RESEARCH PAPER

Removal of Chromium Ions from Polluted Water by Highly Active Surface ZnO/ Activated Carbon: Kinetic and Thermodynamic Model

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ABSTRACT

In this study, Activated carbon was prepared by simple method using stem a Punica granatum. The nano ZnO was prepared by Silybum marianum leaves extract and zinc sulfate ($ZnSO_4$) (source of zinc oxide nanoparticles) with calcination at temperature at 600 °C. The activated carbon and nano ZnO as a binary composite were prepared by mixing a certain different ratio of activated carbon and zinc oxide nanoparticles by ultrasonicification. FTIR spectroscopy, Field-Emission Scanning Electron Microscope techniques (FESEM) and X-ray diffraction were used to characterize the synthesized compounds. The experimental data were fitted into two kinetic models: pseudo-first order and pseudo-second order. It was observed that pseud-second order describe the adsorption better than pseudo-first order kinetic models. Negative values of the thermodynamic functions (ΔG, ΔH, ΔS) of the adsorption declared that it is spontaneous, exothermic and the position of the adsorbed Cr^{+3} ions is more regularly after the adsorption process.

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INTRODUCTION

Environment" means all living organism that surroundings, such as natural forces, which provides that condition for the development and growth, danger and damage [1]. It also means surrounding everything that effects on organism during its lifetime or it is sum total of water, air and land and also their relationship with the human being. It involves all the physical and biological surrounding and their interactions [2]. So, pollutants entrance to a natural environment leads to disorder, instability, damage or discomfort of the ecosystem i.e. physical systems or living organisms known as the environmental pollution [3].

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Environmental pollution can be; water pollution, light pollution, air pollution, noise pollution, soil pollution, thermal pollution, radiation pollution, and known as pollutants [4]. Water pollution, known as the water bodies pollution (for example rivers, lakes, oceans and ground water) is the most significant environmental problems. Human is the main source of it, due to the activities such as agricultural, industrial and domestic processes. Contaminates are happen in directly and indirectly into water bodies without enough remediation to remove harmful compounds [5]. The presence of heavy metals is one of the major concerns and that used target pollutants in research studies of the well- documented human health problems associated to these compounds and also their high toxicity [6,7]. Adsorption is the potent treatment processes as comparing with other technologies, for the remediation of different contaminates from aqueous environment due to the low-cost factor, moreover it can isolate the small amounts of toxic elements that exist in a large volume of solutions. Different adsorbents have been commercialized and modified to treat the waste water [8, 9]. A number of commercial activated carbons have been utilized as received and after chemical modifications for Cr(VI) adsorption. Several works have been reported for the development of low-cost activated carbon from renewable resources, and how to water decontamination in friendly environmental manner. Waste materials that are produced from the agriculture and industry operations have been used as activated carbon precursors for the removal of Cr(VI) [10].

In the present study, use activated carbon and zinc oxide nanoparticles and their composite to

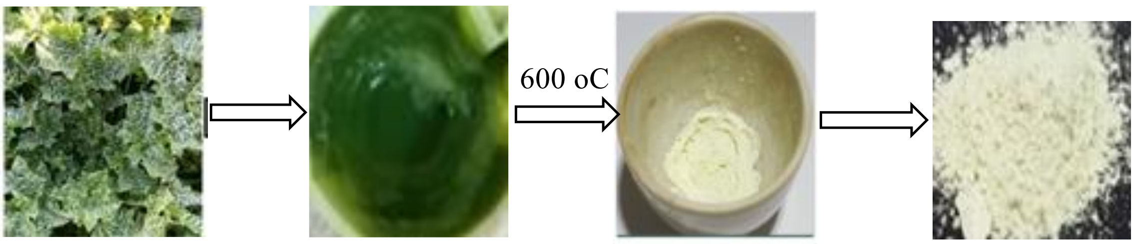

Fig. 1. Steps of the preparation of zinc (II) oxide nanoparticles using Silybum marianum leafs Extract.

