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Research Article

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Adsorption of Pb^{+2} and Zn^{+2} ions from oil wells onto activated carbon produced from rice husk in batch adsorption process

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ABSTRACT

In this work, the adsorption of Pb^{+2}& Zn^{+2} ions onto activated carbon produced from rice husk(RHAC) was studied, and the efficiency of RHAC has been compared with efficiency of raw rice husk(RH) and commercial activated carbon(CAC) for removal the heavy metal ions from waste oil water which comes out from the oil industry in basrah city. The effects of operating parameters were studied such as (contact time, adsorbent size, adsorbent dose, initial concentration of adsorbate, temperature, pH and rotation speed), and the optimum operating parameters in batch adsorption process were determined. At the optimum conditions the adsorption efficiency is arranged by (RHAC > CAC >RH) which removed 96.26, 95.71, 81.06% of Pb^{+2} ions, and 92.51, 83.32, 53.28% of Zn^{+2} ions

Key words: Adsorption, Activated Carbon, Rice Husk, Heavy metals, Waste Oil Water.

INTRODUCTION

Heavy metal ions pollution has become one of the most important environmental problems. The metals having specific gravity more than 5gm/cm^3 are considered as heavy Metal. The presence of heavy metals in the environment has been of great concern because of their increased discharge, toxic nature and adverse effect on human being. All heavy metal cause various disorders in human being [1].

Most of the heavy metals are carcinogenic, a problem assumed to be related to their electronic structure. Even the metals considered to be essential for all forms of life may become problematic when in excess[2]. Heavy metals enter in to the food chain through the bioaccumulation from the contaminated water, soil and air, they cannot be degraded and destroyed[3]. The permissible limit for Pb^{+2} in waste water as given by Environmental protection Agency (EPA) is 0.05 mg/L[4]. and the maximum concentration limit for Zn is 1mg/L as in USEPA[5].

Adsorption has application for the removal of heavy metals from aqueous solutions. The adsorption of toxic metals onto the agricultural waste and waste materials provides economical and eco-friendly technique for metal removal from aqueous solutions[6].

Adsorption on activated carbon (AC) has been found to be an effective process for removal of heavy metal ions, but the commercial AC is too expensive. Consequently numerous low cost materials has been used to produce an activated carbon such as seed shell of palm tree[7] dates stones[8] waste tires [9]oil palm fibre[10] pine ,oak woods, olive seeds[11] apricot stones[12] waste seeds husks of Moringaoleifera[13] coconut shell[14] ArundoDonax canes[15] pistachio-nut shells[16]and coir pith [17].

In this study, the efficiency of AC produced previously from rice husk(RHAC) for removal of Pb^{+2}& Zn^{+2} were investigated, and compared with raw rice husk(RH) and commercial activated carbon (CAC). The effects of operating parameters were studied such as (contact time, adsorbent size, adsorbent dose, initial concentration of adsorbate, temperature, pH and rotation speed).

EXPERIMENTAL SECTION

2.1 Materials

Zinc Chloride with purity (97%) and Sodium Hydroxide with purity (97.5%) was supplied from THOMAS BAKER (Chemicals) Company. Lead Chloride with purity (99%) was supplied from BDH Company. Hydrogen chloride with purity (37 %) was supplied from Scharlab.S.L Company.

2.2 Source of waste oil Water

After measuring the concentrations of heavy metal ions in waste oil water from different locations (West Qurna, nahran Bin Umer, Barjessia) by using atomic absorption , were found that different concentrations as shown in Table(1).

Table (1): Heavy metal ions concentration in different oil location in basrah city.

Location	Pb^{+2}	Zn^{+2}
Nahran Bin Umer	4	42
West Qurna	3	7.4
Barjessia	4.5	16.2

For simulated waste oil water, solutions were prepared with lower and higher concentrations of these four heavy metal ions in the locations mentioned above.

2.3 Preparation of standard solutions

The stock solutions of 1000 mg/L (ppm) of Pb(II) and Zn(II) were prepared by dissolving 1.3557 gm of $PbCl_2$ and2.1273 gm of $ZnCl_2$ in 1000 ml volumetric flasks and fill up to the mark with distilled water.

The diluted concentrations were prepared from stock solutions for carrying out experiments. Following the equation below :

$$N_1 * V_1 = N_2 * V_2 \tag{1}$$

And then a certain volume (10 ml) of oil has been added to all above solution with efficient agitation.

2.4 The calibration curve method of analysis.

In 25 ml volumetric flasks were prepared a series of standard solutions containing 5 , 10 , 15 , 20 , 25 , 30 , 35 , 40 , 45 , 50 , 55 , 60 , 65 and 70 ppm of heavy metal ions. After determining the absorbance by AAS , making a plot of absorbance vs. concentration using EXCEL software. The results and the equations which was described calibration curve are shown in Figure (1) .

2.5 Analyze a sample of heavy metal ions by using atomic absorption spectrophotometer (AAS)

The concentration of metal ions was measured by using atomic absorption spectrophotometer (BUCK Scientific, Model 210 VGP**)**. In atomic absorption spectroscopy, metal atoms were vaporized into a flame, and the metal vapor absorbed radiation from the specific hollow cathode lamp in proportion to the number of atoms present. Beer's Law was followed in the part-per-million range (remember that ppm means mg of metal/liter of solution).

