Egypt.J.Chem. **Vol. 63**, No.2, pp.425-431 (2020

Egyptian Journal of Chemistry
http://ejchem.journals.ekb.eg/

The Removal Of Zinc Ions From Their Aqueous Solutions By Cr_2o_3 Nanoparticles Synthesized Via The UV-irradiation Method

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A modification of an UV-irradiation method is used to synthesis of Cr_2O_3 nanoparticles. It is a simple and easy way to produce small particles of chromium oxide at a range of 2 – 30 nm according to the transmission electron microscopy (TEM) and X-ray diffraction (XRD) characterizations. In this study, the synthesized nanoparticles are used as an adsorbent for zinc ions from their aqueous solutions under effect of different temperatures 15, 25, 35, 45 and 55 °C. The adsorption process of zinc ions is endothermic (ΔH is 10.33 kJ/mol) and its data fitted well with the Freundlich isotherm model (R_2=0.9601). The data of adsorption show non-spontaneously in nature when the thermodynamic parameter ΔG is positive (1.515 kJ/mol). However, the ΔG changes to a negative value with the temperature rising and the process begins spontaneously because the adsorption capacity increases with increase in temperature.

Keywords. Cr_2O_3 nanoparticles, chromium oxide, UV-irradiation, zinc ion, adsorption.

Introduction

The manipulation of particles into a nanoscale produces novel and improved physicochemical properties compared with the so-called bulk solid [1, 2]. These unique properties of nanoparticles are exhibit due to the high aspect ratio, shape, crystallinity and the shape of the surface edges [3-5].

Two stable chromium oxides can exist in the environment that are trivalent chromium (Cr III) and hexavalent chromium (Cr VI). Since its first successful experiment in the chemistry of dyes by Augustus Schultz, It has remained the sole leather-tanning chemical [6]. Later, chromium oxides (Cr_2O_3) have attracted great attention due to their contribution in many applications, such as coating for high temperature [7], the UV and microwave shielding [8], green pigments [9], solar energy collectors [10], photonic and electronic devices, heterogeneous catalysts [11, 12] and hydrogen storage [13]. Moreover, as many nanometal oxides, such as aluminum oxides [14], titanium oxides [15], cupper oxides [16], magnesium oxides [17], iron oxides [18, 19] and cerium oxides [20] have been shown an axcellent heavey metal adsoption from aqueous solutions, the spherical Cr_2O_3 nanoparticles demonstrates a remarkable capacity in water treatment to extract azo-dye pollutant [21]. The Cr_2O_3 nanospheries with excellent dye absorptions are therefore expected to be useful in alternative technologies for absorption.

According to the advantage of the Cr_2O_3 nanoparticles, they have been synthesised by several developing techniques inclouding the sol-gel process [22-24], mechanochemical process [25], precipitation-gelation [26, 27], sonochemical reactions [28], solid thermal decomposition [29, 30], bio method [31], nano casting method [32], laser irradiation method [33], gas condensation

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Received 7 /12/2019 Accepted 12/12/2019
DOI: 10.21608/ejchem.2019.17003.2042

[34] and microwave method [35]. Each method has features that affect particle size, morphologies, dispersion and so on. For example, the irregular morphologies and particle aggregation were obtained using the plasma method [36]. It had also been reported ageing chromium sulfate for long periods of time produced particle sizes in the micrometre range [37, 38]. Moreover, some methods are complicated, sensitive to the surrounding environment, cost effective, the high temperature needed and advance lab [39].

In the current study, we report for the first time, the synthesis of chromium oxide nanoparticles using the UV-irradiation technique. It is a simple, cheap, one-step process and high efficiency. XRD was obtained the size and crystallographic structure of nanoparticles, and TEM was used to study the morphology and size of particles. Moreover, these nanoparticles were studied to be adsorbent for zinc ions and they proved to have high efficiency for removing zinc ions from their solutions.

Experimental

Materials

The chemicals of (KCr$(SO_4)_2$·٦H٢O) and $ZnCl_2$ were used as received from Sigma-Aldrich. Deionized water was used throughout the experiment steps.

