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Removal of Cd(II) and phenol using novel cross-linked magnetic EDTA/chitosan/TiO_2 nanocomposite

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ABSTRACT

In the present study, a novel cross-linked magnetic EDTA/chitosan/TiO_2 (MECT) was prepared as eco-friendly and efficient bioadsorbent for the removal of Cd(II) ions and phenol from aqueous solution. Magnetic chitosan was improved by surface functionalization and cross-linking of it with EDTA and photocatalytic with TiO_2. The nanocomposite was characterized by FE-SEM, EDX, FTIR and XRD techniques and Cd(II) ions adsorption and phenol degradation under varied experimental conditions were investigated. Results revealed that MECT nanoparticle with an average diameter of 40 nm had the best performance in adsorption of Cd(II) and degradation of phenol at optimum pH values of 5–6. Moreover, the adsorption kinetics proceeded according to the mechanism of the pseudo-second-order model. The maximum adsorption capacity of Cd(II) obtained from Langmuir model was 209.205 mg g^{-1} and phenol degradation efficiency was up to 90%. Reusability of MECT was tested and the adsorption and degradation capacities were not affected after five cycles. The paper suggests that the MECT is a promising recyclable nanocomposite for the removal of hazardous pollutants from contaminated water.

1. Introduction

The limitation of water resources, water crisis and the increasing level of heavy metal ions and organic pollutants that are discharged into the environment as industrial wastes, which would endanger the public health and ecological systems (Gorjian & Ghobadian, 2015). Many toxic heavy metals and aromatic compounds as a result of industrial activities, primarily plating, mining, manufacturing of batteries, metallurgy, dyeing and petroleum refining are released into the natural environment (Ahmaruzzaman, 2011). Phenol and cadmium have received considerable attention due to their high toxicity, causing excessive damage to human health, persistence and the biomagnification effects on ecology (Goss, Tubeileh, & Goorahoo, 2013). In addition, United States Environmental Protection Agency (USEPA) has listed these as priority pollutants (PROTECTION, 2011).

Common technologies used to remove heavy metals and organic pollutants from the contaminated water were chemical precipitation (Fu & Wang, 2011), chemical oxidation/reduction (Argun, Dursun, Karatas, & Gürü, 2008; Santos, Yustos, Gomis, Ruiz, & Garcia-Ochoa, 2006), ion exchange (Gode & Pehlivan, 2006), membrane filtration (Landaburu-Aguirre, Pongrácz, Perämäki, & Keiski, 2010), reverse osmosis (Mohsen-Nia, Montazeri, & Modarress, 2007) and solvent extraction (Lertlapwasin, Bhawawet, Imyim, & Fuangswasdi, 2010). These methods are highly inefficient due to incomplete degradation, high costs, the production of secondary pollutants, and the generation of toxic sludge. As a result, adsorption and advanced oxidation processes have been proposed as an efficient and economical method to remove metal ions and organic pollutants from wastewater (Monier & Abdel-Latif, 2012).

In recent years, research has been conducted for a beneficial and environmentally friendly material (Zhao, Repo, Yin, & Sillanpää, 2013). Chitosan is produced by deacetylation of chitin and is one of the most abundant biopolymers in nature, with it's unique properties such as biodegradability, biocompatibility, non-toxicity and chelation metal ions by amino and hydroxyl functional groups (Muxika, Etxabide, Uranga, Guerrero, & de la Caba, 2017). To obtain improved adsorption performance, prevent it from swelling and dissolving in acidic media and recovery of adsorbent from treated water, required to be modified chemically (Sobahi, Abdelaal, & Makki, 2014). The process of adsorbing metal ions on nano-adsorbent is due to the amine ($-NH_2$) and hydroxyl (OH^-) chitosan groups and the carboxyl group that trap metal Cd ions on the surface of the nanocomposite.