2.6 Batch adsorption processes

Adsorption experiments were carried out in double neck(125 ml) flask using 100 mL metal bearing solution with a certain dosage of the AC and installed in the water bath(Memmert Gmbh Type WMB 22). The pH values were controlling by adding 0.1 N NaOH or 0.1 N HCl. And stirred for different rotation speed using Variable-Speed Bench top, model 5850, Eberbach. Before the metal solution analyzed using AAS was filtered through filter paper.

The efficiency of each bed was measured in the case of batch adsorption with different parameters such as the effect of temperature (8 – 55Ċ), Contact time (2 -30 minutes), PH (3-11), Adsorbent Dose (1- 5 gm), Adsorbent Diameter (0.075 -1.14 mm), Rotation speed (0 -1500 rpm) and Initial Concentration of heavy metal ions (10-60 ppm), and comparison between the effect of operating conditions on adsorption of heavy metal ions by CAC, RHAC and RH.

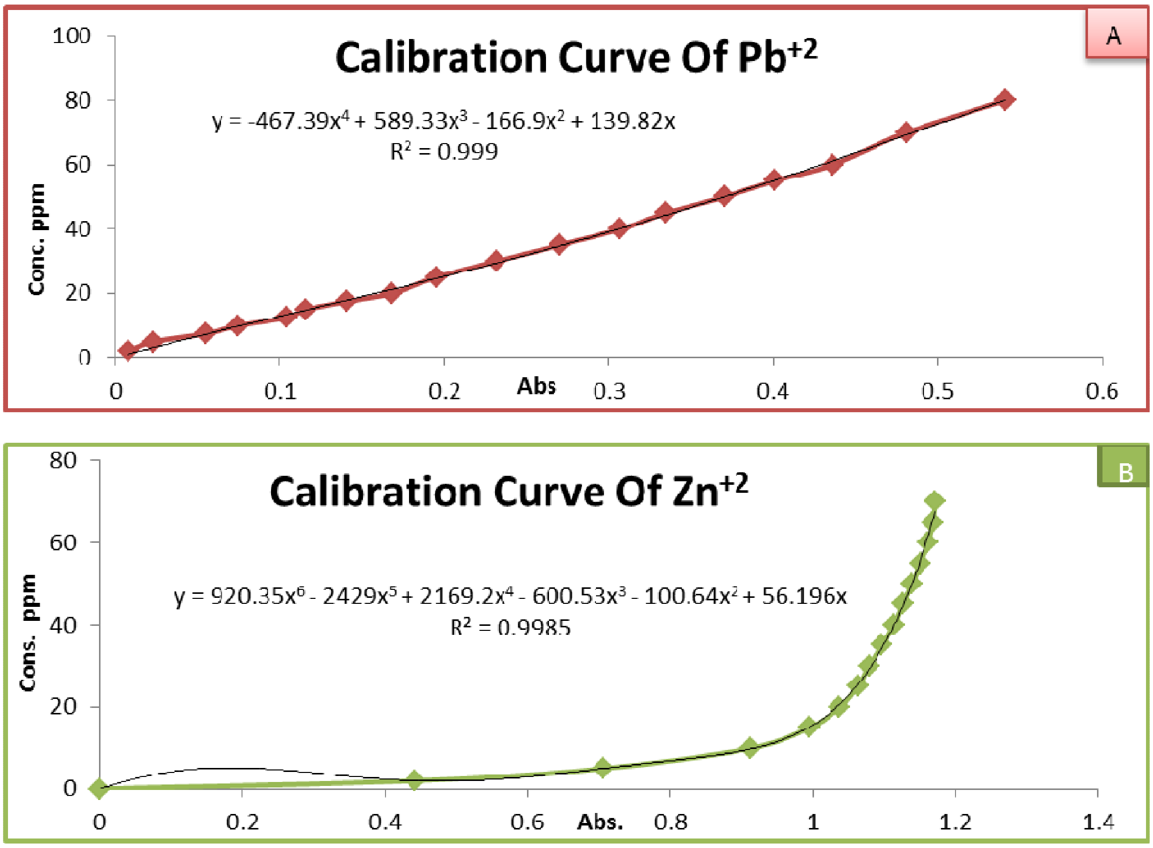
RESULTS AND DISCUSSION

3.1 Efficiency of Adsorption

The Removal Percentage (R.P.%) which described the efficiency of adsorbent to adsorbed a heavy metal ions is calculated by following equation [18]:

$$R.P.\% = \frac{C_i - C_f}{C_i} * 100 \qquad (2)$$

Where :C_i and C_f are the initial and final concentration in (ppm), respectively.



Figure(1): Calibration Curves of heavy metal ions

3.2 Effect of contact time

The effect of contact time on the adsorption of heavy metal ions (H.M.I.) was investigated. The experimental were done under the conditions of constant temperature (25^{0}C), adsorbent dose(1gm), particle size (0.3), rotation speed (600 rpm), PH(2.9), initial concentrations (50ppm) and contact time(0-30 min), the experimental data are presented in figure (2).