Synthesis of chromium oxide nanoparticles

Cr_2O_3 nanoparticles were synthesized by the UV-irradiation method [40] as shown in Fig. 1. The photocell contains a 125 W UV mercury lamp with a wavelength of 365 nm and a pyrex tube, which was a reactor, was cooled in an ice bath to avoid the temperature rising as a result of the UV-irradiation. A complex solution of chromium was gotten after dissolving 0.3 g of (KCr$(SO_4)_2$·٦H٢O) in 30 ml of deionized water. The solution was irradiated for 30 minutes and then a precipitate of brown color CrOOH was shown. The precipitation was separated and washed several times with deionized water using a centrifuge. A black-green precipitate of chromium oxide nanoparticles was obtained, after dry the material for a day and calcine it in an oven at 450 ^oC for 2 hours.

Characterization

The nanoparticles of chromium oxide were studied by (XRD-6000) that was operated at 30 mA and 40 kV to generate radiation at a wavelength of 1.5406 Å. JEOL JEM-2100 TEM measurement was used to study the size and morphology of nanoparticles.

Adsorption experiment

(5 - 25 mg/l) of zinc ion solution was used to study the adsorption of zinc on Cr_2O_3 nanoparticles. The solution was prepared by dissolving $ZnCl_2$ in deionized water. 0.05 g of nanoparticles were added to 10 ml of zinc solution at each concentration. The mixture was shaken for 60 min at 15, 25, 35, 45 and 55 ^oC.

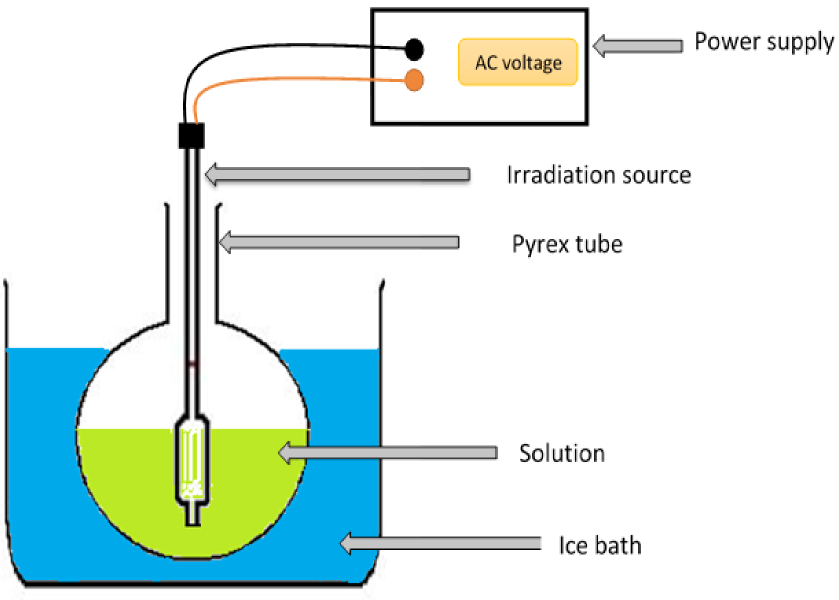

Fig. 1: Synthesis of chromium oxide nanoparticles using the UV-irradiation method.

Results and Discussion

XRD of synthesized chromium oxide nanoparticles is shown in figure 2. The peaks are shown only for Cr_2O_3 at a high degree of purity and peaks for other materials are not detected. The result of XRD displays sharp peaks that indicate high crystallinity nanoparticles. According to the Debye-Scherrer formula [41], the average particle size was calculated to be 16.7 nm.

TEM characterization was obtained the exact size of the Cr_2O_3 nanoparticles. Figure 3 shows that the nanoparticles have clear morphological boundaries with different sizes at around 2 – 30 nm. The result shows a good agreement with the XRD calculation.

The adsorbent phase of the retained concentration of zinc ions was determined according to the following equation:

$$Q_e = (C_e - C_o) V_{sol} / M \quad (1)$$

where is equilibrium ion concentration (mg/l), is equilibrium capacity (mg/g), is concentration of initial ion solution (mg/l), is solution volume (l) and is mass adsorbent (g).

