(11)</sup>.

$$\% \text{ H} = \frac{m3 - m2}{0.5} \times 100$$

**Iodine index :** Measuring the inner surface area of activated carbon. (50 mL) of iodine solution (0.02N) was placed in a volumetric flask and 0.1g of activated carbon was added to it. The mixture was stirred for 10 min before filtering. 10 mL of the filtrate was taken and added to it. 2 drops of the starch solution was prepared in advance to obtain a purple solution. Then, volumetric doses were made of a standard sodium thiosulfate solution (0.1N) in the burette and after changing the purple color to a colorless solution, the volume of sodium thiosulfate was calculated, the iodine index was obtained from the mathematical formula next:

$$\text{Index } I_2 = \left( \frac{N0 \times Nth \times Vth}{2 \times VI2} \right) \times \left( \frac{M12 \times Vads}{mac} \right)$$

**Methylene blue indicator :** A measurement of the surface area of the activated carbon, which is an indication of the ability of activated carbon to adsorb large particles. 0.1g of activated carbon was placed in a conical flask and (100 mL of methylene blue (MB) at a

concentration of (25 mg/L), and the mixture was placed in a vibrating water bath at a temperature of (25°C) for 2 hrs after which the mixture was filtered and the remaining (MB) concentration was measured and the (MB) index was expressed by the following mathematical formula: <sup>(12)</sup>

$$\text{Index}_{(\text{MB})} = \frac{ci - cf}{mac} \times 100$$

**Zero charge point pH :** (50 mL) of distilled water was put into five flasks and the pH was adjusted at (2,4,6,8 and 10), then (0.05g) of activated carbon was added and the flasks were left stirred at a temperature The room until the pH stabilized and the final pH was determined, and (pH pzc) is determined from the intersection of the curve that represents the relationship between the initial pH pHi and the amount of pH change ΔpH.

#### Study of the factors affecting adsorption

**The effect of the adsorbent mass :** Adding different weights of activated carbon samples (0.02, 0.04, 0.06, 0.08 and 0.1g) to (50 mL) of (PPD) and (Pb<sup>+2</sup>) at a concentration of (100 mg/L) and placed in a vibrating water bath at a temperature of (25°C) and for 3hrs after that, the solution was filtered, the residual concentration measured, and the adsorption percentage was calculated using the following mathematical equation <sup>(13)</sup>.

$$\% \text{ Removal} = \frac{C_0 - C_e}{C_0} \times 100$$

**Effect of time on adsorption :** Several solutions of (50 mL) volume were prepared with a concentration of (100 mg/L) of (PPD) and (Pb<sup>+2</sup>) and (0.1g) of activated carbon was added to it and placed in a vibrating water bath at (25°C) with time different (15, 30, 60, 90, 120 and 150 min) and filtering the solution after the specified time and measuring the remaining concentration, and the amount of adsorption was calculated at each time Qe from the following equation <sup>(14)</sup>

$$Q_e = \frac{C_0 - C_e/v}{mac}$$

**Effect of temperature :** Prepare several solutions of volume (50 mL) with a concentration of (100 mg/L) for each of (PPD) and (Pb<sup>+2</sup>) and add to it (0.1g) of activated carbon samples and put them in a vibrating water bath at different temperatures, which are (25, 35 and 45°C) for 3h, the solutions were filtered and the remaining concentration measured.

**Effect of primary concentration :** The effect of concentration and application of isotherms (Langmuir and

Freundlich) was studied by preparing several solutions with a volume of (50 mL) and different concentrations (100, 300, 500 and 700 mg/L) of (PPD) and (Pb<sup>+2</sup>) adding to it (0.1g) of carbon samples. The activator was placed in a vibrating water bath at a temperature of 25°C for 3h, then the solutions were filtered and the concentration measured after adsorption and the amount of adsorption at each concentration was calculated using the following equation <sup>(13)</sup>.

$$Q_t = \frac{(C_0 - C_e)V}{mac}$$

#### Preconcentration

**Batch method :** Prepare three standard solutions of different volumes (300, 600 and 900 mL) of (Pb<sup>+2</sup>) at a concentration of (1.0 mg/L) and at pH = 6, add to them (1.0 g) of activated carbon and shake continuously for 3 hrs at room temperature. The solution was filtered and the lead concentration in the filtrate was measured using an atomic absorber.

**Column method :** A suitable separation column with a diameter of 2 cm and a height of 40 cm was prepared, and activated carbon was placed inside between two layers of fiberglass, with a height of 3 cm. At room temperature and at a flow rate of (3 mL) per minute, the remaining lead ions in the solution were determined from the column.

## RESULTS AND DISCUSSION

#### Define surface functions

**Infrared spectroscopy :** FT-IR of the raw material appeared wide band at (3325cm<sup>-1</sup>) elongation back to Vibration of the OH group of polymeric compounds in alcohols or carboxylic acids present in lignin or cellulose <sup>(15)</sup> and a bundle at (2901cm<sup>-1</sup>) vibration deformation belongs to alpha CH and a bundle at (1725cm<sup>-1</sup>) and (1311cm<sup>-1</sup>) vibration deformation belongs to the group C=O and CO respectively in the carbonyl group or presence of carboxylic bonds and band at (1630 cm<sup>-1</sup>) C=C expansion vibration in alkenes, and band at (1205 cm<sup>-1</sup>) and (1027 cm<sup>-1</sup>) due to OH bending vibration and CO expansion on respectively in carboxylic acids <sup>(16)</sup>. From the FT-IR spectrum of the samples of activated carbon obtained after treating the raw material with phosphoric acid and zinc chloride and burning at 450°C, the beam positions of the active groups such as OH and C=O changed and some of them disappeared as aliphatic CH, due to the structural change of the surface of The raw material and the formation of other additional functional groups, which leads to changing the vibrations of the bonds at different frequencies <sup>(17)</sup>. And that the original carbon

