Synthesis and Characterization of Zinc Oxide Nano particles for the removal of Cr (VI)

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Abstract: Hexavalent Chromium has been considered to be toxic and hazardous due to its carcinogenic properties. Yet various methods used for removal of Cr(VI) from industrial wastewater include filtration, chemical precipitation, electrode position, membrane systems or even ion exchange process, and adsorption. Nanotechnology is the most effective in treating environmental wastes because of the reduced amount of material needed for removal, and it is considered to be environmentally friendly. Its application in the future is enhancing as it is less toxic and gives better performance. The present work was conducted for the synthesis of Nano size zinc oxide for the removal of hexavalent chromium Cr (VI). Batch experiments were performed to investigate the effects of Cr (VI) concentration, pH of solution, adsorbent dose, solution temperature, and contact time variations on the removal efficiency of Cr (VI). Zinc oxide nano material was synthesized by simple heating process using polyethylene glycol (PEG). FTIR analysis and TEM microscopy were applied for determination of particle size and characterization of produced nanoparticles. The results showed that the removal efficiency decreased with increasing Cr (VI) concentration, and increasing pH of solution and increased with increasing adsorbent dosage and increasing contact time. The optimum solution temperature that gave the maximum percentage removal of Cr (VI) was 60 oC.

Key words: Adsorption, Nano-technology, Zinc Oxide, Chromium (VI), Simple heatimg method.

1 INTRODUCTION

In developing countries, water resource pollution by heavy metals from industrial wastewater and aqueous solutions is a serious problem. Several industrial wastewater streams may contain heavy metals such as Pb, Cr, Cu, Zn, Co, Ni, etc. including the waste liquids generated by metal finishing or the mineral processing industries [1]. The toxic metals, probably existing in high concentrations (even up to 500 mg/L), must be effectively treated/removed from the wastewaters[2]. If the wastewater were discharged directly into natural waters it will constitute a great risk for the aquatic ecosystem. It is well known that some metals can have toxic or harmful effects to human beings and environments [3].

Chromium causes water pollutions since it is found largely in leather industry, electroplating, pigment production and in batteries production[4]. Nowadays, in general, trivalent chromium (Cr (III)) is used for chromium tanning process. However, some small tanneries using old method in which hexavalent chromium (Cr (VI)) is used. Cr (VI) is high toxic and causes diseases Doses of hexavalent chromium greater than 10 mg/kg diet affect mainly the gastrointestinal tract, kidneys, and probably the hematopoietic system[5]. When a similar dose is introduced parenterally, the principal effect is on the kidney, mainly in the proximal convoluted tubules, without evidence of glomerular damage[6]. Toxic effects from trivalent chromium have been reported only following parenteral administration [7].

At present, a number of technologies can be used to remove heavy metals from the aqueous solution such as filtration, adsorption, chemical precipitation, ion exchange, membrane separation methods and electroremediation methods [8].

Adsorption has many advantages over other methods including recovery of metal value, selectivity, sludge-free operation, cost effectiveness and meeting of strict discharge specification However, most of these methods might not be efficient in removing heavy metal at

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very low concentrations, and could be relatively expensive. These methods are also not effective due to their secondary effluent impact on the recipient environment. Hence, the simple, effective, low cost and eco-friendly techniques are required for the fine tuning of effluent wastewater treatment [9-10].

Different types of adsorbents can be used such as activated carbon, silica gel, synthetic polymers and nanomaterial [11].

Nano technology is successfully applied to treat various organic and inorganic water contaminants. Nanomaterial are applicable in the areas of reduction of environmental burden, reduction or treatment of industrial and agricultural wastes and non-point sources pollution control that involves controlling water pollution problems [12].

Nanomaterial alters physical properties on a Nano scale due to their high specific surface area to volume ratio and greater density of reactive and adsorptive sites [13]. There are different types of nanomaterial metals, metal oxides and alloys [14]. They are used as catalysts, adsorbents, membranes, and additives to increase activity and capability due to their high specific areas and Nano sized effect [15]. Nanomaterial are more effective in treating environmental wastes because they reduce the amount of material needed and they are environmentally friendly applications in the future as they are less toxic and give better performance [16].