The isotherm of zinc adsorption deals with the linearized Freundlich isotherm as seen in Figure 4. The relationship between the Zn^{+2} concentration at equilibrium and the of chromium oxide nanoparticles is given by

(2)

Where and were known by the Freundlich constants, and are the adoption of capacity and intensity, respectively. The linear fitting of the isotherm data was shown excellent fitted the Freundlich isotherm (R^2=0.9601). The calculations were shown that the constant values of and were 4.142 and 1.821, respectively. The multilayer adsorption was indicated by value.

Langmuir isotherm equation is shown below:

(3)

where a and b are adsorption energy constants and are known by the Langmuir constants. Figure 5 shows that the linear fitting of Langmuir isotherm data for zinc adsorption in its solution did not undergo the Langmuir isotherm according to the low value of R^2 which is 0.5593. This happened due to the Langmuir isotherm. It is correct for single-layer adsorption onto a surface with a limited number of homogeneous energy sites [42].

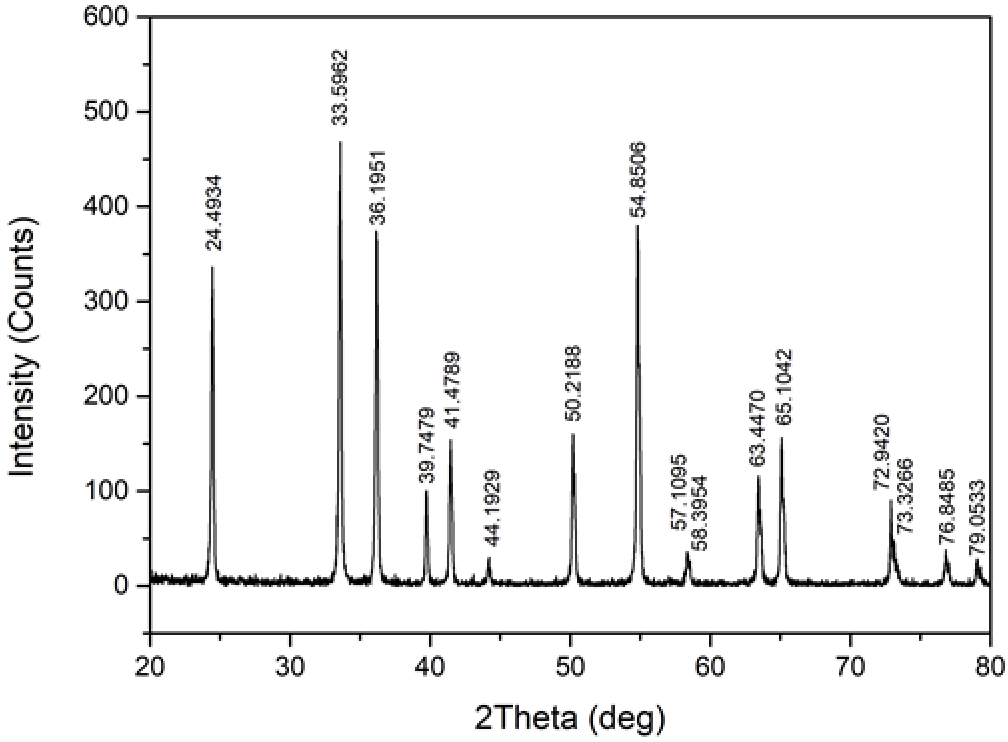

Fig.2: XRD pattern of the Cr_2O_3 nanoparticles.