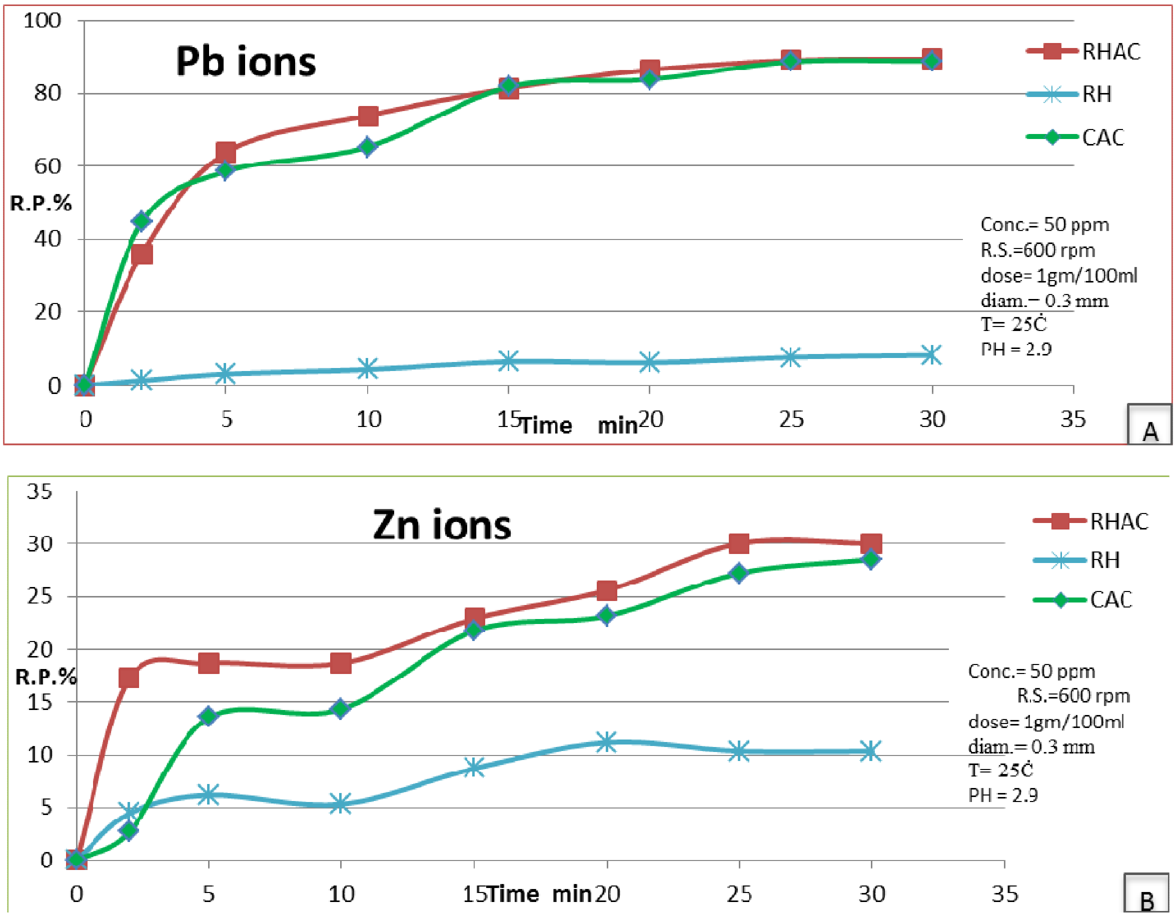


Figure (2):Effect of time contact on the adsorption of heavy metal ions

The results shown that the R.P. of adsorption first increases with increasing in contact time, then remains almost constant. This may be due to the availability of the uncovered surface area of the adsorbents, since the adsorption kinetics depend on the surface area of the adsorbents. The adsorption of heavy metal ions takes place at the more reactive sites. As these sites are progressively filled the more difficult the sorption becomes[19].

The saturation time is determined for adsorption of heavy metal ions on the RHAC with different dosage, the experimental data are presented in Figure (3) and Table (2) .

Table(2):The saturation time of adsorption of H.M.I. on RHAC

Dose	1gm/100ml	2gm/100ml	3gm/100ml	4gm/100ml
H.M.I.	Time min	Time min	Time min	Time min
Pb^{+2}	45	15	15	20
Zn^{+2}	30	15	15	15

At saturation time, the adsorption reached to equilibrium state when the process reached to equilibrium that means the number of molecules arriving on the surface of the adsorbent equals the number of molecules that are leaving.

The equilibrium time indicated to the maximum adsorption capacity of the adsorbent under identified operating conditions, no more H.M.I. was further removed from the solution.