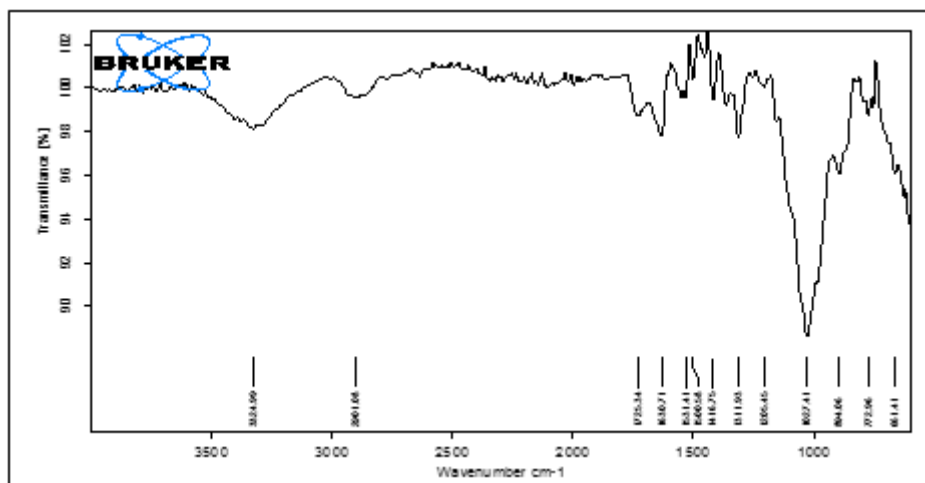


Fig. 1 : FT-IR spectrum of the raw material.

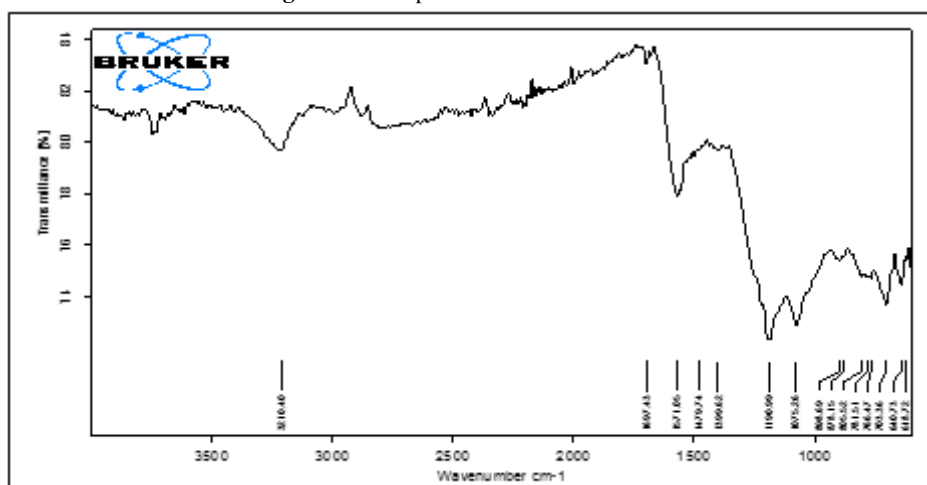


Fig. 2 : FT-IR of (CHP) before adsorption.

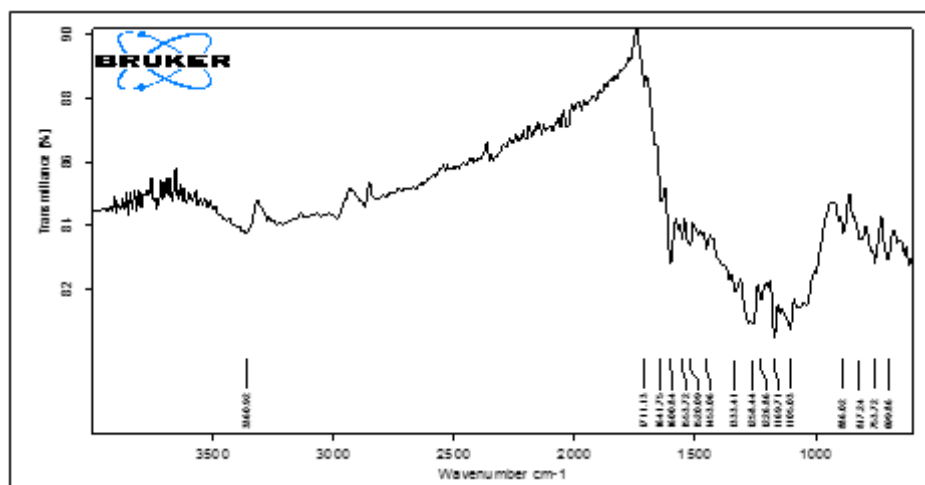


Fig. 3 : FT-IR of (CZn) before adsorption.

structure was transformed into polycyclic aromatic structures when exposed to high temperatures, which led to a widening of the interlayers between the crystals of activated carbon<sup>(18)</sup> and the FT-IR spectrum of activated carbon with phosphoric acid (CHP) after adsorption of para-phenylene diamine (PPD) dye. For activated carbon

with zinc chloride (CZn) after the adsorption of lead ions ( $Pb^{2+}$ ), we notice a significant change in the position of the bundles for some functional groups, and the OH functional group band disappeared, and this is evidence that these functional groups contributed significantly to the adsorption process. The position of the beams of the

functional groups indicates that a reaction or ion exchange has taken place between the ions of the adsorbent and the functional groups on the surface of the activated carbon, specifically the OH and C=O groups <sup>(15)</sup>.

**Scanning electron microscopy :** SEM was used to study the surface formation of the raw material and the prepared activated carbon before and after adsorption. The high temperature and contains many pores and gaps of different sizes and shapes, as these pores can provide excellent surfaces for adsorption of particles of pollutants, and the reason for the availability of these pores is due to the dissolution of lignin and cellulose at high temperatures, in addition to the evaporation of volatile compounds present <sup>(19)</sup>. From (SEM) images of (CHP) after (Pb<sup>2+</sup>) adsorption and SEM images of (CZn) after (PPD) adsorption, we find that the structural formation has changed dramatically and that most of the large pores and gaps have been filled and covered with particles of adsorbent materials.