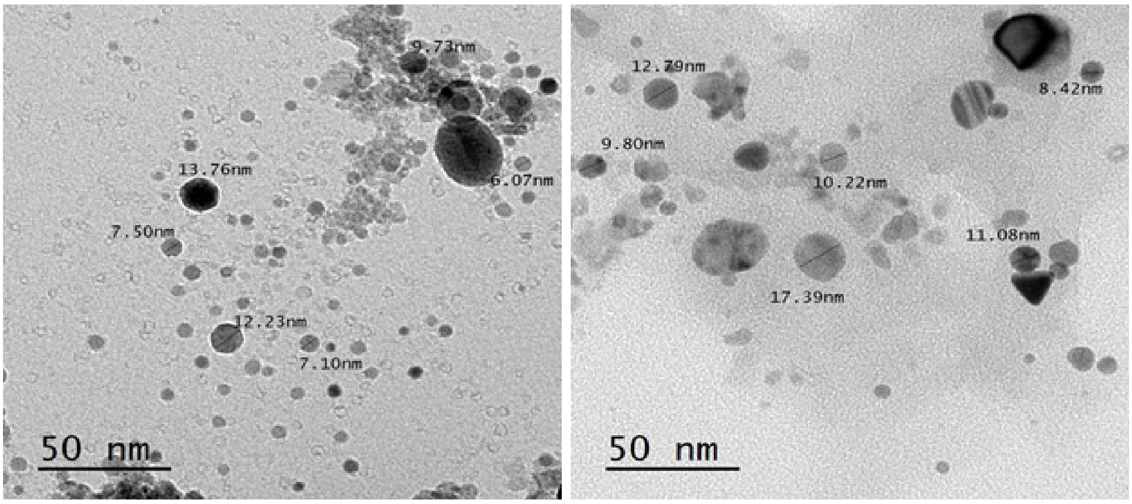

Fig.3: TEM images of the Cr_2O_3 nanoparticles.

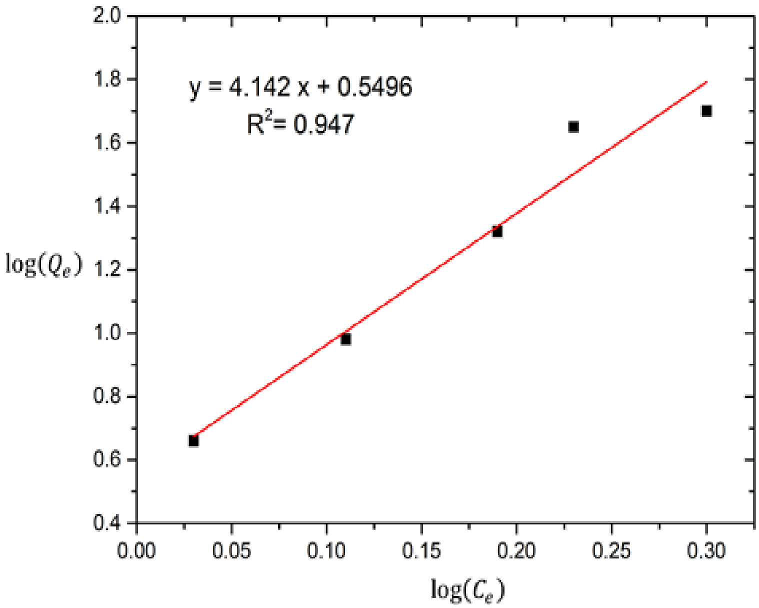

Fig.4: Adsorption equation of Freundlich isothermal at 298 K.

The temperature was also considered as an effect parameter for the zinc adsorption on Cr_2O_3 nanoparticles. Different temperatures, which were 15, 25, 35, 45 and 55 ^{o}C, were used in the experiment. The results show that the adsorption efficiency increases with temperature rising because of an increase in the surface activity that means the process is positive endothermic (*ΔH*).

Gibs free energy of adsorption (ΔG), enthalpy (ΔH), and entropy (ΔS) had been calculated through the following equations:

(4)

(5)

(6)

where is an equilibrium constant, R equals 8.314 J/mol K, which is gas constant, is a concentration of solid-phase at equilibrium, is an equilibrium concentration in solution (mg/l) and is a temperature (K). The plot of van't Hoff as shown in Figure 6 gave the values of both ΔH and ΔS from the slope of the linear fitting.