The aim of the present work is to synthesis zinc oxide nanoparticles and to use it in the removal of Cr^{+6} from waste water. Full characterization of the ZnO nanoparticle was carried out using FTIR, and SEM analysis. Batch adsorption experiments were carried out as a function of content time, solution pH, solution temperature, the concentration of Cr^{+6} ions, and the adsorbent dosage.

2 MATERIALS AND METHODS:

2.1 Materials:

Zinic acetate was supplied by Riedel-deHaen AG.D3016 Seelze. Polyethylene glycol 4000 was (PEG 4000, Carbowax 4000). Potassium chromate salt was used to make all chrome standard solutions used in the experiments. A stock solution of 1000 mg/L was prepared by dissolving the powder in distilled water. Working standards ranging from 20 mg/L to 100 mg/L Were then prepared by appropriately diluting the stock solution. The pH of the metal solution was adjusted to that required by the experiment using 1M HCl and 1M NaOH.

2.2 Preparation of Nano Zinc Oxide particles:

Reagent were analytical grade and used without further purification. In analytical procedure, 10 ml of 0.6M zinc acetate aqueous solution was mixed with 8 gm of polyethylene glycol in a round bottom flask. The solution was heated under stirring at 70°C for 20 min to obtain homogeneous viscous material. The materials were heated in a furnace at 800°C for an hour [17]. Then, the product of Nanoparticles was analyzed by standard method [18].

2.3 Characterization of Nano Zinc Oxide Particles:

2.3.1FTIR spectroscopy studies:

The Fourier Transform Infrared Spectrum (FTIR) of Nano Zinc Oxide particales was analyed in wide range wavelength between 600 cm -1 and 4000 cm -1 by FTIR- 8400 S Shimadzu.

2.3.2 TEM (Transmission electron microscope):

Transmission electron microscopy image was obtained for Nano Zinc Oxide particales by TEM "JEOL TSM 6360 LA."

2.4. Adsorption isotherm experiment:

Batch adsorption experiments were carried out in a 250 ml glass bottles by adding 0.1-0.8 g of adsorbent (Nano ZnO particles) and 50 ml of chrome solution of specific concentration. The concentration of Cr(VI) solution was varied from 20 to 100 mg/l. All experiments were done at room temperature. The samples were shaken at 150 rpm in a mechanical shaker for a contact time ranging from 45 to 240 min. The pH of the solutions was ranged from 2 to 10.5. Then, the effect of temperature was studied in range from 25°C to 100°C. After each experiment, the contents were filtered through a filter paper. Concentrations of chrome ions in the filtrate were then determined by atomic absorption spectrophotometer.

The percentage removal of hexavalent chromium solution was calculated by using the following equation:

$$\% \text{ removal} = C_i - C_e / Ci * 100 \quad (1)$$

The amount of chrome adsorbed using the adsorbent (Nano ZnO) at equilibrium, q_e (mg/g), was calculated by the following mass balance relationship:

$$qe = (C_i - Ce) * V/m \quad (2)$$

Where C_i and C_e are the initial and equilibrium liquid-phase concentration of chrome, respectively (mg/l), V the volume of the solution (l), and W is the weight of the adsorbent used (g).

3. Results and Discussions

3.1 Infrared Spectroscopy (FTIR):

The FTIR analysis permits spectrophotometric observation of both ZnO Nano powder without PEG and ZnO Nano powder with PEG in the rang 600-4000 cm^{-1} and served as a direct mean for the identification of the functional groups on the surface. Figures (4.1 and 4.2) show the Fourier transformed spectrum of ZnO Nano powders at room temperature without PEG and with PEG respectively. The sharp different peaks of the synthesized products indicate their good crystallinitty.No characteristic peaks were observed other than ZnO. It indicates that the high purity of the ZnO nanoparticles is obtained. It can be seen that the intensity of the diffraction peaks increases and becomes shaper with adding poly ethylene glycol (PEG)[19].