#### Ash content and moisture

Ash is an inorganic substance that acts as an impurity that clogs the pores on the surface and thus reduces the adsorbent surface area <sup>(11)</sup>. We note that the activated carbon with phosphoric acid contains a very small percentage of ash, which enhances the quality of the carbon compared to the activated carbon with zinc chloride, and the ash percentage increases with the increase in the activator. As for the moisture content, the values were between 1.0% to 5.6%, which indicates that the activated carbon prepared for the different models does not easily capture moisture and an indicator of the quality of the obtained activated carbon, especially activated carbon with zinc chloride, where the ratio was from 1% to 2%. These values also indicate on the easy storage capacity of activated carbon.

#### Iodine and methylene blue index

The results shown in Table 2 indicate that the iodine value increases with the increase in the concentration of the activator and that the activated carbon with zinc chloride has the best iodine adsorption capabilities up to (761 mg/g) and that the activated carbon models whose iodine value falls within the range of 500 to 1500 is recommended for the removal of fine pollutants <sup>(20)</sup>. We note that the blue methylene index increases with the increase of activation for activated carbon with zinc chloride. As for activated carbon with phosphoric acid, the blue methylene index decreases with the increase in activation and the percentage of removal was very high, which confirms that activated carbon appears Great efficiency in removing large and small particles.

**Table 1 :** Values of ash content and moisture.

AC	C HP1	C HP2	C HP3	C Zn1	C Zn2	C Zn3
Ash content %	2	2	4	6	10	12
Moisture content %	3.6	4.8	5.6	1.0	1.0	2.0

**Table 2 :** Values of iodine and methylene blue index.

AC	C HP1	C HP2	C HP3	C Zn1	C Zn2	C Zn3
Iodine values(mg/g)	380	507	571	571	634	761
M.B values(mg/g)	24, 990	24, 980	24, 970	24, 960	24, 970	24, 980

**Table 3 :** shows the values of (pH pzc).

AC	C HP1	C HP2	C HP3	C Zn1	C Zn2	C Zn3
pH PZC	5.2	5.0	5.4	6.0	5.5	5.8

**Table 4 :** Freundlich and Langmuir constants on the surface of CHP.

Adsorbent	Langmuir			Freundlich		
	R <sup>2</sup>	Q <sub>max</sub>	kl	R <sup>2</sup>	n	kf
PPD	0.929	454.5	0.05	0.998	1.7	33657
Pb <sup>2+</sup>	0.957	526.3	0.02	0.997	1.4	20104

**Table 5 :** Freundlich and Langmuir constants on the surface of CZn.

Adsorbent	Langmuir			Freundlich		
	R <sup>2</sup>	Q <sub>max</sub>	kl	R <sup>2</sup>	n	kf
PPD	0.917	434.9	0.06	0.996	1.8	40741
Pb <sup>2+</sup>	0.923	434.9	0.04	0.994	1.7	30424

**pH of the zero charge point (pH pzc) :** Determining the acidic function at (pH pzc) is very important to know the pH value at which the adsorbent surface is neutral. When the pH value is higher than (pH pzc) the charge of the adsorbent surface is negative and when the pH value is Less than (pH pzc) the adsorbing surface charge is positive, thus improving the adsorption efficiency of pollutants bearing a positive charge at a pH higher than (pH pzc) and the adsorption of pollutants bearing a negative charge at a pH less than (pH pzc) <sup>(21)</sup> was obtained pH pzc values by determining the points of intersection between the curves pH<sub>i</sub> and ΔpH.

#### Factors affecting adsorption

**Adsorbent mass :** the results shown in Figs. 15 and 14 indicate that the percentage of adsorption increases with the increase in the mass of the adsorbent surface and continues to increase until it reaches close values, and the reason is due to the increase in the adsorbent surface area, which leads to an increase in the number of functional sites for the bond With the adsorbent

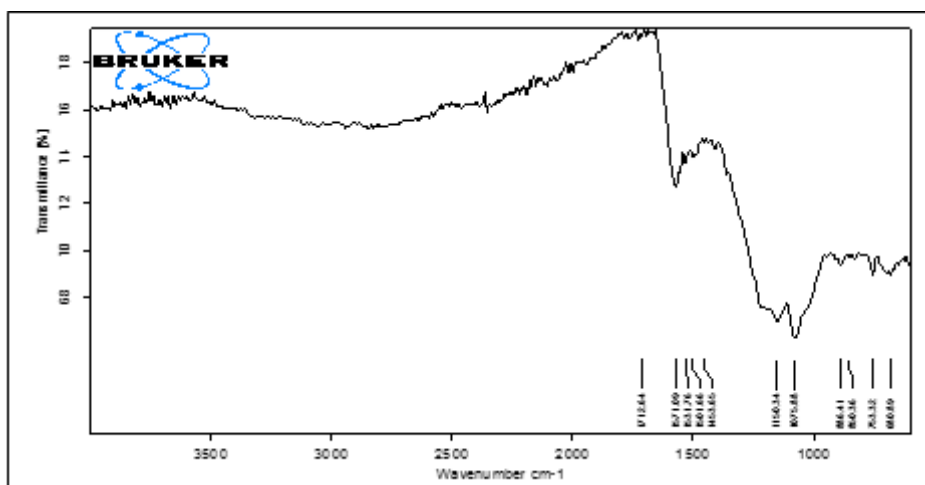


Fig. 4 : FT-IR of (CHP) after PPD adsorption.