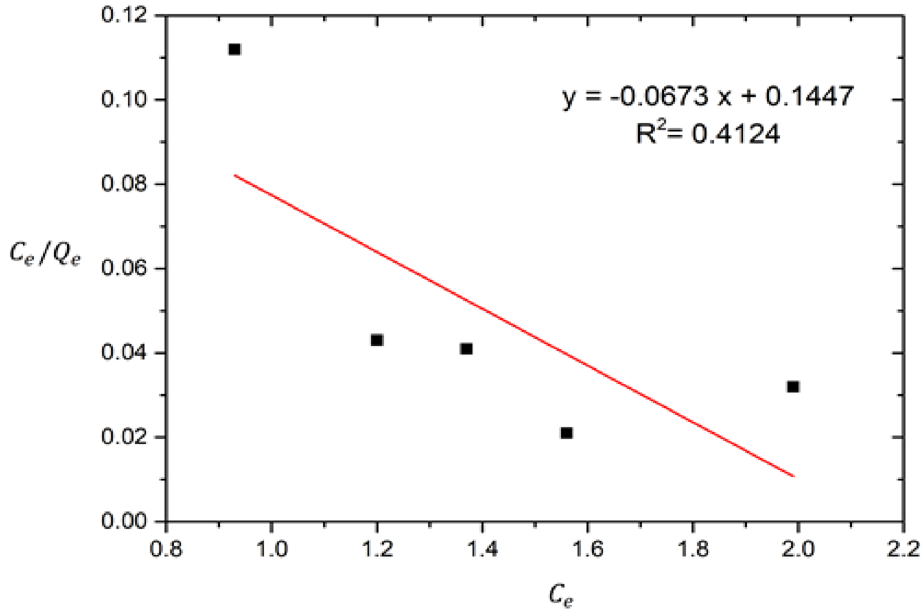

Fig.5: Adsorption equation of Langmuir isotherm at 298 K.

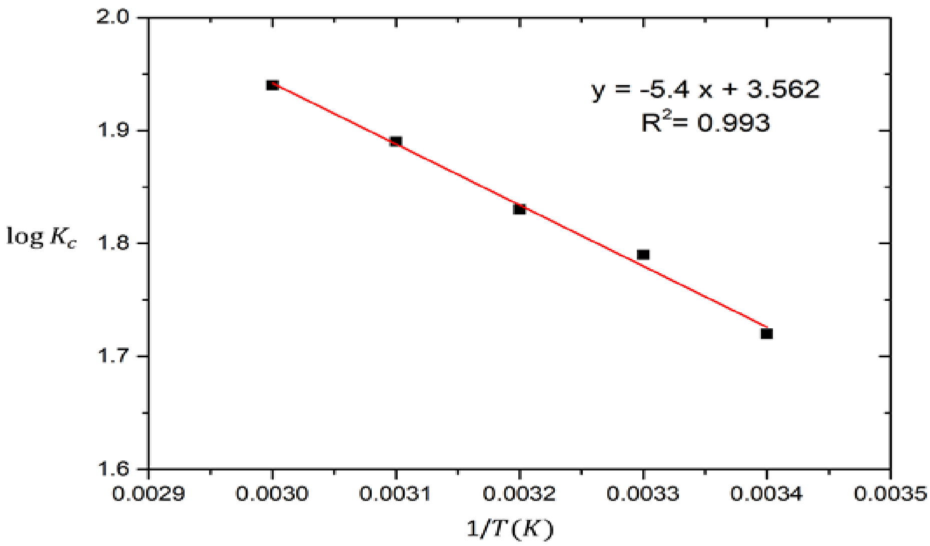

Fig.6: Relation between log and 1/T for the adsorption of zinc ions

The calculation values show that the ΔH is 10.33 kJ/mol and the ΔS is 29.61 J/(mol·K). These values indicated that the adsorbed molecules had a constant motion on the surface and were attributable to be absorption as well as adsorption. The high temperature showed facilitated the adsorption of zinc. The value of positive ΔG for the adsorption (1.515 kJ/mol) at 298 K indicated that the adsorption happened non-spontaneously in nature, but when the temperature had risen, the process began spontaneously (ΔG value is negative) because the adsorption capacity increased with temperature increasing.

Conclusion

The UV-irradiation method technique proved to be a perfect way to produce small particles of chromium oxide in nanoscales with an excellent crystallinity structure. Due to high surface area of Cr_2O_3 nanoparticles, they were proved to have good adsorption for zinc ions due to comparing the data fitted of both the Freundlich isotherm model and the Langmuir model. Moreover, increasing temperature plays a crucial role to change the thermodynamic parameter ΔG into negative value because of adsorption capacity increase.

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