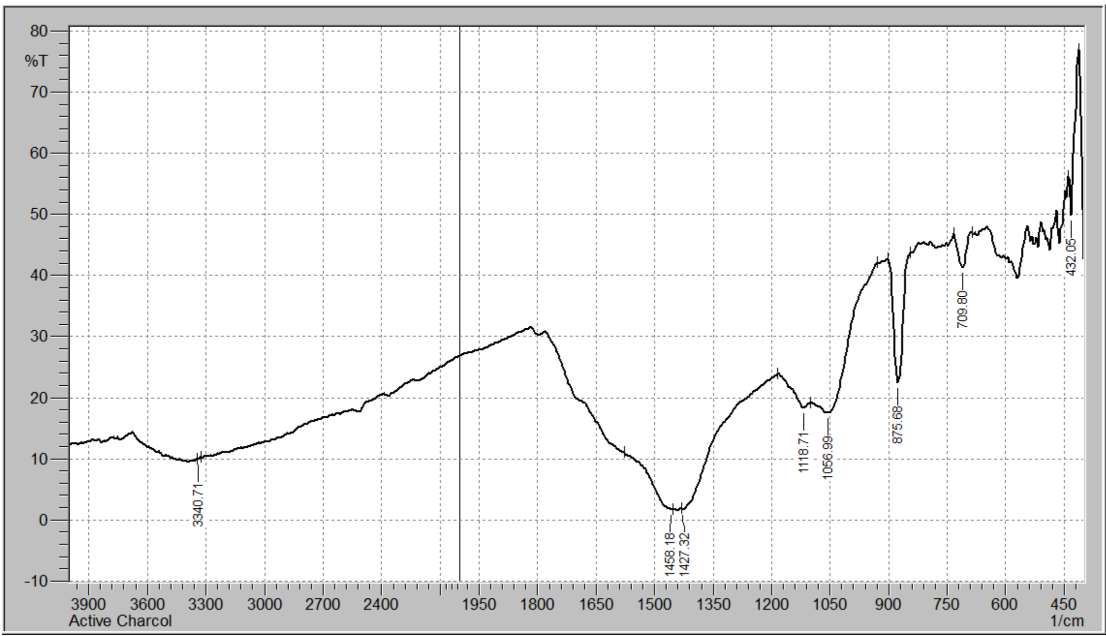

Fig. 2. FTIR spectra of activated carbon

the adsorption of Cr^{+3} from polluted water have investigated, and study the adsorption kinetic with thermodynamics function.

MATERIALS AND METHODS

Preparation the activated carbon

The charcoal was obtained from the local garden - Iraq by burning the stem of the Punica granatum. For obtained Activated carbon, the Punica granatum charcoal (500 g) was grinded well to become a powder. Drying the charcoal powder with air for 24 hours, after that, carefully mix calcium chloride and water in a 1:3 ratio, then cover the charcoal powder completely with the calcium chloride solution under stirring to get a cohesive paste. The paste was covered and left for 24 hours, and it was placed in an oven (200 °C) for 3 hours to obtain activated carbon.

Synthesis of Zinc (II) Oxide nanoparticles

Zinc (II) sulfate ($ZnSO_4$) (0.5) g was dissolved in (100 mL) of deionized H_2O with continuous stirring, and was added to (20 mL) of plant extract gradually with continuous stirring at room temperature then, raise temperature of solution to (70 ^{0}C). Adjusts pH of the solution by adding potassium hydroxide (0.1 M) approximately (20-25 mL) where precipitate with a light green color of zinc hydroxide nanoparticles formed, separate using centrifuge and washed with deionized water several times and absolute ethanol to remove impurities, dry in an oven at (80 ^{0}C) for (1.5) hours, and calcinaeted in the oven at 600 °C and zinc oxide nanoparticles were formed. The steps are shown in Fig. 1.

Preparation ZnO /Activated carbon as a binary composite

Using impregnation method, the ZnO / Activated carbon composites were synthesized (0. 3g activated carbon: 0.3g ZnO nanoparticles). An impregnated aqueous solution was prepared by suspended 0.3g of activated carbon in and 0.3g of ZnO nanoparticles in 20 mL THF at room temperature with constant stirring; the mixture was placed in ultrasonic apparatus. After 2 hour the nanoparticles are completely suspended and the solvent was evaporated to obtain a ZnO / Activated carbon as a binary composite.