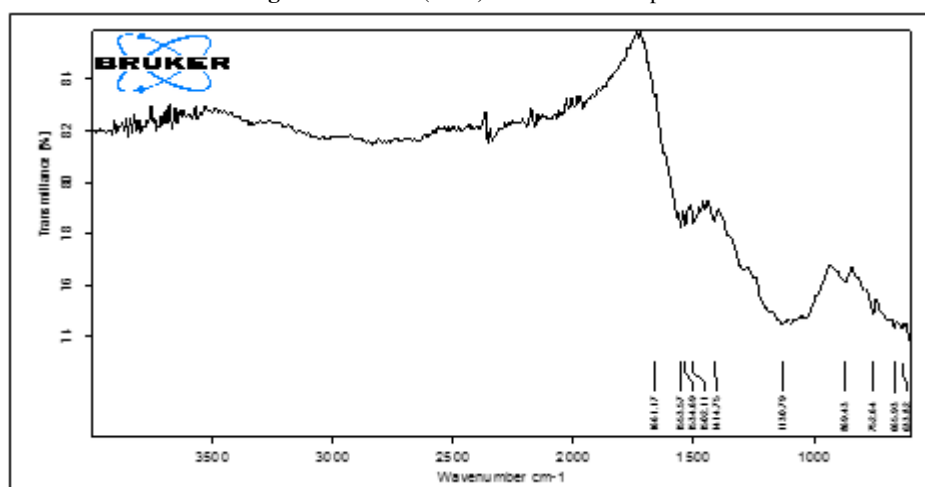


Fig. 5 : FT-IR of (CZn) after  $Pb^{2+}$  adsorption.

material and continue to increase with the use of larger doses of the adsorbent until a layer of ions is formed covering the surface, preventing adsorption again <sup>(22)</sup>.

#### The effect of contact time

The results shown in Figs. 16 and 17 indicate that the adsorption occurs rapidly during the first thirty minutes, and the reason is due to the presence of a large number of vacant adsorption sites on the outer surface of the adsorbent material, which facilitates rapid adsorption during that time period. Then we note that the adsorption rate decreased after the thirty minute and the process became slow as the adsorption sites on the surface reached saturation, which causes a decrease in the number of adsorption sites and also a decrease in the number of un adsorbed molecules <sup>(16, 19)</sup>. Where the results recorded that the equilibrium time for activated carbon with phosphoric acid (CHP) was at 90 min, while the equilibrium time for activated carbon with zinc chloride (CZn) was at 120 min. However, activated carbon with zinc chloride provided more pores.

#### The effect of temperature

The results shown in Figs. 18 and 19 indicate that the percentage of adsorption increases with the increase in temperature, and this can be explained by the fact that the increase in temperature leads to a decrease in the viscosity of the solution in addition to the liberation of functional aggregates and thus increasing the pores on the surface. The adsorbent material, as well as the increase in the rate of diffusion of the adsorbent molecules on the surface of the adsorbent material due to the increase in its kinetic energy with the increase in temperature, and the possibility of an absorption process occurring in conjunction with the adsorption process, which is called saturation and means that the process of adsorption and absorption occurs together <sup>(23)</sup>.

#### The effect of the initial concentration

The results shown in Figs. 20 and 21 indicate that the percentage of adsorption decreased with the increase of the initial concentration, reaching the highest adsorption rate at the lowest concentration of 100 mg/l. The reason

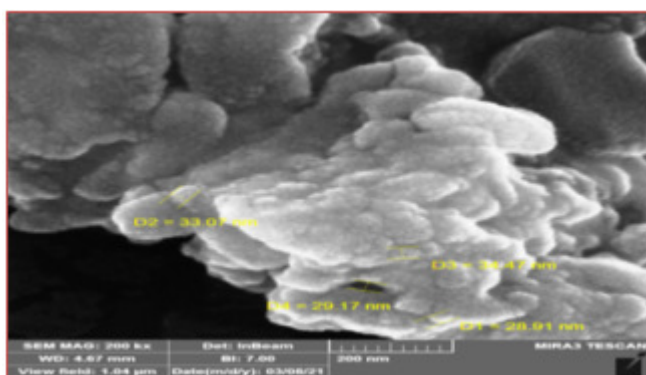


Fig. 6 : SEM of the raw material.

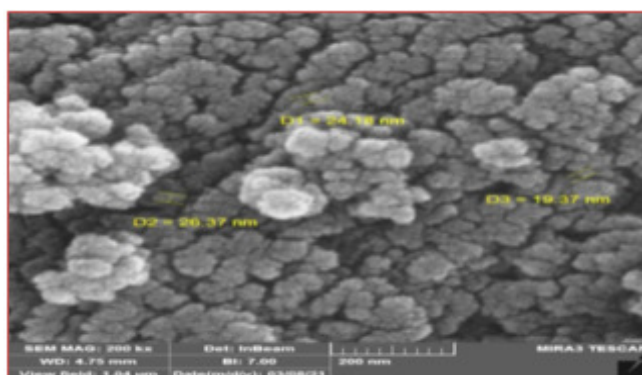


Fig. 9 : SEM of (CHP) after adsorption of Pb<sup>2+</sup>.

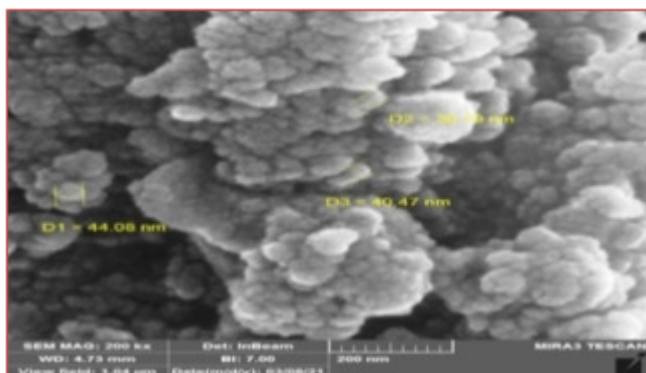


Fig. 7 : SEM of (CHP) before adsorption.

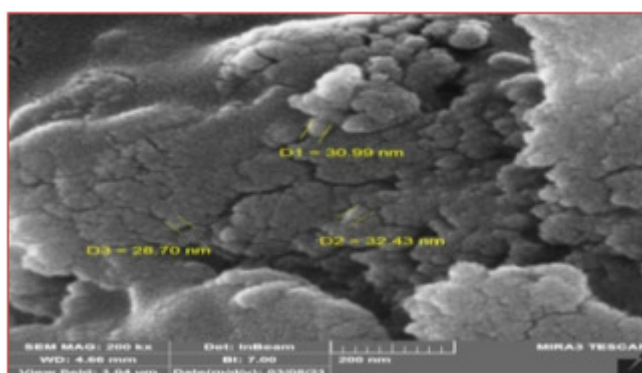


Fig. 10 : SEM of (CZn) after adsorption of PPD.