Typical methods such as filtration and centrifugation result in absorption loss and the release of nanomaterials in water, which may

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cause unknown damage to the environment (Fan et al., 2012). The use of magnetic field is a new method for the separation of nanoparticles from aqueous environments. Therefore, the combination of chitosan with magnetic cores and use the external magnetic field for separation adsorbent from the sorption system has solved environmental problems (Zhang et al., 2017). Usually, magnetic adsorbents have been prepared via emulsion cross-linking method, which use different cross-linkers such as glutaraldehyde (Ge & Hua, 2016), epichlorohydrin (Reddy & Lee, 2013) and ethylene glycol diglycidyl ether (Li & Bai, 2006). However, the cross-linking process has caused notably decreased adsorption metal ions because the amino groups on chitosan are involved in the chemical reaction (Dzul Erosa, Saucedo Medina, Navarro Mendoza, Avila Rodriguez, & Guibal, 2001).

In order to improve the adsorption ability of magnetic chitosan have been modified with thiourea (Zhou, Wang, Liu, & Huang, 2009), xanthate (Zhu, Hu, & Wang, 2012) and isatin (Monier, Ayad, Wei, & Sarhan, 2010) groups, etc., and chelating agents such as ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic (DTPA) (Repo, Warchol, Kurniawan, & Sillanpää, 2010) and ethylene glycol tetraacetic acid (EGTA) (Zhao et al., 2013). Zhao et al. (2015) have recently reported a green and economic method for one kind of magnetic EDTA- and/or DTPA- modified chitosan adsorbents via emulsion cross-linking technique. EDTA and DTPA were not only as the cheaper cross-linkers with lower toxicity for the environment compared to other cross-linkers but also due to have functional groups have been useful in the chelating process of metal ions (Zhao et al., 2015). For the removal of organic pollutants, photocatalytic oxidation process by using semiconductor material of TiO_2 has been as an efficient method for the degradation of organic pollutants due to non-toxicity, economical, high stability and excellent photocatalytic (Chen et al., 2012). Nevertheless, practical application of TiO_2 was limited because of the strong tendency to agglomerate (Xiang, Wang, He, & Song, 2015). In order to overcome this weakness, the synthesis of TiO_2 nanomaterials on chitosan have attracted great attention (Chen et al., 2012; Xiang et al., 2015). In another study, a novel composite of thiourea-modified magnetic ion-imprinted chitosan/TiO_2 (MICT) was prepared through the combination of ion-imprinted technology and photodegradation technology, which has been shown to have suitable efficiency for the removal of cadmium and 2,4-dichlorophenol (Vunain, Mishra, & Mamba, 2016).

However, all these works have had numerous drawbacks, for example, preparation adsorbents by cross-linkers and compound with high toxicity, expensive modification methods, removing just one type of pollutant and the synthesis of micro-sized particles, which could impact the removal efficiency.

In the present study, a novel cross-linked magnetic EDTA/chitosan/TiO_2 (MECT) nanocomposite was prepared for the removal of Cd(II) metal ions and phenol as hazardous materials from aqueous solution. In MECT nanocomposite, EDTA not only was as an environmentally friendly cross-linker and magnetic nanoparticles embedded in chitosan, but also the modification of chitosan by chelation groups of EDTA at the same time. The MECT was characterized by FTIR, FE-SEM, EDX and XRD techniques and parameters affecting the removal behavior have been investigated to receive the optimum conditions for adsorption and degradation capacities. Finally, kinetic models and adsorption isotherms were evaluated and the reusability of MECT was studied after five cycles.

2. Materials and methods

2.1. Materials

Chitosan (deacetylation 75–85%; and medium molecular weight of 1526 g mol^{-1}), $FeSO_4{\cdot}7H_2O$ (Purity ≥99.0%) and $FeCl_3{\cdot}6H_2O$ (Purity ≥99.0%) were obtained from sigma-Aldrich. Degussa P-25 TiO_2 with an average particle size of 21 nm as a photocatalyst. All other chemicals used in this study were of analytical grade and supplied by Merck (Germany). Distilled water was used for preparation stock solutions.