Studying the factors affecting adsorption process

Effect of contact time on Chromium ions Adsorption

The time that is required for the adsorption process to reach equilibrium at temperature of 25 °C and was determined by using five volumetric flasks with a volume of (100 mL) and containing (100 mL) polluted water contain a Cr^{+2} ions with initial concentration of (Cr^{+2} =0.9745 mg/L). Adsorbent amount of 3 g of activated carbon, ZnO nanoparticles and binary composite activated carbon /ZnO were added into each flask and covered and placed in a water bath shaker at constant temperature of (25°C) K at speed of (150) rpm at various time intervals (20, 30, 40,

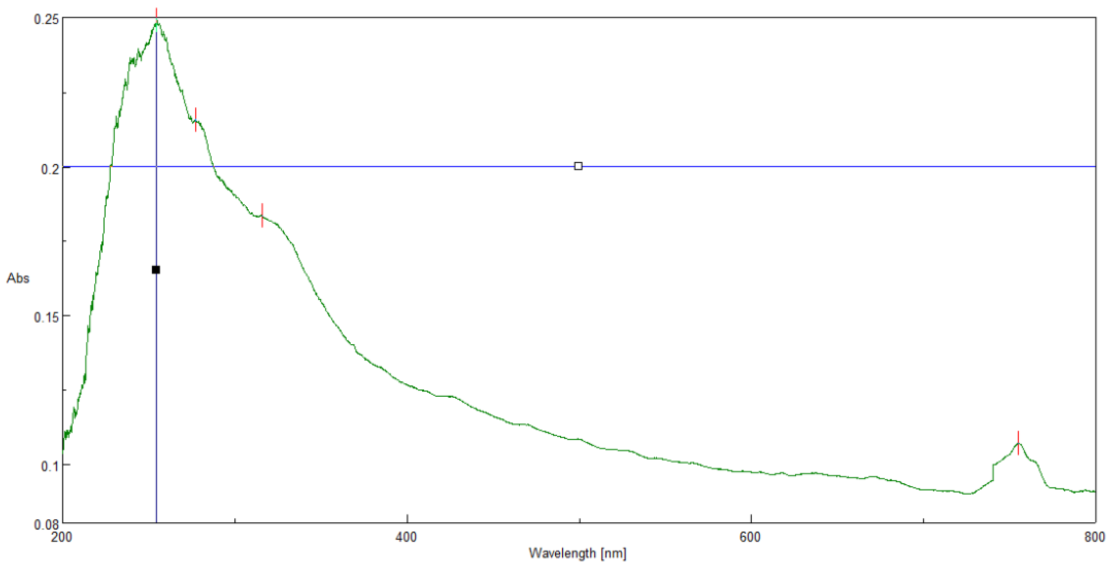

Fig. 3. UV-Vis spectroscopy of ZnO nanoparticles.

50, 60 and 80) min. Then filtered the solutions and finally measure the concentration of Cr^{+3}ion in polluted water to reach equilibrium using atomic absorption spectrophotometer at λ_{max} of (280-400 nm) for all ions.

The effect of surface weight

The influence of surface weight has studied using (1, 1.5, 2, 2.5 and 3) gram from prepared activated carbon, ZnO nanoparticles and binary composite activated carbon /ZnO for the removal of heavy metal ions (Cr^{+2}, Cu^{+2} and Cd^{+2}) ions using a fixed (150 mL) of (Cr^{+3} = 0.9745 mg/L), temperature at 25 °C, stirring speed at 150 rpm. The contact time for adsorption was 100 min for all cases.

Effect of temperature

In order to investigate the temperature effects on adsorption the experiments are carried out at different temperatures (25, 30, 35, 40, 45 and 50) °C to remove Cr^{+3} ions from polluted water. The adsorption equilibrium constant (K) calculate by using Vent Hoff Arrhenius equation 1.

$$\ln xm = \frac{-\Delta H}{RT} + \text{Constant} \quad (1)$$

Where x/m is maximum adsorption (mg/g), constant represented vent Hoff constant.

RESULT AND DISCUSSION

Samples characterization

Infrared Spectra Analysis

Fourier Transform Infrared Analysis (FTIR) for the activated carbon spectrum showed weak broad bands at 3440 cm^{-1} belong to O–H stretching, C–H bonds of the aromatic ring moderate intensity at 2927–2981 cm^{-1}. Band at 1643 cm^{-1} and 1427 refers to C=O /C=C bonds, while 1049 cm^{-1} for the C–O bonds of the aromatic ring compound (Fig. 2) [11].

UV-Vis Spectroscopy

The prepared ZnO nanoparticles exhibit an absorbance peak at about 254.4 nm (Fig.3) which corresponds to the particle size of 111 nm.