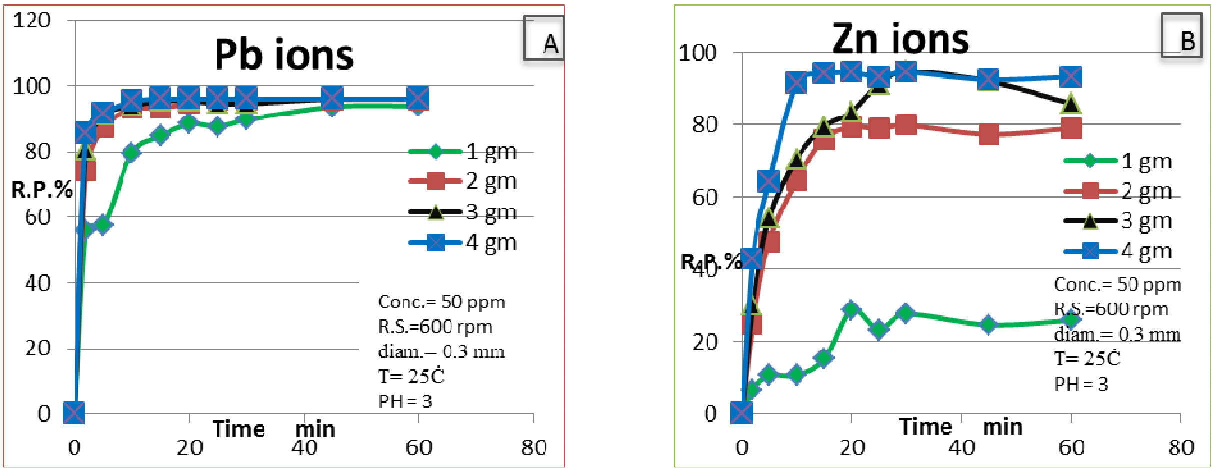


Figure (3): The saturation time of adsorption of H.M.I. on RHAC

3.3 Effect of temperature

The efficiency of adsorption of heavy metal ions was studied with different temperature ranging (8-55ºC), while the other operating parameters were kept constant at initial concentration (50 ppm), rotation speed (600 rpm), pH (3), adsorbent dose (1gm), contact time (15min.) and adsorbent size (0.3 mm). The experimental data are shown in Figure (4).

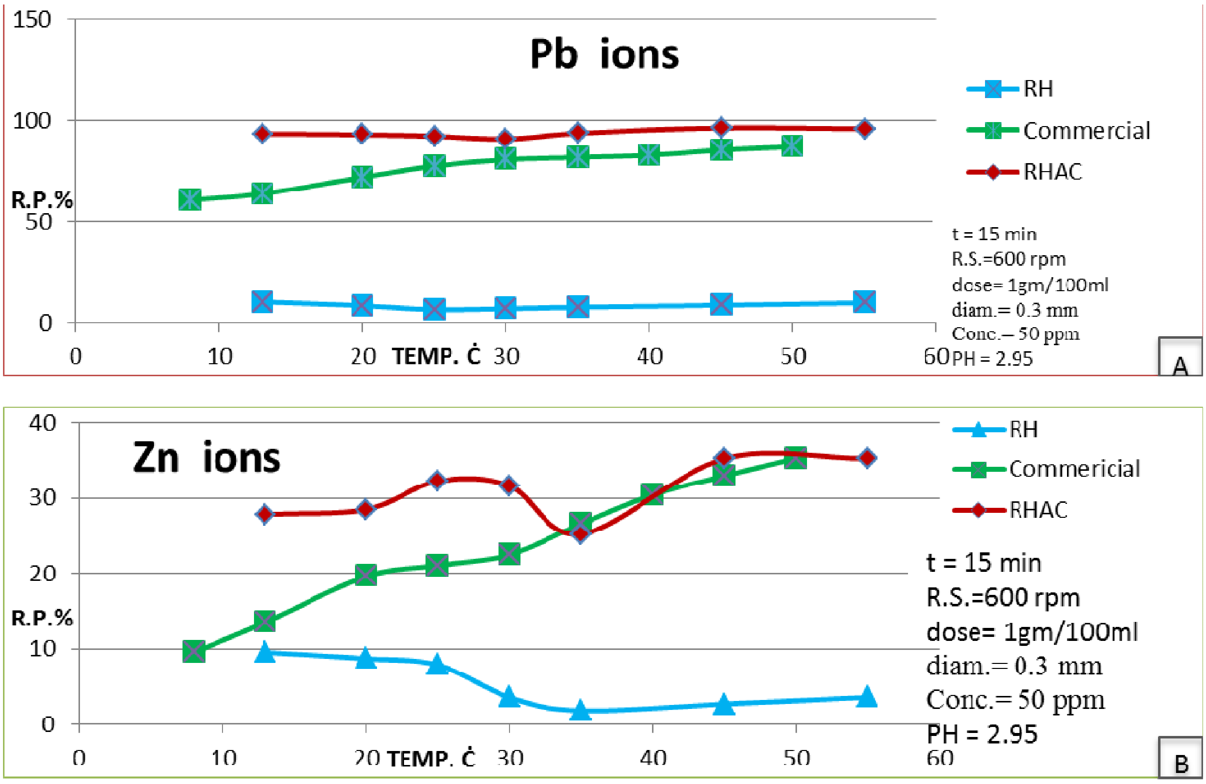


Figure (4):Effect of temperature on the adsorption of heavy metal ions

The plots of R.P. as a function of temperature shows that, an increasing of adsorbed amount of H.M.I with increasing temperature. But the adsorption capacity does not largely depend on temperature.

The enhancement in adsorption with rise in temperature may be attributed to increase in the number of active surface sites available for adsorption, increase in the porosity and in the pore volume of the adsorbent[20]. The enhancement in adsorption may also be a result of an increase in the mobility of the H.M.I. with an increase in their kinetic energy[21]. An increase of temperature increases the rate of diffusion of the adsorbate molecules across the external boundary layer and within the internal pores of the adsorbent particle, due to decrease in the viscosity of the solution[21,22].

3.4 Effect of pH

The pH of the aqueous solution was an important variable, the experimental work were done under the conditions of constant temperature (28^{0}C), adsorbent dose(1gm), particle size (0.3), rotation speed (600 rpm), initial concentrations (50ppm), contact time(15 min) and pH(3-11), the experimental data are presented in Figure (5).