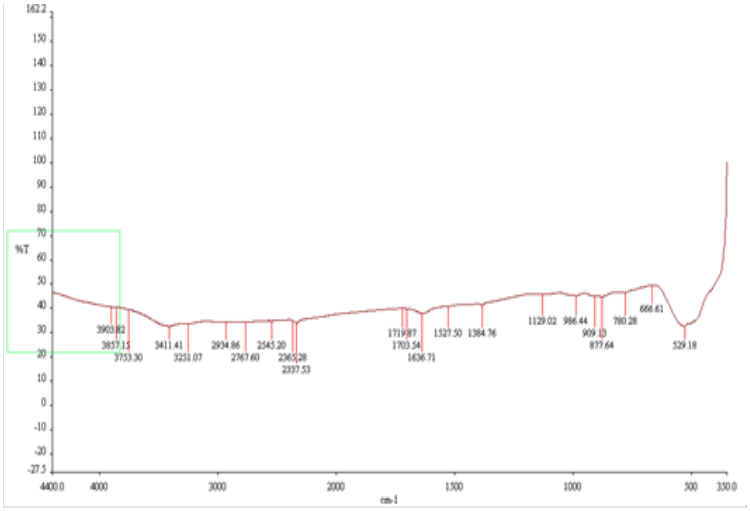

Figure 1: FTIR of ZnO Nano powders at room temperature without PEG

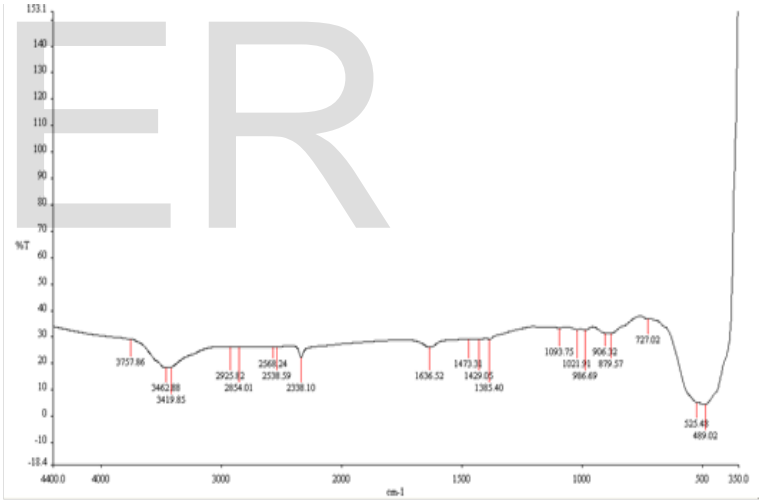

Figure 2: FTIR of ZnO Nano powders at room temperature with PEG

3.2 Transmission Electronic Microscopy (TEM):

The TEM bright field image for ZnO Nano powder with PEG shown in Figure (3) has revealed that the powder is composed of hexagonal and uniform shaped particles, with an average size from 38.8 to 45.5 nm.