XRD diffraction

X-ray diffraction spectroscopy was performed for ZnO nanoparticles. The main peaks that appear for the zinc oxide nanoparticles can be observed, as shown in the Fig. 4. In comparison with Fig. 5 and the return for the ZnO/activated carbon composite, we had shown that the peaks of the ZnO nanoparticles were not influenced and maintained their position and width with a slight decrease in their intensity. This indicates that the ZnO nanoparticles have good dispersion in case of activated carbon.

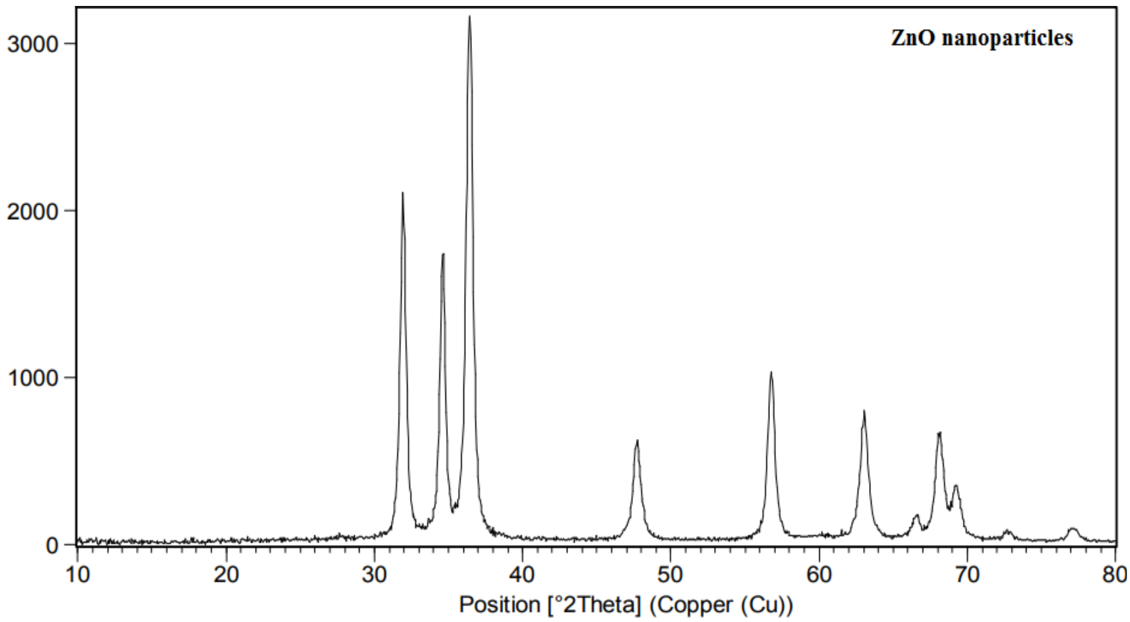

Fig. 4.XRD plot of ZnO nanoparticles.

FESEM image

In general, the Field-emission Scanning Electron Microscope technique gives information about the shape of the surfaces and size nanoparticles of the prepared nanomaterials. Figs. 6 and 7 gave information about the surface of the prepared samples difference in the shape and size of nanoparticles. The FESEM images also showed the clear effect of activated carbon on reducing the accumulation of ZnO nanoparticles

Adsorption of Cr^{+3} ions

The effect of contact time, surface Weight and temperature on the Cr^{+3}ions adsorption from polluted water was studied by activated carbon that prepared from Punica granatum, in addition to zinc oxide nanoparticles and the binary composite prepared from ZnO nanoparticles/ activated