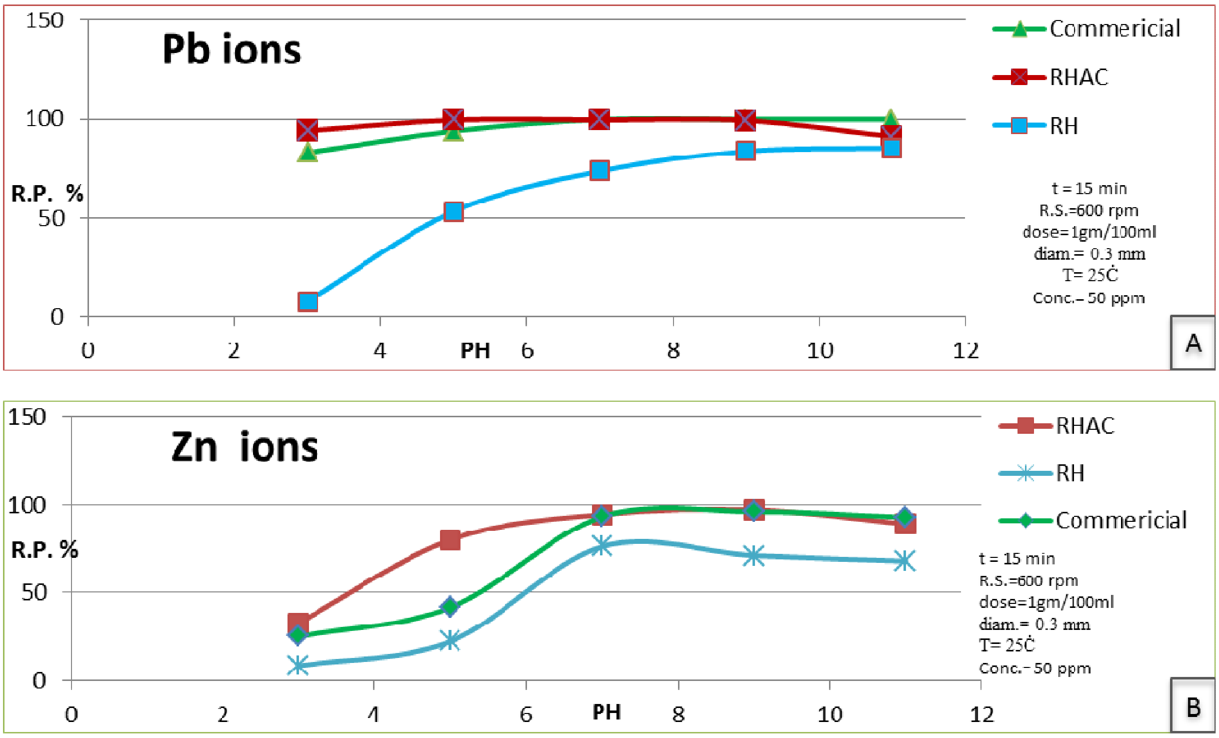


Figure (5):Effect of pH on the adsorption of heavy metal ions

It has been found that the adsorption increases with increase in pH until the optimum pH is reached, the optimum pH of maximum adsorption for H.M.I. on different adsorbent is listed in Table (3).This may be due to the fact that at higher pH values, the surface of adsorbent becomes negative which enhances the adsorption of positively charged H.M.I. through electrostatic force of attraction between the carbon surface and the adsorbate were increased [23].

Table(3): The optimum value of pH of H.M.I. adsorption

H.M.I.	CAC	RHAC	RH
Pb^{+2}	7-9	5-7	7-9
Zn^{+2}	9	7-9	7

3.5 Effect of initial concentration

Adsorption experiments were carried out at different initial H.M.I. concentrations ranging from 10 to 60 ppm to study the effect of initial concentration , other conditions of experimental work are kept constant at rotation speed (600 rpm), pH (3.5), adsorbent dose (1gm), contact time (15min.), temperature (25^{0}C), and adsorbent size (0.3 mm). All the adsorption efficiencies obtained are shown in Figure (6) .