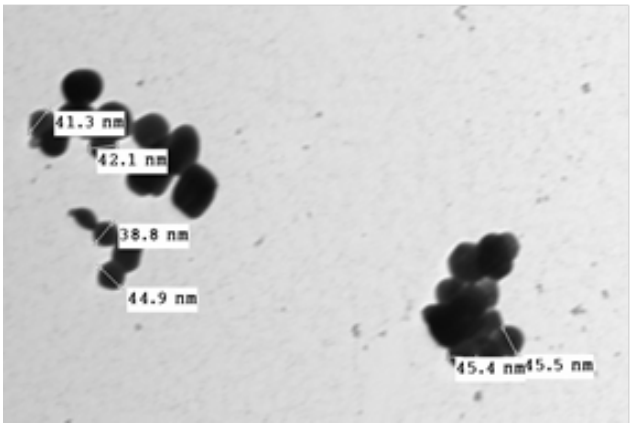

Figure 3: TEM on ZnO Nano powder with PEG

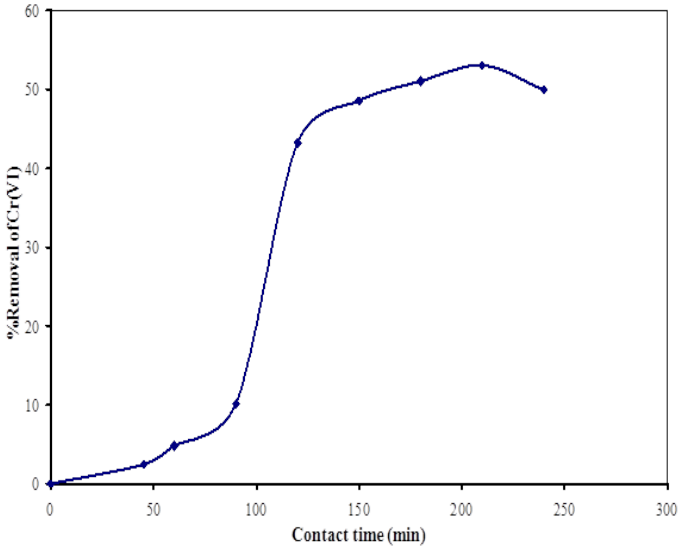

Figure 4: Effect of contact time on Cr (VI) percentage removal

3.3 Factors affecting the removal of Cr (VI) ions:

The influences of several operational parameters such as initial concentration of Cr (VI) ions, dose of nano material, pH of solution, contact time, and temperature of solution were investigated for the remval of Cr(VI) ions.

3.3.1 Effect of contact time:

Figure (4) indicates that percentage removal of Cr(VI) was increased by increasing contact time before equilibrium was reached. This is probably due to larger surface area of the sorbent available at the beginning for adsorption of C r(VI) ions. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transferred from the exterior to the interior sites of the adsorbent Particles [20]. The effect of contact time on Nano ZnO sorbent was measured for times of 45 to 240 min. Equilibrium occurs at time of 210 min in which maximum removal percent of Cr(VI) was attained (53.1%).

3.3.2 Effect of initial concentration of Cr (VI) ions:

The initial concentration of metal ion provides an important driving force to overcome all mass transfer resistances of metal ions between the aqueous and solid phases. The adsorption of Cr(VI) ions on Nano ZnO sorbent was carried out at different initial Cr(VI) ion concentrations ranging from 20 to 200 mg/l. Figure (5) clearly shows that by increasing the concentration gradually there is a decrease in the percentage removal for sorbent. As the ratio of sportive surface to ion concentration decreased with increasing metal ion concentration and so metal ion removal was reduced. At low initial concentration of metal ions, more binding sites are available. But as the concentration increases, the number of ions competing for available binding sites in Nano ZnO increased [21].

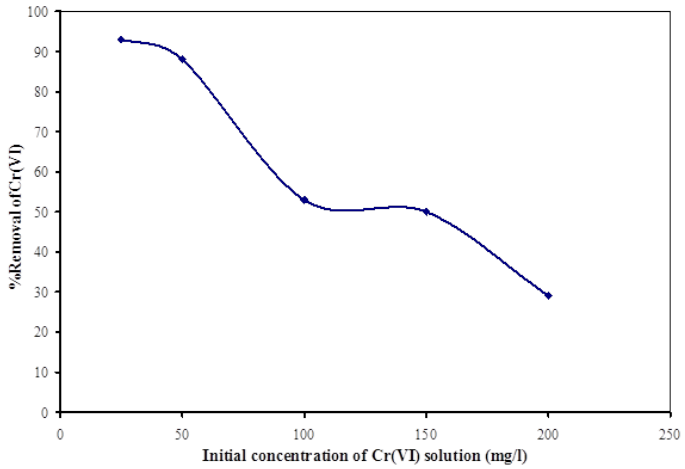

Figure 5: Effect of initial concentration of Cr (VI) solution on percentage removal of Cr(VI)