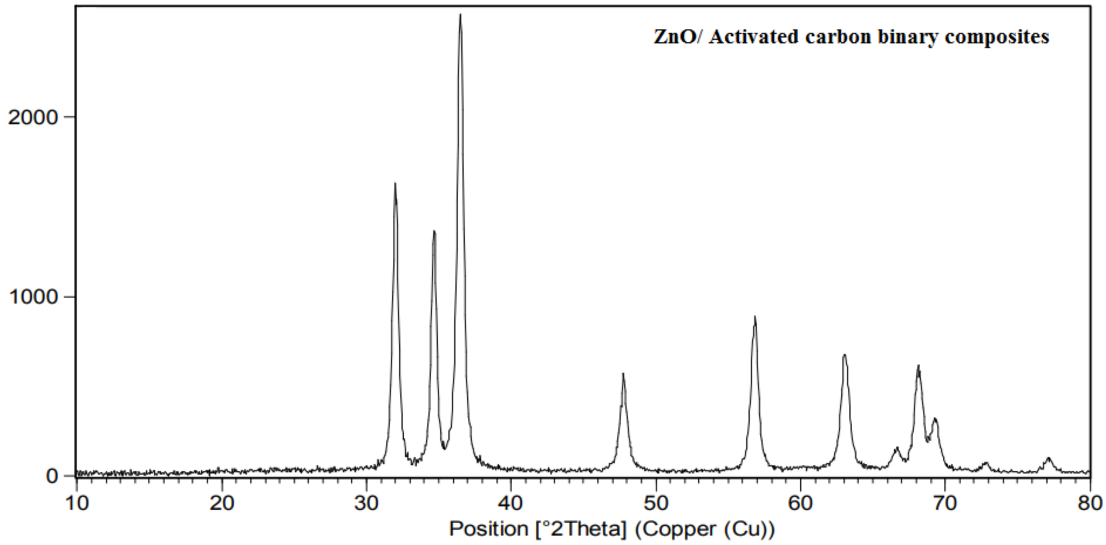

Fig. 5.XRD plot of ZnO/ activated carbon binary composite.

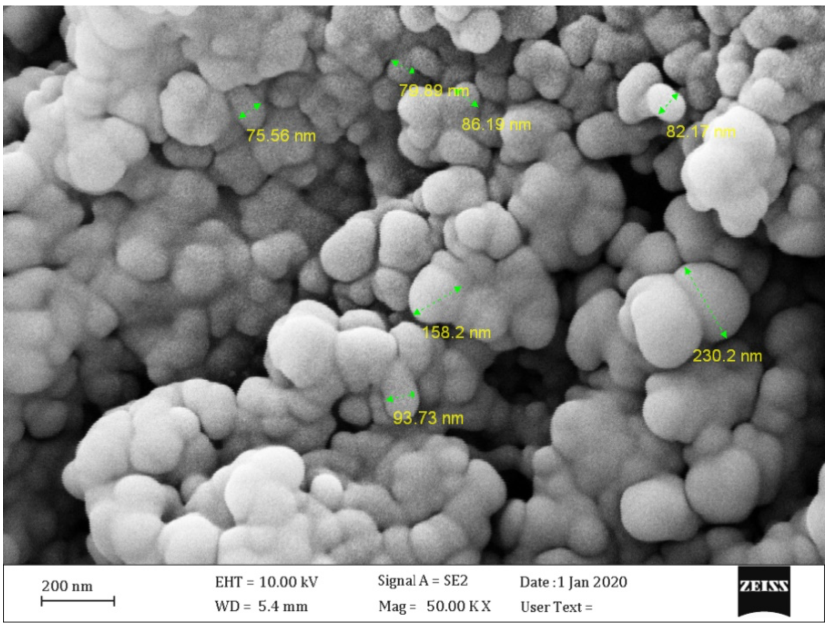

Fig. 6. FESEM images of ZnO nanoparticles

carbon. Initial concentration of Cr^{+3} ions in polluted water before carrying out the adsorption process by atomic absorption was Cr^{+3} equal 0.9745 mg/L.

Effect of Contact Time on Adsorption

The residual heavy metal ions concentrations in the polluted water were determined by atomic absorption and the percent of removed metal ions (R%) in the solution was calculated using Equation 2:

$$\% \text{ Removed} = \frac{C0 - Ct}{C0} X\ 100 \quad (2)$$

C_0 is initial concentration of chromium ions and C_t residual concentration of chromium ions after t time.

It is clear from Fig. 8 that the adsorption process of Cr^{+3} ions was enhanced by using ZnO/ activated carbon composite, also we can note the percent of removal Cr^{+3} ions was increased with increasing contact time.