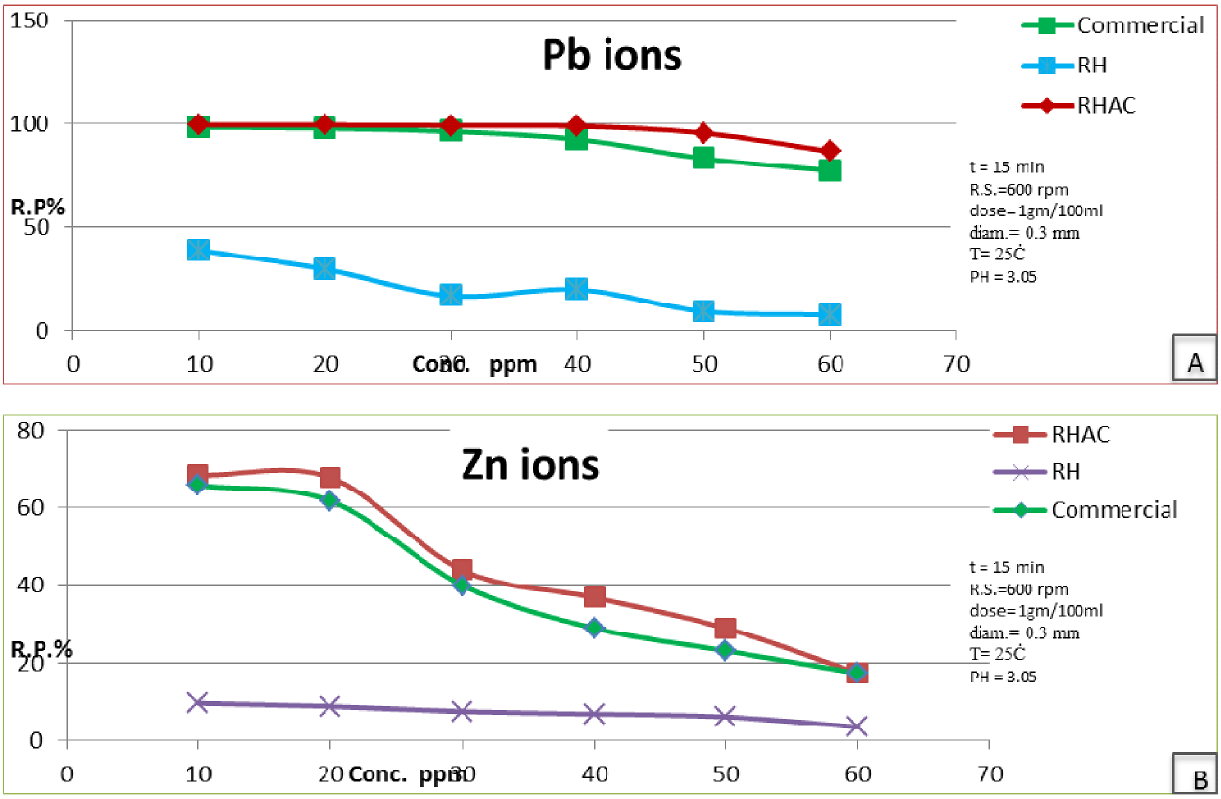
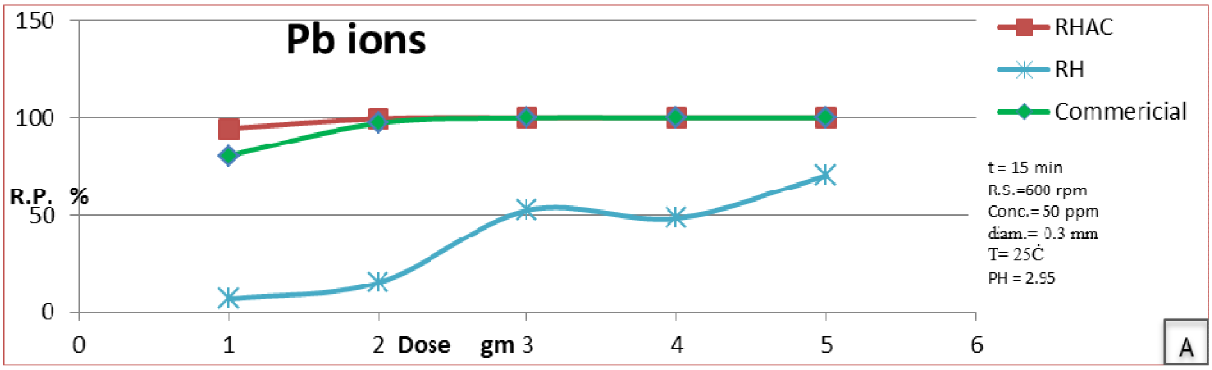


Figure (6):Effect of initial concentration on the adsorption of heavy metal ions

The results are shown that the removal percentage of H.M.I. (efficiency) decreases, with the increase in H.M.I. concentration while the amount of H.M.I. removed will be increased. This is so because the initial H.M.I. concentration provides the driving force to overcome the resistance to the mass transfer of H.M.I. between the aqueous and solid phase resulting in higher probability of collision between metal ions and active sites. The increase in initial concentration also enhances the interaction between adsorbent and adsorbate [24,25].

3.6 Effect of adsorbent dose

The effect of adsorbent dose on H.M.I. adsorption was investigated with different adsorbent dosage ranging (1-5 gm), the other conditions of experimental work are kept constant at contact time (15min.), rotation speed (600 rpm), pH (3), temperature (25^0C), initial concentration(50ppm) and adsorbent size (0.3 mm). All the adsorption efficiencies obtained are shown in Figure (7).



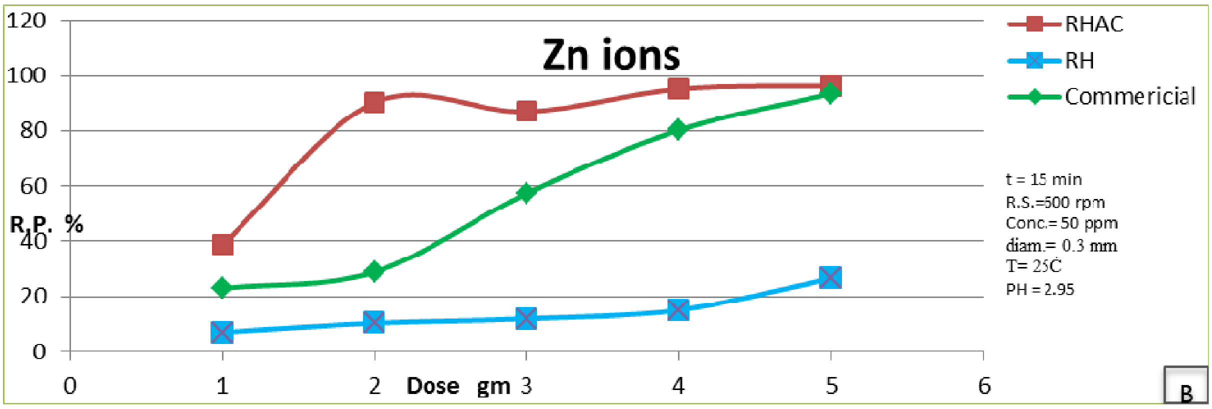


Figure (7):Effect of adsorbent dose on the adsorption of heavy metal ions

The adsorption capacity increased with increasing adsorbent dosage until a certain value , any further addition of the adsorbent beyond this value did not cause any significant change in the adsorption. The optimum adsorbent dosages were determined and listed in Table (4)