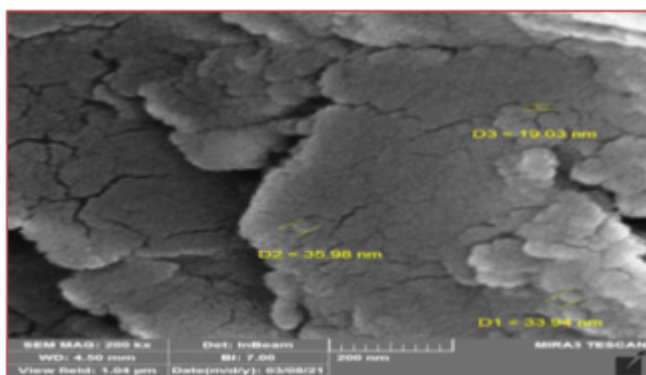


Fig. 8 : SEM of (CZn) before adsorption.

is that most of the vacant adsorption sites on the surface of the adsorbent have Saturated, so competition between the adsorbent molecules increases, and thus the adsorption rate decreases at high concentrations <sup>(24)</sup>. Although, the percentage of adsorption decreases with the increase in the initial concentration, the adsorption capacity  $Q_e$  increases with the increase in the initial concentration of the adsorbent. Particles of substances adsorbed on the adsorbent surface <sup>(25)</sup>.

**Langmuir isotherm :** The practical adsorption results of the adsorbents were applied to the two used adsorbent surfaces by using the linear Langmuir equation.

$$\frac{C_e}{Q_e} = \frac{1}{Q_{max} \cdot K_l} + \frac{C_e}{Q_{max}}$$

Table 6 : False first-order coefficients.

AC	Adso rbent	R <sup>2</sup>	K <sub>1</sub> ×10 <sup>-1</sup>	Q <sub>e</sub> Experimental	Q <sub>e</sub> Theoretical
CHP	PPD	0.997	0.70	49100	25591
	Pb <sup>2+</sup>	0.990	0.67	48200	25591
CZn	PPD	0.974	0.45	49300	13874
	Pb <sup>2+</sup>	0.951	0.33	48900	13039

Table 7 : False second-order coefficients.

AC	Adso rbent	R <sup>2</sup>	K <sub>1</sub> ×10 <sup>-5</sup>	Q <sub>e</sub> Experimental	Q <sub>e</sub> Theoretical
CHP	PPD	0.999	0.50	49100	50000
	Pb <sup>2+</sup>	0.999	0.60	48200	50000
CZn	PPD	0.999	0.60	49300	50000
	Pb <sup>2+</sup>	0.999	0.50	48900	50000

The values of  $Q_{max}$  and  $K_l$  were obtained from the slope and cut-off of the linear relationship between  $C_e$  versus  $C_e/Q_e$ .

**Freundlich isotherm :** The practical adsorption results of the adsorbents were applied to the used adsorbent surfaces by using the linear Freundlich equation <sup>(26)</sup>.

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e$$

The Freundlich constants  $n$  and  $K_f$  were obtained from the slope and cut off linear relationship between  $\ln Q_e$  versus  $\ln C_e$  and the value of the correlation coefficient  $R^2$  for the adsorption process was obtained.

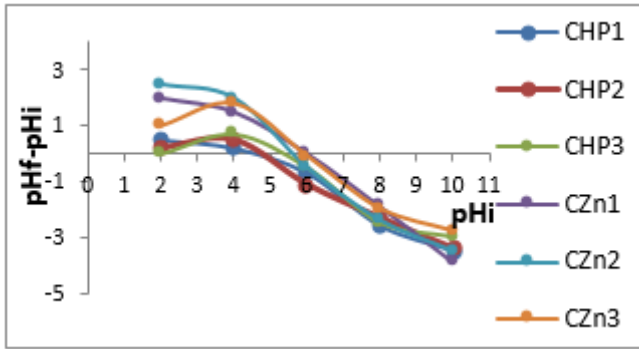


Fig. 11 : shows the (pH pzc) of the activated carbon samples.

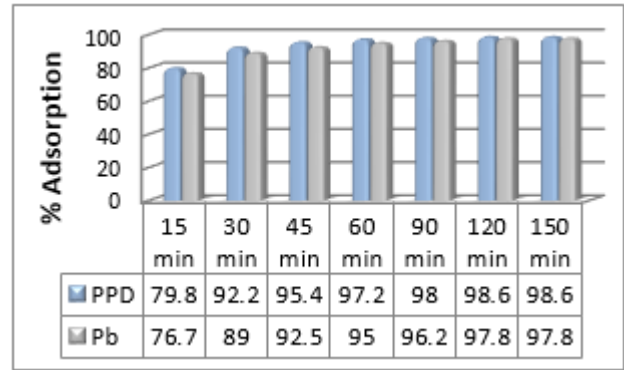


Fig. 15 : Effect of contact time on the percentage of removal on the surface of (CZn).

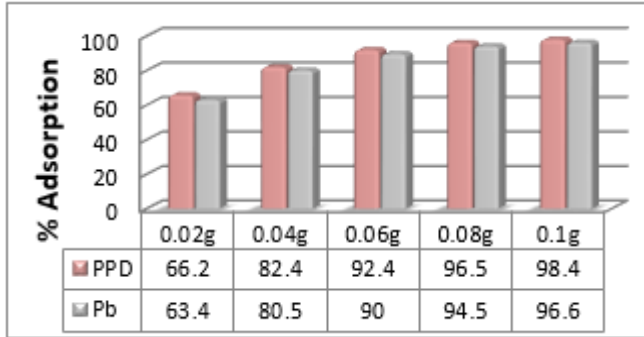


Fig. 12 : Effect of (CHP) mass on the removal rate.