Effect of Surface Weight

The effect of surface weight is a crucial factor to determine the ratio of adsorption rate capacity adsorption on the concentration of Cr^{+3} ions, this study was found that the capacity of adsorption of metal ions was highest when using the amount of

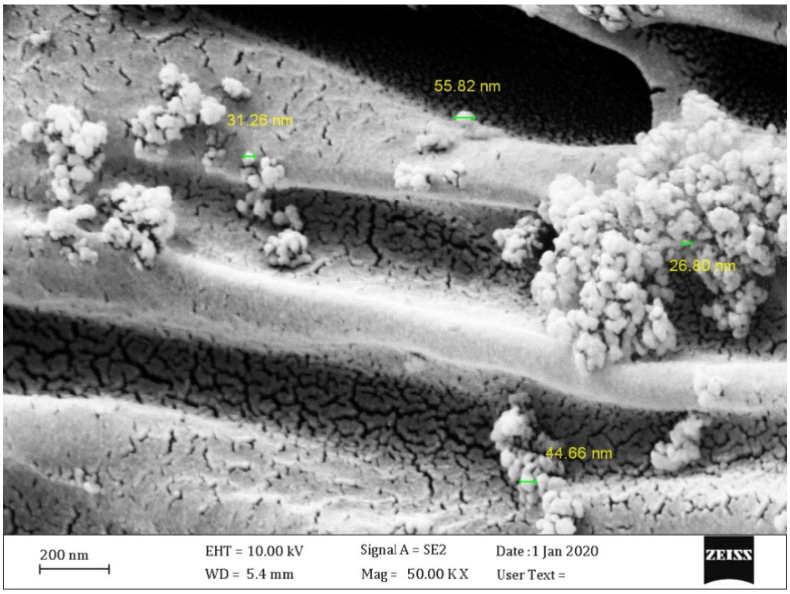

Fig. 7. FESEM images of ZnO/ activated carbon composite

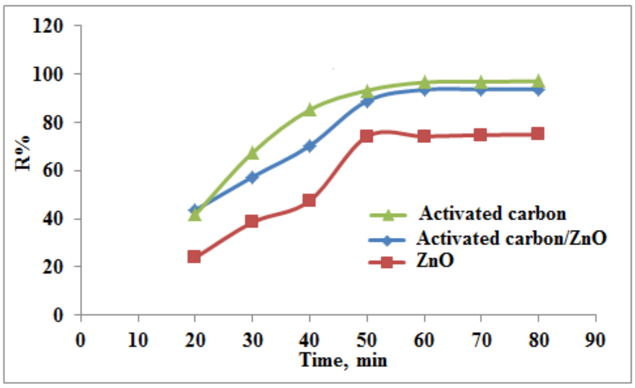

Fig. 8. The effect of contact time on the % removed of Cr^{+2}

3 grams of nanomaterial.

Effect of temperature on the Cr^{+3} Adsorption

The temperature had a manifest effect on the adsorption of chromium ion for all synthesized samples. To study the effect of temperature on the removal of Cr^{+3} percentage, works were done at different temperatures, (25, 30, 35, 40, 45 and 50) °C, using optimum surface weight 3 g, contact time 80 min and initial concentration 0.9745 mg L^{-1}. The effect of temperature on Cr^{+3} removals can be noticed from Fig. 10, by means increase of