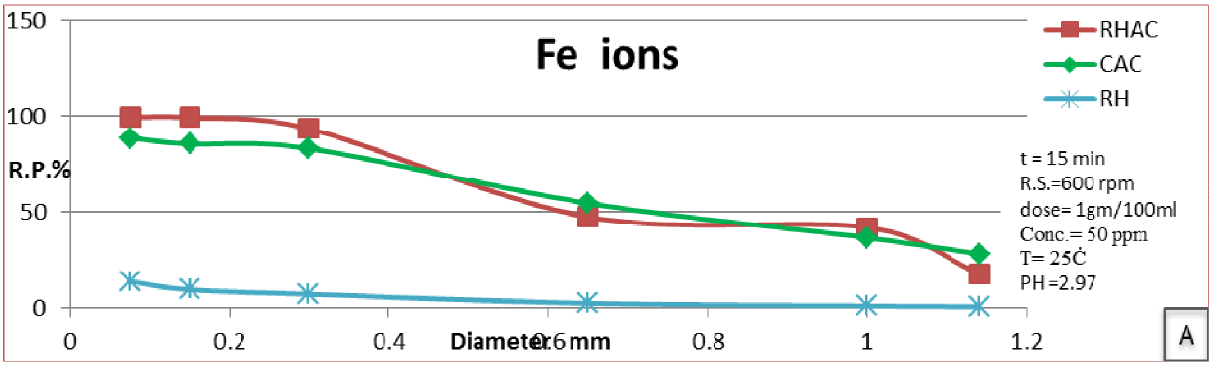
Table(4): The optimum value of adsorbent dose (gm/100 ml of H.M.I.)

H.M.I.	CAC	RHAC	RH
Pb^{+2}	4	3	5
Zn^{+2}	5	4	5

An increase in the adsorption with adsorbent dosage can be attributed to greater surface area and the availability of more adsorption sites[18,25], then there was no further increase in adsorption for either metal ions. This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles [18].

3.7 Effect of adsorbent size

Effect of adsorbent size on adsorption of H.M.I. was investigated by conducting different experiments at different adsorbent diameter (0.075-1.2mm), while the other conditions of experimental work were kept constant at pH (2.97), rotation speed (600 rpm), adsorbent dose (1gm), contact time (15min.), temperature (25^0C), and initial concentration (50 ppm). The experimental data are presented in Figure (8).



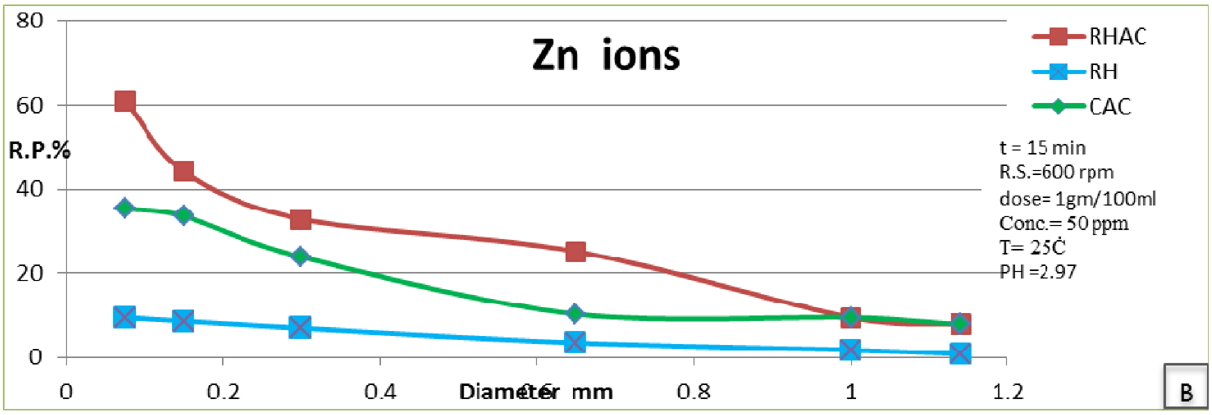


Figure (8):Effect of adsorbate diameter on the adsorption of heavy metal ions

The results shown that the R.P. of H.M.I. increased with decreasing particle size. This is due to the total surface area increasing with decreasing in particle size, which provided more adsorption sites for the metal ion. The shattering of larger particles causing to open tiny cracks and channels on the surface of the adsorbent materials, resulting in more accessibility to better diffusion between liquid and solid phases .

3.8 Effect of rotation speed

The effect of rotation speed on H.M.I. adsorption was investigated. The experimental work were done under the conditions of constant temperature (25^0C), adsorbent dose(1gm), particle size (0.3), PH(2.95), initial concentrations (50 ppm), contact time(15min) and rotation speed (0-1500 rpm), the experimental data are presented in Figure (9).