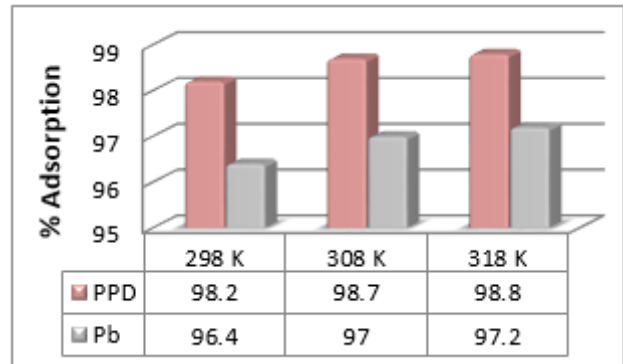


Fig. 16 : Effect of heat on the percentage of removal on the surface of (CHP).

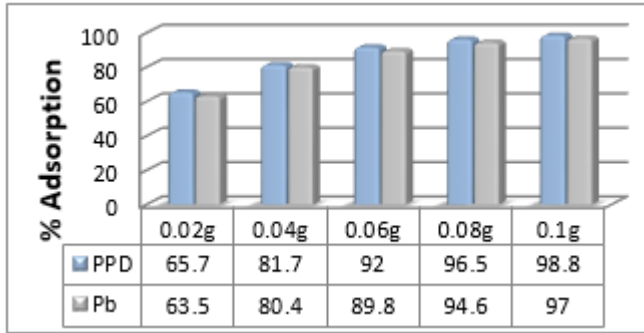


Fig. 13 : Effect of (CZn) mass on the removal rate.

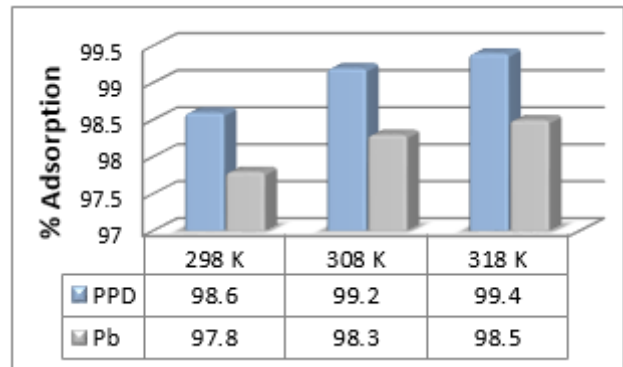


Fig. 17 : Effect of heat on the percentage of removal on the surface of (CZn).

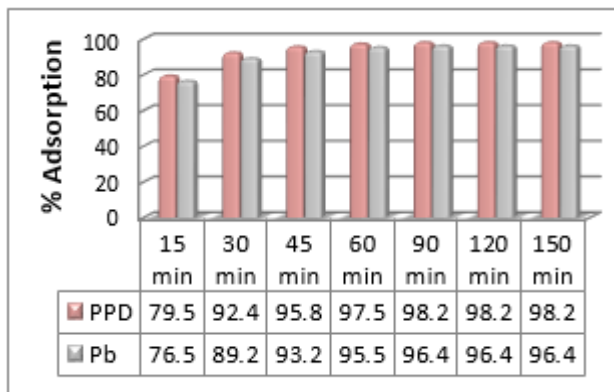


Fig. 14 : Effect of contact time on the percentage of removal on the surface of (CHP).

The results in Tables 4 and 5 indicate that the different adsorption processes on the prepared adsorbent surfaces apply to them in part by the Langmuir adsorption equation, which gave good linear correlation coefficients between (0.9571-0.9168). The different adsorption processes gave

excellent linear correlation coefficients between (0.9983-0.9965). We note that the values of n representing the intensity of adsorption were greater than one, which indicates that the adsorption is physical, as if (n<1) means that the adsorption is chemical and (n>1) means that the adsorption is physical<sup>(23)</sup>.

**Adsorption kinetics study**

**False first order :** The false first order equation was applied to the various adsorption processes by using the following equation:

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t$$

**False second-order :** The pseudo-second-order



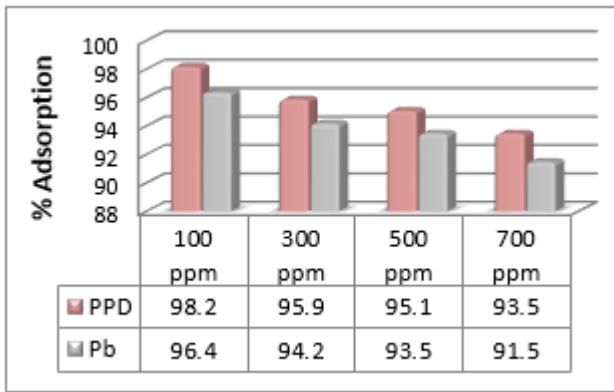


Fig. 18 : Effect of concentration on the percentage of removal on the surface of (CHP).

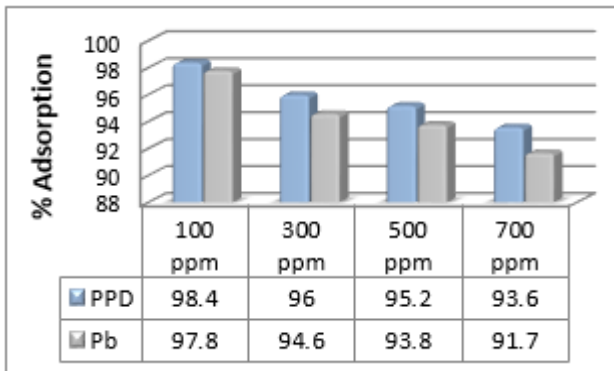


Fig. 19 : Effect of concentration on the percentage of removal on the surface of (CZn).