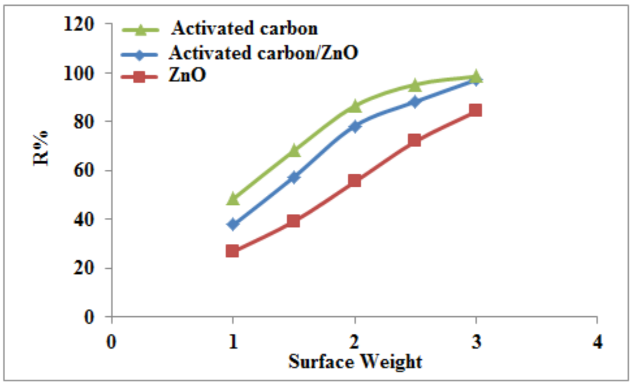

Fig. 9. The effect of surface weight on the percent removed of Cr^{+3} ions

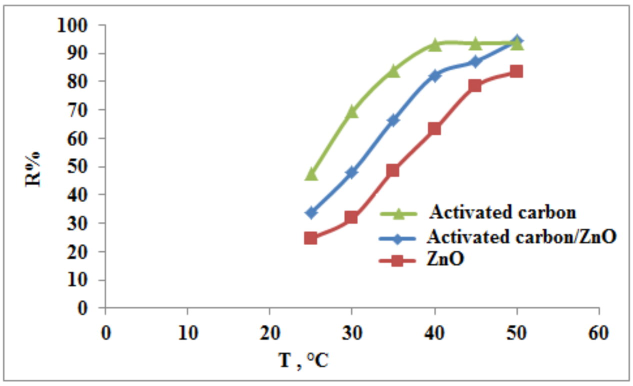

Fig. 10. The effect of temperature on the % removed of Pb^{+2} ion

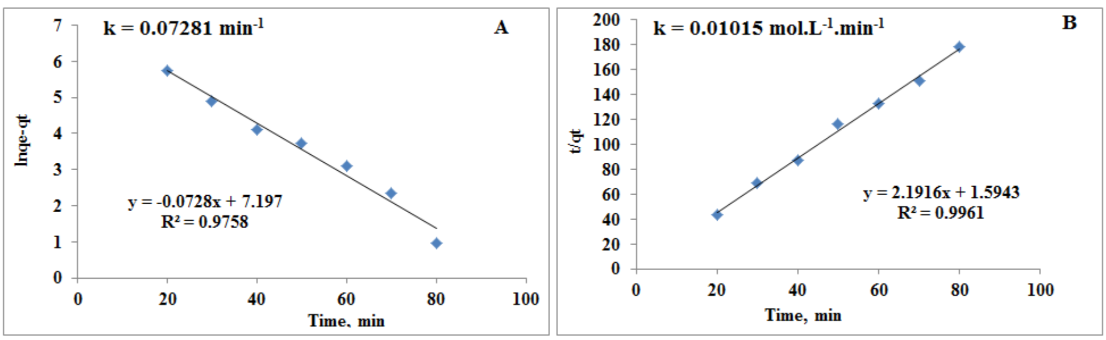

Fig. 11. Pseudo-second order (A); Pseudo-second order (B) plots for Cr^{+3} ions adsorption

removal efficiency with increasing temperature exhibit that the Cr^{+3} adsorption processes is an exothermic [12].

Adsorption Kinetics

The Lagergren equation was used to derive the rate constant of the chromium ion adsorption process on the surface of activated carbon and it's their composite. The pseudo-first-order kinetic model equation is shown as:

$$\ln(qe - qt) = lnqe - k1t \qquad (3)$$

Where qe is absorbed Cr^{+3} ions at equilibrium and qt is absorbed Cr^{+3} ions at time (mg g^{-1}) and k1 is the first-order rate constant (min^{-1}).

The pseudo-second-order kinetic model is shown as:

$$\frac{1}{qt} = \frac{1}{kq2e} + \frac{t}{qe} \qquad (4)$$

The adsorption kinetics of chromium ions (Cr^{+3}) on the activated carbon, zinc oxide nanoparticles and their binary composite surface at a temperature of 298 K and an initial concentration