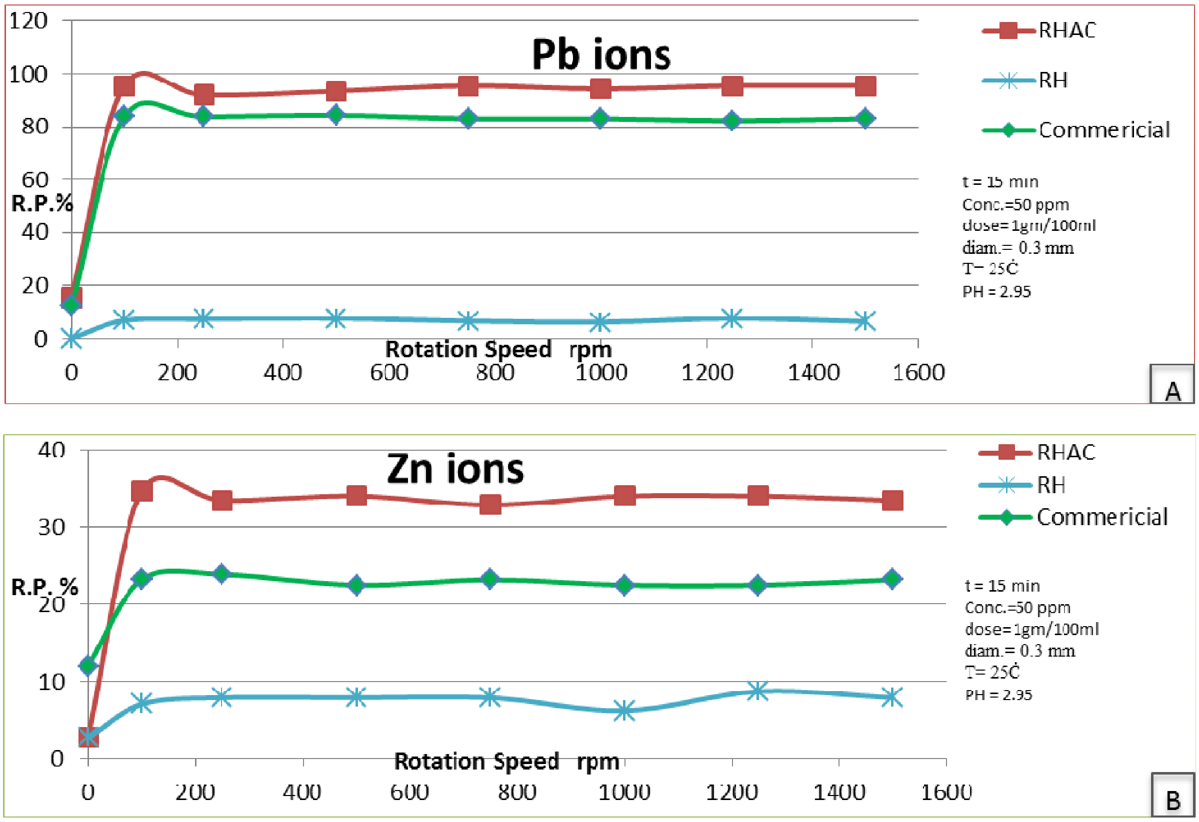


Figure (9):Effect of rotation speed on the adsorption of heavy metal ions

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The adsorption capacity increased with increasing rotation speed. Due to the fact that rotation facilitates proper contact between the metal ions in solution and the adsorbent binding sites and consequently promoting effective transfer of adsorbate ions to the sorbent sites[19].Without rotation speeds the resistance to mass transport is in the bulk solution ,and a thin liquid film surrounding the adsorbent particles offered resistance to mass transport by diffusion . As the rotation speeds increased, there would be decrease in the thickness of the boundary film thereby decreasing the effect of film diffusion[26].

4.1 Comparison of adsorption process in optimum condition

adsorption of Pb ions

The operational parameters were kept constant at (adsorbent dose 3gm, PH 7, adsorbent diameter 0.15 mm, rotation speed 250 rpm, initial concentration 50 ppm, Temperature 55 Ċ and contact time 45 min).

Table (5) Adsorption of Pb ions on the different adsorbents.

Adsorbent	RHAC	CAC	RH
R.P. %	96.26	95.71	81.06

Efficiency of different adsorbents were used to adsorb Pb^{+2} ion arranged: RHAC > CAC >RH

adsorption of Zn ions

The operational parameters were kept constant at (adsorbent dose 3gm, PH 7, adsorbent diameter 0.15 mm, rotation speed 250 rpm, initial concentration 50 ppm, Temperature 55 Ċ and contact time 45 min).

Table (6): Adsorption of Zn ions on the different adsorbents.

Adsorbent	RHAC	CAC	RH
R.P.%	92.51	83.32	53.28

Efficiency of different adsorbents were used to adsorb Zn^{+2} ion arranged: RHAC > CAC > RH

CONCLUSION

The adsorption capacity first increased with increases in contact time until reached the saturation time then remained constant. The rotation speed causing a good contact between the H.M.I. in solution and the adsorbent active sites and consequently providing effective transfer of adsorbate ions to the sorbent sites. And an important factor in the adsorption processes is pH which the adsorption increased with increasing in pH until the optimum pH is reached. Also the adsorption capacity increased with increasing temperature, adsorbent dose while the adsorption capacity decreased with increased in adsorbent size and initial concentration of heavy metal ions .

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