2.2. Preparation of magnetic chitosan (MEC) and magnetic EDTA/chitosan/TiO_2 nanocomposite (MECT)

Fe_3O_4 nanoparticles were prepared by chemical co-precipitation of Fe^{2+} and Fe^{3+} ions by ammonia solution according to the previous study (Chen, Yang, Ma, & Wu, 2011). $FeCl_3{\cdot}6H_2O$ and $FeSO_4{\cdot}7H_2O$ with the molar ratio of 2:1 were dissolved in distilled water at 60 °C during stirring and under argon gas. Drops of NH_2OH (8 M) were added to the solution and the mixture was stirred for 30 min. The black Fe_3O_4 MNPs were washed three times with 5% NH_4OH and then twice with distilled water. Finally, they were dried in a vacuum at 70 °C.

The water/oil (W/O) emulsion cross-linking method was used for the preparation of MEC (Zhao et al., 2015). First, 0.7 g of chitosan was dissolved in 50 ml of acetic acid (5 wt%), then 0.3 g of the previously prepared Fe_3O_4 MNPs was fully dispersed in the chitosan solution under ultrasonication vibration for 20 min. The above solution was dropped slowly to the W/O emulsion which was composed of 50 ml distilled water, 100 ml of hexane and emulsifiers (4 ml Span-80 and 2 ml of butanol) and stirred until it became brightly colored. After that, 0.5 g of EDTA was suspended in 100 ml of methanol, and drops added into the emulsion. The mixture was vigorously stirred and refluxed at 60 °C for 6 h. Next, the cross-linked magnetic EDTA/chitosan were separated using a magnet, mixed with 100 ml ethanol and stirred for another 6 h. The products were washed with 0.1 M NaOH, distilled water, 0.1 M HCl, again distilled water, and ethanol. Eventually, MEC nanoparticles were dried at 60 °C in vacuum for 12 h.

The TiO_2 nanoparticles were heat-treated at 400 °C for 1 h. 0.2 g of MEC and 0.1 g of nano-TiO_2 were ultrasonicated in 100 ml distilled water with acetylacetone (acac) as dispersant and OP-10 as an emulsifier for 2 h. MECT nanocomposites were prepared at 60 °C.

2.3. Characterization

Field Emission Scanning Electron Microscope (FE-SEM) and Energy Dispersive X-ray Spectroscopy (EDX) (MIRA3-XMU, TESCAN, Czech Republic) were taken to analyze the morphology and chemical characterization of the nanocomposites. Functional groups were identified by Fourier transform infrared (FTIR) spectrophotometry (Equinox 55, Bruker, Germany). The phase and crystallinity were characterized by powder X-ray diffraction (XRD) analysis were obtained by X-ray diffractometer (EQUINOX 3000, Intel, France) in the range of $2\theta = 5–120^{\circ}$ at room temperature. Cd(II) ions concentration in solution was measured by an inductively coupled plasma optical atomic emission spectrometer (ICP-OES) (VISTA-MPX, Varian, USA) and phenol concentration determined by UV–vis spectrophotometer (Cary 5000, Varian, USA).

2.4. Adsorption and degradation experiments

All experiments were carried out by mixing 30 mg adsorbent with 30 ml solution of Cd(II) ions and phenol with known concentrations on a shaker (150 rpm) under an UV-A lamp (the wavelength of 365 nm, the light intensity was 4.42–8.9 mW cm^{-2} and placed at a distance of 10 cm above the solution) at room temperature.

The effects of various parameters were studied such as metal ion concentration (50–300 mg L^{-1}), phenol concentration (15, 25, 50 and 100 mg L^{-1}) and different contact times in the pH range of 3–9.

The adsorption capacity (q_e) and degradation efficiency (D_e) of MECT nanocomposite were calculated by Eqs. (1) and (2):

$$q_e = \frac{(C_0 - C_e)}{M} V \times 100 \quad (1)$$