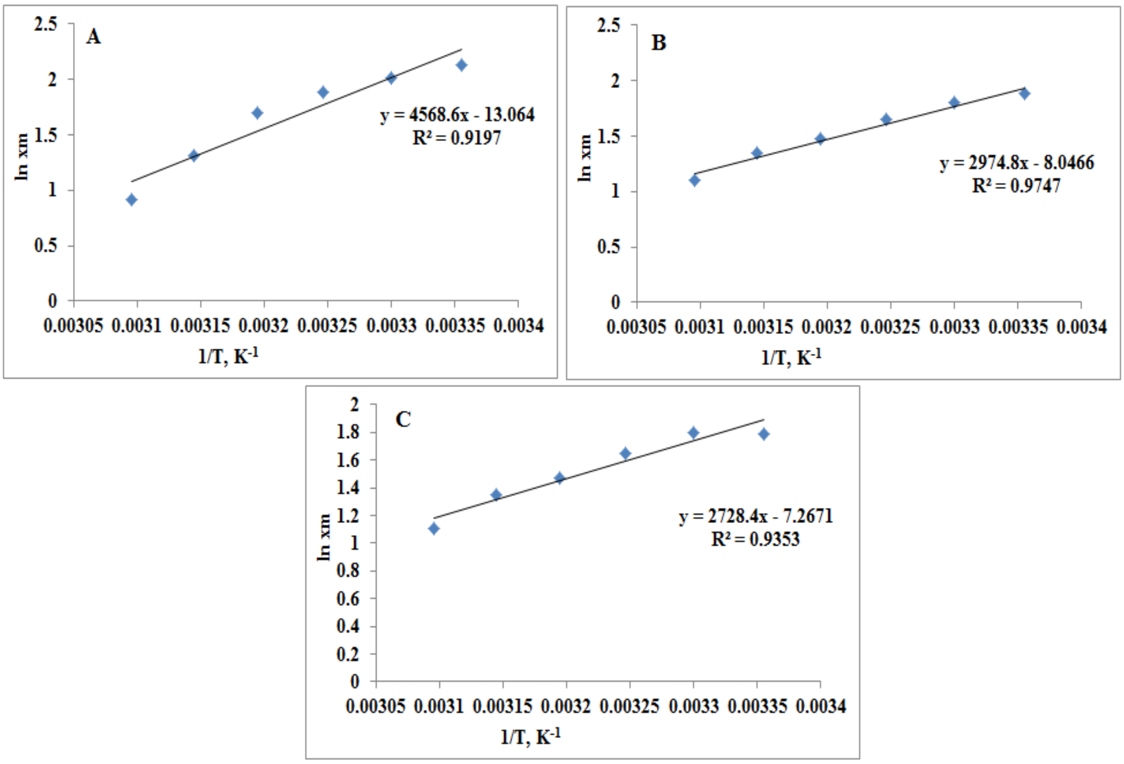

Fig. 12. Plot of ln xm versus 1/T to estimate the thermodynamic parameters for the adsorption of Cr^{+3} on(A) activated carbon, (B) ZnO nanoparticles, and (C) ZnO/ activated carbon composite

Table 1. Thermodynamic parameters of Cr^{+3} ion adsorption onto activated carbon.

T	ΔG, KJ mol^{-1}	ΔH, KJ mol^{-1}	ΔS, J $mol^{-1}k^{-1}$
298	-5.281		
303	-5.081		
308	-4.828	-37.983	-0.108
313	-4.426		
318	-3.466		
323	-2.471		

Table 2. Thermodynamic parameters of Cr^{+3} ion adsorption onto ZnO nanoparticles.

T	ΔG, KJ mol^{-1}	ΔH, KJ mol^{-1}	ΔS, J $mol^{-1}k^{-1}$
298	-4.656		
303	-4.538		
308	-4.216	-22.684	-0.0604
313	-3.825		
318	-3.564		
323	-2.959		

Table 3. Thermodynamic parameters of Cr^{+3} ion adsorption onto ZnO/ activated carbon composite.

T	ΔG, KJ/mol	ΔH, KJ/mol	ΔS, J $mol^{-1}k^{-1}$
298	-5.4747		
303	-5.3275		
308	-5.24487	-24.837	-0.0642
313	-5.01919		
318	-4.37856		
323	-3.80151		

0.9745 mg L^{-1}were studied. The results of the adsorption kinetics study showed, according to the pseudo first order, by drawing (ln qe-qt) against time see Fig. 11, k value and ln qe were obtained from the slope and the intercept of the plot, respectively.

It was spotted that pseud-second order describes the adsorption with high correlation factor (R^2) better than Pseudo-second order kinetic models.

Interpretation of thermodynamic functions

The effect of temperature on the adsorption of chromium ion on the surfaces prepared was studied at temperatures (25, 30, 35, 40, 45 and 50 °C). When plotting the values of (ln xm) against (1/T), we get a straight line whose slope is equal to the heat of adsorption (ΔH) according to the Vent Hoff Arrhenius equation (equation 1). Fig. 12 and Tables 2 and 3 and 4. We get the Gibbs free energy through the equation 5:

$$\Delta G = -nRTLn\ qe/Ce \quad (5)$$

Hence, the value of the change of entropy is obtained from the Gibbs equation for equilibrium:

$$\Delta G = \Delta H - T\Delta S \quad (6)$$

CONCLUSION

In our concluded that the prepared surface ZnO NPs by Silybum marianum leaves extract and zinc sulfate (ZnSO4) have a highly surface activity for removal of pollutants. The work confirm the results observed that Negative values of the thermodynamic functions (ΔG, ΔH, ΔS) of the adsorption declared that it is spontaneous, exothermic and the position of the adsorbed Cr+3 ions is more regularly after the adsorption process. Beside that pseud-second order describe the adsorption better than pseudo-first order kinetic models.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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