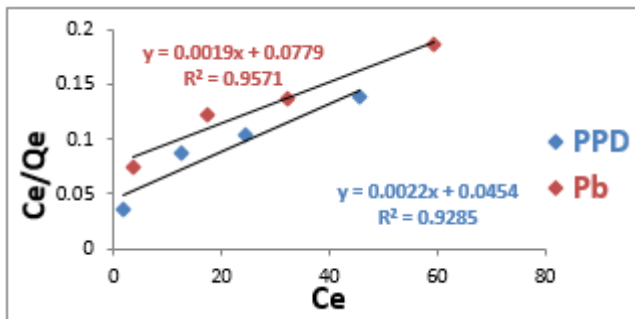


Fig. 22 : Lancomyer isotherm to remove (Pb<sup>2+</sup>) and (PPD) on the surface of CHP.

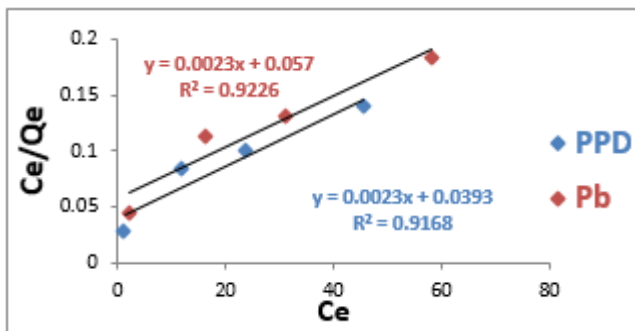


Fig. 21 : Lancomyer isotherm to remove (Pb<sup>2+</sup>) and (PPD) on the surface of CZn.

equation has been applied to various adsorption processes by using the following mathematical equation<sup>(27)</sup>.

$$t/Q_t = 1/K_2 \cdot Q_e^2 + t/Q_e$$

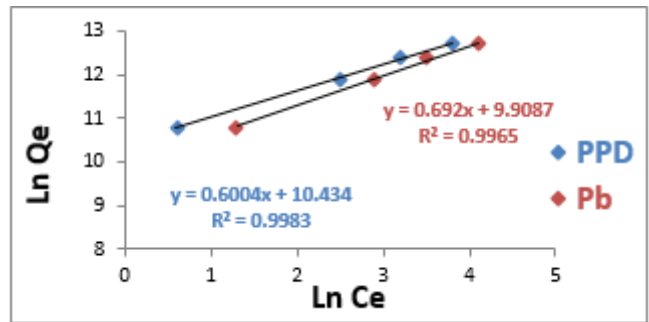


Fig. 22 : Freundlich isotherm to remove (Pb<sup>2+</sup>) and (PPD) on the surface of CHP.

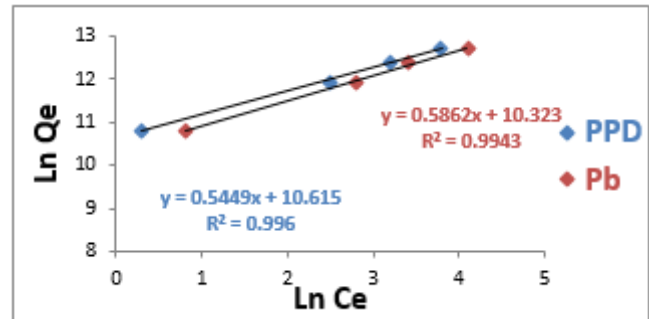


Fig. 23 : Freundlich isotherm to remove (Pb<sup>2+</sup>) and (PPD) on the surface of CZn.

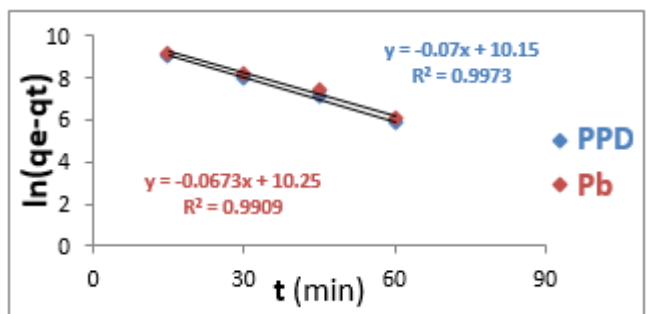


Fig. 24 : Pseudo-first order of removal of Pb<sup>2+</sup> and PPD on the surface of CHP.

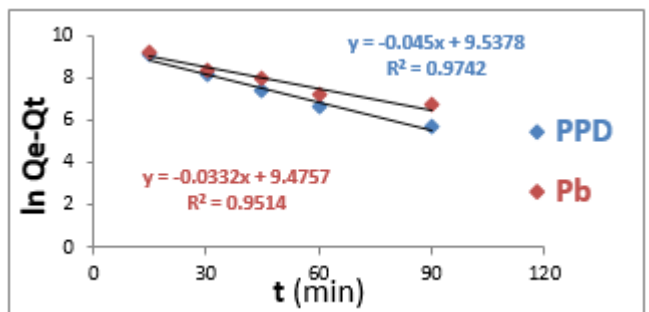


Fig. 25 : Pseudo-first order of removal of Pb<sup>2+</sup> and PPD on the surface of CZn.

From the results obtained in Table 6, we note that the correlation coefficients ( $R^2$ ) for the first false order were confined between (0.9965 - 0.99514), but the theoretical  $Q_e$  value calculated from the linear relationship does not agree with the practical  $Q_e$  value, which confirms that the adsorption processes are not subject to false first place. We note in Table (7) that ( $R^2$ ) of the false second

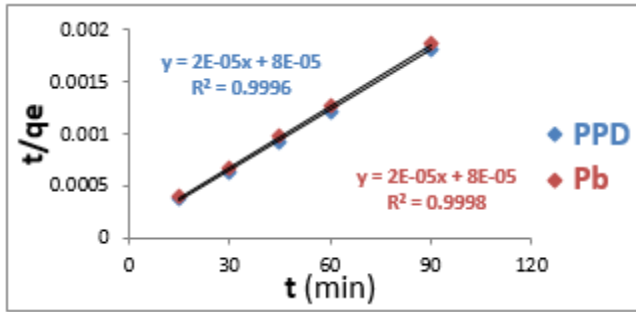


Fig. 26 : Second order of removal of Pb<sup>2+</sup>, PPD on the surface of CHP.