3.3.3 Effect of sorrbent dose:

The effect of the sorbent dose was studied by varying the sorbent amounts from 0.1 to 0.8 g/50 ml. It is obvious from Fig. (6) that the percentage removal of Cr(VI) increases from 45 to 53% with an increase in the dose of Nano ZnO sorbent from 0.1 to 0.5 g and remained nearly constant at adsorbent quantities higher than 0.5 g. This behavior is expected, since increasing the amount of sorbent, increases the area and sites available for adsorption thus making easier penetration of Cr(VI) to the adsorption sites and more metal ion removed. The high adsorption capacity exhibited by ZnO is explained by its nano-scale particle size which results to alarger surface area [22]. Since the quantity of metal ion is constant, an increase in the amount of adsorbent above a quantity that can completely adsorb the available Cr(VI) had no apparent effect on further increase of percent adsorption[23].

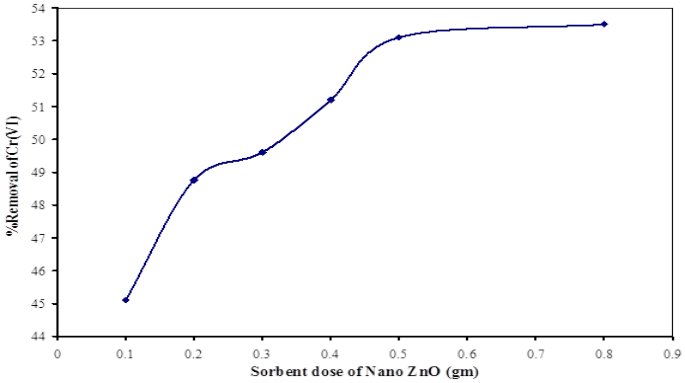

Figure 6: Effect of sorbent dose of Nano ZnO on percentage removal of Cr(VI)

3.3.4 Effect of pH

The pH of the solution is an important variable which controls the adsorption of the metal ions at the solid-water interface. Hence, the influence of pH on the adsorption of Cr^{+6} ions onto Nano ZnO sorbent was examined in the pH range of 1 – 10.5. These results were represented in Fig. (7) which shows that the adsorption capacities of Cr^{+6} ions onto adsorbent increased significantly, with decreasing pH value and the maximum removal of Cr^{+6} ions was 96.1% by adsorbent for contact time (210 min) were carried out at pH of 2.5. High removal of Cr(VI) at low pH is probably due to reduction of hexavalent chromium to trivalent chromium ions, which is easier in removal [24].

$$Cr_2O_7^{-2} + 14H^+ \rightarrow 2Cr^{+3} + 7H_2O \qquad \textbf{(4.1)}$$

The favorable of low pH can be attributed to the neutralization of negative charges on the surface of the adsorption by excess hydrogen ions, thereby facilitating the diffusion of hydrogen chromate ions $(HCrO_4)^-$ and their subsequent adsorption. By increasing pH $(HCrO_4)^-$ species shifts to forms $(CrO_4)^-$ and $(Cr_2O_7)^{-2}$. The decrease in adsorption of Cr (VI) by increasing pH is due to completion between the anions $(CrO_4)^-$ and OH^- [25-26].

