Treatment of synthetic wastewater containing Cr(VI) using novel magnetic nanocomposite of Chitosan/EDTA/CeZnO under UV irradiation

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ABSTRACT

Because to the increasing use of chromium in various industries, water pollution with chromium has become a significant problem. Hexavalent chromium (Cr (VI)) is known as a toxic substance for aquatic organisms, animals and humans and as a carcinogen, so it is very important to treat this type of wastewater. In the present study, a new magnetic nanocomposite EDTA/Chitosan/CeZnO (MEC-CeZnO) was synthetized and used to remove heavy metal ions of Cr (VI) from an aqueous solution. The morphology, structure, and properties of the new MEC-CeZnO magnetic nanocomposite were identified by SEM, EDX, and XRD methods and the effect of various parameters such as initial pH, contact time and initial Cr (VI) concentration on system efficiency was investigated. The results showed that MEC-CeZnO nanoparticles with an average diameter of less than 45 nm, had the best performance of Cr (VI) regeneration at an input concentration of 10 mg/L, pH of 3 and retention time equal to 180 minutes. Also, process kinetic studies showed that the results of Cr (VI) reduction process follow the second-order kinetic model. Finally, the reusability of nanocomposites was tested in 5 cycles; the results showed a high efficiency of 90% of nanocomposites in the reduction of metal ions.

KEYWORDS

Magnetic chitosan, Nanocomposite, EDTA, Hexavalent chromium, Industrial wastewater

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1. Introduction

The rapid growth of industrialization has led to the release of toxic heavy metals into receiving water sources. Among heavy metals, chromium (Cr) is one of the toxic pollutants produced by plating, leather tanning, metal fabrication, textile and chromate industries[1]. In 2007, the US Environmental Protection Agency (EPA) reported a maximum of 100 g / L of chromium in drinking water, and the World Health Organization (WHO) set a maximum of chromium in natural waters and wastewater at 0.05 mg / L and a maximum concentration. The permissible chromium in irrigation water is reported to be 0.01 mg / L. Extensive physical and chemical processes for the removal of chromium from wastewater such as filtration[2], electrochemical deposition[3], adsorption[4, 5], reduction by iron nanoparticles[6], and membrane systems or ion exchange processes[7, 8] in Is available. Among these methods, ion adsorption is the most economically desirable method, while it is also technically easy[9].

Chitosan is a polymer that has excellent properties for the adsorption of heavy metal ions due to the presence of amino groups (-NH_2) in its structure that interact with metal ions in solution by ion exchange and complex reactions[10]. EDTA not only acts as a cheap and environmentally friendly binder but also as a multi-toothed ligand along with chitosan helps in the adsorption of metal ions[4]. In order to remove organic pollutants and reduce heavy metals, advanced oxidation process using Ce-modified ZnO has been recognized as an efficient method[11]. Alizadeh et al. Used an EDTA-modified chitosan magnetic composite and TiO2 photocatalyst to simultaneously remove cadmium heavy metal and phenol organic matter, and the best state of cadmium heavy metal adsorption was obtained at pH = 6-5 at 209 mg / g [4]. In the present study, a new MEC-CeZnO magnetic nanocomposite was synthesized to remove Cr (VI).

2. Methodology

The chemicals used, including chitosan and ferrous sulfate, were purchased from Sigma-Aldrich and zinc nitrate, cerium nitrate and other chemicals used by the German company Merck.

To prepare the nanocomposite, first Ce-modified ZnO photocatalytic particles were produced by sol-gel method [11] and Fe3O4 magnetic nanoparticles were produced by chemical co-precipitation method[12]. The Fe3O4 magnetic nuclei were then attached to the chitosan polymer chain by an EDTA linker. Finally, mixtures containing magnetic chitosan and CeZnO nanoparticles were combined and the nanocomposite was prepared.