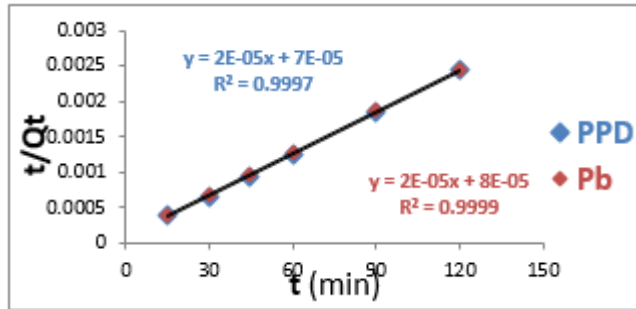


Fig. 27 : Second order of removal of Pb<sup>2+</sup>, PPD on the surface of CZn.

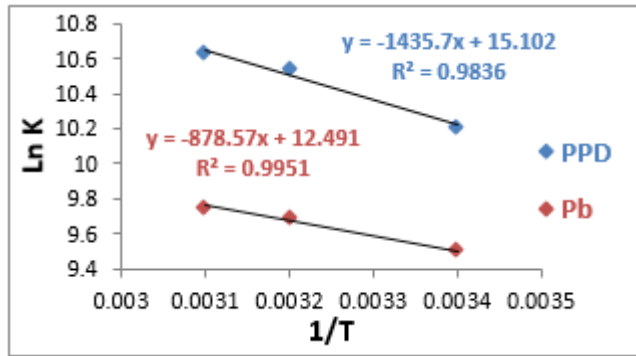


Fig. 28 : Vant-Hof relationship for the removal of Pb<sup>2+</sup> and PPD on the surface of CHP.

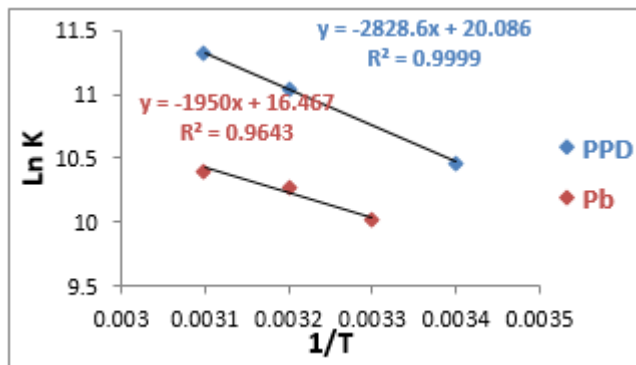


Fig. 29 : Vant-Hof Relationship for the removal of Pb<sup>2+</sup> and PPD on the surface of CZn.

order is confined between (0.9999-0.9994) and that the theoretical (Qe) value is close to the practical (Qe) value, which confirms that the adsorption processes are subject to the false second order.

Table 8 : Thermodynamic functions of adsorption on the surface of CHP.

T <sub>k</sub>	PPD			Pb <sup>2+</sup>		
	ΔG	ΔH	ΔS	ΔG	ΔH	ΔS
298	-25.5	+11.9	+125.6	-23.6	+7.3	+103.9
308	-26.7			-24.7		
318	-28.0			-25.7		

Table 9 : Thermodynamic functions of adsorption on the surface of CZn.

T <sub>k</sub>	PPD			Pb <sup>2+</sup>		
	ΔG	ΔH	ΔS	ΔG	ΔH	ΔS
298	-26.2	+23.5	+167.0	-24.6	+16.2	+136.9
308	-27.9			-26.0		
318	-29.6			-27.3		

Table 10 : Percentages of removal of (Pb<sup>2+</sup>) using activated carbon by a Preconcentration method in the Batch.

	CHP			CZn		
	V (mL)	Con (mg/L)	% R	V (mL)	Con (mg/L)	% R
V (mL)	300	600	900	300	600	900
Con (mg/L)	1.0	1.0	1.0	1.0	1.0	1.0
% R	100	100	100	100	100	100

Table 11 : Percentages of (Pb<sup>2+</sup>) removal using activated carbon by column Preconcentration method.

Adsorbent	V (L)	Con.(mg/L)	% R
CHP	3.0	1.0	100
CZn	3.0	1.0	100

**Thermodynamic :** The thermodynamic functions of the adsorption process of (Pb<sup>2+</sup>) and (PPD) were calculated from aqueous solutions using activated carbon with phosphoric acid (CHP) and activated carbon with zinc chloride (CZn). Where the value of the adsorption enthalpy (ΔH) and the value of the adsorption entropy (ΔS) were calculated using Vant Hoff equation <sup>(21)</sup>.

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT}, K = \frac{Q_e}{C_e}$$

From the graph between Ln k vs. 1/T the value of ΔH and ΔS was obtained from the slope and cut-offs of the straight line equation, respectively. The value of the free energy ΔG was also calculated from Kibs' mathematical equation <sup>(145)</sup>.

$$\Delta G = \Delta H - T \cdot \Delta S$$

We note in Tables 9 and 8 that the value of the heat of adsorption (ΔH) is positive, which indicates that all adsorption processes are endothermic and that all values were less than (40 kg/mol) indicating that the nature of adsorption on adsorbent surfaces is physical (23). Negative (ΔG) values indicate that the adsorption processes occur spontaneously. We note that the values

of ( $\Delta S$ ) are positive, which indicates that the adsorbed molecules are less regular on the adsorbing surface than they are in the solution.

**Batch method:** From the obtained results shown in Table 9, we note that the concentration of lead ion in the leachate solution is (0.0 mg/l), which proves the importance of the concentrated adsorption process by the Batch method and the possibility of its application in getting rid of the small concentrations of different elements.

**Column method :** The results obtained and shown in Table 11 indicate that the concentration of lead ion in the solution descending from the column is equal to (0.0mg/l), which confirms that the application of column Preconcentration is of great benefit to get rid of the small concentrations of ions in large quantities of water We note that the flow rate was (3 ml) per minute compared to the height of the coal inside the column (3 cm), meaning that for every 1 ml the flow rate was 1 cm the height of the coal, where the flow rate could be increased by increasing the height of the coal inside the column.

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