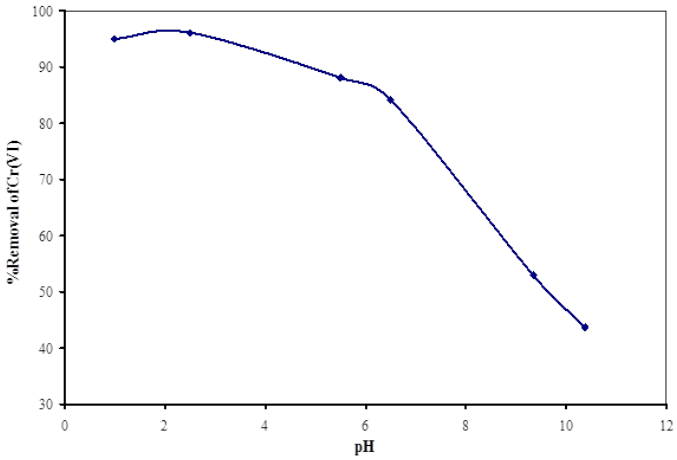

Figure 7: Effect of solution pH on the percentage removal of Cr (VI)

3.3.5. Effect of temperature:

Temperature is a highly significant parameter in the adsorption process. Experiments were performed at different temperatures (25, 40, 60, 80 and 100°C) at contact time of equilibrium of 210 min. It was observed that the percentage of adsorption increases from 53.1 to 58.98 for Hexavalent Chromium ions with the rise in temperature from 25 to 60°C but the percentage of adsorption decreases from 58.98 to 56.7% with the rise in temperature from 80 to 100°C. It is evident from Figure (8) where the maximum adsorption 58.98 at 60°C in case of Nano ZnO. That adsorption process does not usually operate at high temperature (more than 60°C) and this is due to the damage of active binding sites and because of high operational cost. At first adsorption increases with the rising temperature because this adsorbent is not homogenous and implying the active energy of adsorption sites is different[27]. Therefore, at low temperature, the adsorption sites with lower active energy were occupied first, and the other sites with higher active energy were occupied as the temperature increases [28]. The rise of adsorption capacity with temperature was due to the increase in kinetic energy of adsorbent particles. Thus, the collision frequency between adsorbent and adsorbate increases, which results in the enhanced adsorption onto the surface of the adsorbent. Secondly, at high temperature due to bond rupture of functional groups on adsorbent surface increases active adsorption sites, which may also lead to enhanced adsorption [29].

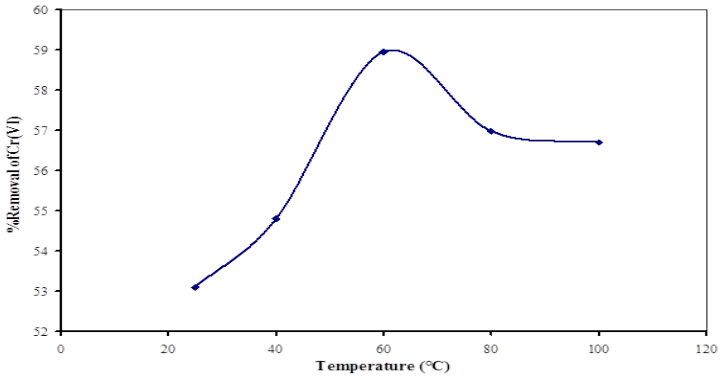

Figure 8: Effect of temperature on the percentage removal of Cr(VI)

4. Conclusions:

- In this study, Nano zinc oxide material was synthesized by simple heating method using poly ethylene glycol (PEG).
- The synthesized ZnO nanoparticles were in the range of 38-45 nm in size.
- This method was found to be rapid and economically for large production.
- The maximum adsorption percentages of Cr (VI) ions using adsorbent were achieved within 210 minutes.
- The adsorption percentages of Cr(VI) ions increased by increasing adsorbent dose to 0.5g then future increase was not effective .
- As the initial concentration of ions increased, the percentage removal using Nano zinc oxide decreased.
- The best temperature for the maximum adsorption of Cr (VI) was 60 ^{o}C carried out at pH (2.5).
- Finally, the results show that the synthesized zinc oxide nano material can be used for the treatment of aqueous solutions containing chromium fasten and effective.

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List of symbols

Symbol	Description	Units
C_e	Equilibrium copper concentration	mg/L
C_i	Initial copper concentration	mg/L
m	Mass of adsorbent	g
q_e	amount of copper adsorbed at equilibrium	mg/g
V	Volume of solution	L