For experiments, Cr (VI) stock solution was prepared at a concentration of 500 mg / L by dissolving 1.414 g of potassium dichromate salt in one liter of distilled water. Other required concentrations of chromium solution were made from the mother solution by sequential dilution method. Changes were made depending on the studied parameters such as initial pH (7-3), process time (180, 120, 60, 30 min) and chromium ion concentration (40, 30, 20, 10 mg / L). The samples were placed in a quartz chamber for complete mixing on a UV mixer. At the end of the experiments, the nanocomposite was separated from the solution by a magnet and finally the colorimetric method was used to measure the metal ions remaining in the solution.

3. Discussion and Results

The shape and structure of the synthesized nanocomposites in this study were determined using TEM, SEM, EDX, XRD and BET analyzes. The specific surface area and the average pore diameter of MEC-CeZnO nanocomposite were 210 g / m^2 and 45 nm, respectively, indicating the successful synthesis of the nanocomposite, due to the increase in surface area and the reduction of pores compared to the synthesized CeZnO particles.

One of the important parameters in the efficiency of the photocatalytic process is the initial pH of the solution. Therefore, in this study, its effect on the removal of Cr (VI) was studied by changing the initial pH of the solution. pH was studied at three different levels (3, 5, 7) at initial concentrations (10, 20, 30 and 40 mg / l) and at a constant concentration of 500 mg / L nanocomposite and a residence time of 180 minutes. At different concentrations, with increasing pH, the efficiency of the process in removing Cr (VI) decreases. For example, at a concentration of 10 mg / L with increasing pH, the efficiency decreased by 20%, from 77% at pH = 3 and to 58% at pH = 7 in 180 minutes.

In order to investigate the effect of increasing concentration on Cr (VI) removal efficiency, concentration changes were tested at four different levels (10, 20, 30 and 40 mg / L) and each at different pH (3, 5 and 7). Also, the concentration of nanocomposite used was constant and equal to 500 mg / L and the residence time was 180 minutes. At pH = 3, with increasing concentration from 10 to 40 mg / l, the removal efficiency decreased by 33% and from 77% at 10 mg / L to 44% at 40 mg / L. The results indicate that the removal efficiency decreases with increasing concentration.

The effect of process retention time on Cr (VI) adsorption on Cr at initial concentration of 10 mg / L and pH = 3 was investigated and the results showed that over time, Cr (VI) removal efficiency increased and 77% efficiency in 180 minutes achieved. The highest rate of chromium removal was 45% in the first 30 minutes and a 32% increase in efficiency from 30 to 180 minutes.

The efficiency of the nanocomposite during reuse was evaluated in 5 cycles. For this purpose, 5 containers with a volume of 100 ml with pH = 7 containing Cr (VI) with a concentration of 40 mg / L were prepared and 500 mg / L of nanocomposite was added to the first container. After 180 minutes, the nanocomposite was collected by magnet and washed with 0.1 M NaOH and distilled water and added to the next sample container. At the end, the final adsorption of Cr (VI) solution from each cycle was read in a spectrophotometer. The results show that the efficiency of the photocatalyst after five reuses to remove chromium had an efficiency of over 90%.

The rate of the reduction process, which is considered in the design of experiments, was evaluated. For this purpose, the Langmuir-Hinshelwood kinetic model, which is commonly used to express the heterogeneous catalytic process, was used[13].

4. Conclusions

By examining the effect of pH parameters, initial Cr (VI) concentration and process time, the best removal performance was obtained at pH = 3, initial concentration of 10 mg / L of Cr (VI) and equilibrium time of 180 minutes.

The results of nanocomposite reuse tests showed a high efficiency of 90% of MEC-CeZnO nanocomposite at the end of 5 cycles. The Cr (VI) reduction process by the MEC-CeZnO magnetic nanocomposite followed the Langmuir-Hinshelwood quadratic kinetic model.

The use of MEC-CeZnO magnetic nanocomposite as a safe and high-efficiency adsorbent will be useful in removing biodegradable contaminants from industrial wastewaters.

5. References

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