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Biosynthesized iron oxide nanoparticles used for optimized removal of cadmium with response surface methodology

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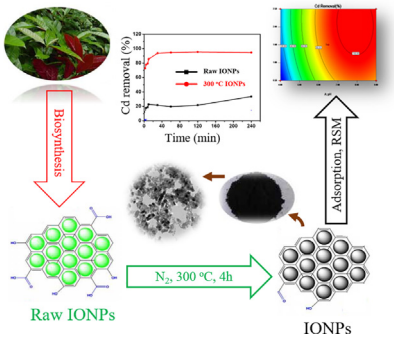
HIGHLIGHTS

- Biosynthesized IONPs were modified by calcination at 300 °C.
- Nanoscale magnetic Fe—O—C composite was successfully synthesized.
- RSM was used to optimize the adsorption of Cd (II) by IONPs.
- The effect of each factor on adsorption was: pH > dosage > ion strength> temperature.
- A 98.50% of Cd (II) (10) was removed by IONPs at optimal conditions.

GRAPHICAL ABSTRACT



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ABSTRACT

To effectively reuse adsorbent in removal of Cd (II), magnetic modification was considered as an alternative. In this study, iron oxide nanoparticles (IONPs) synthesized from the extract of *Excoecaria cochinchinensis Lour* leaves were modified by low-temperature calcination, and used to remove Cd (II). Transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and magnetic properties analysis confirmed the successful synthesis of nanoscale magnetic Fe—O—C composite. Response surface methodology (RSM) served to optimize the adsorption of Cd (II) by IONPs based on Box-Behnken design (BBD). According to the quadratic model, the effect of each factor on the removal of Cd (II) by IONPs was: pH > dosage > ionic strength > temperature. In percentage terms, 98.50% of Cd (II) (10 mg L^{-1}) was removed when the pH, absorbent dosage, temperature and ionic strength conditions were 8.07, 2.5 g L^{-1}, 45 °C, and 0.07 mol L^{-1}, respectively. The adsorption of Cd (II) by IONPs is consistent with pseudo-second order kinetics and Langmuir adsorption isotherm models, indicating that the process of adsorption of Cd (II) by IONPs belongs to monolayer chemical adsorption. The –COOH, –COH, Cπ electron and ≡FeOH may be the binding sites for Cd (II) on the surface of IONPs. Overall, IONPs can be used to remove Cd (II) effectively from aqueous solution in a wide range of conditions.

1. Introduction

Cadmium, a toxic heavy metal, is widespread in the environment due to anthropogenic activities such as mining, industrialization, and farming, which seriously threaten human health (Iqbal et al., 2016). The maximum Cd concentration in drinking water is 0.003 mg L^{-1}

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which is the World Health Organization's preferred guideline (Venkateswarlu and Yoon, 2015). To develop a feasible method for removing Cd (II) from aqueous solution, adsorption has been developed as a wastewater treatment method in recent years due to its operational simplicity and cost-effectiveness (Snoussi et al., 2016). Alternatively, the adsorbents used in the removal of Cd (II) are nanoscale carbon materials, nanoscale iron particles, biochar, apatite and clay (Boparai et al., 2011; Gupta and Saleh, 2013; Jiang et al., 2010; Wan et al., 2018).

Of all the absorbents, iron nanoparticles (Fe NPs) have emerged as the most promising functional materials for removing heavy metals from the environment (Wang et al., 2014a, 2014b; Zeng et al., 2017). Over the past decade the development of green chemistry methods which utilize plant leaf extracts for the synthesis of metal nanoparticles has attracted and focused much research interest (Wang et al., 2014a, 2014b; Weng et al., 2013). Previous studies reported that green synthesized Fe NPs were nanoscale amorphous iron-organic functional group composites (Wang et al., 2014a, 2014b; Weng et al., 2013). Of all the iron species, amorphous iron is a highly unstable form (Chao and Zhou, 1983). However, transforming amorphous iron into crystalline iron and retaining some functional organic groups will help to improve the practical application of green iron nanoparticles.

Calcination is one strategy used to improve the functioning of iron oxide. Fe_3O_4 nanoparticles can be synthesized by pyrolysis of FeO(OH) (Park et al., 2010), and the highly crystalline Fe_3O_4 phase is formed after being calcined at 400 °C (Zhou et al., 2001). However, calcination of Fe NPs synthesized by plant extract, and the variations of Fe species and organic functional groups are not yet clearly understood, hence the need to characterize calcined IONPs. Furthermore, low temperature calcination has proved to be a cost-effective, efficient and environmentally friendly strategy. Overall, it is possible use low temperature calcination to improve the properties of green iron nanoparticles.

Response surface methodology (RSM) is a popular optimization method employed to: firstly, study the relationships between the response and independent variables; and secondly, optimize the optimal level of each variable (Asfaram et al., 2015; Yirsaw et al., 2016). It has the advantages of high precision, low experimental cost and excellent prediction performance. Yirsaw et al. (2016) used RSM to analyze the optimum conditions for removing hexavalent chromium by nanoscale zero-valent iron and established a quadratic model between temperature, pH, dosage, initial concentration and removal rate. Savasari et al. (2015) optimized the removal of Cd (II) from aqueous solution by ascorbic acid modified nanoscale zero-valent iron using RSM. Abbassi et al. (2013) employed RSM to analyze the effect of initial concentration, pH and dosage on the removal efficiency of malachite green dye by clay supported iron nano-particles. Overall, RSM can be used to optimize chemical processes, which can be described with a second order polynomial equation.

Previous studies mainly focused on the synthesis of metal nanoparticles using various plant extracts (Wang et al., 2014a, 2014b; Weng et al., 2013), whereas the modification of green metal nanoparticles has never been reported. In this study, iron oxide nanoparticles (IONPs) were synthesized from the extract of *Excoecaria cochinchinensis Lour* leaves and this was followed by calcinating them at 300 °C. Then the IONPs were used to remove Cd (II) from aqueous solution. The aims of this work were to study: (1) the chemical properties of IONPs; (2) the relationships between the pH, dosage, temperature, ionic strength and the removal rate of Cd (II) using RSM; and (3) the adsorption kinetics, thermodynamics and mechanism of Cd (II) adsorption by IONPs.

2. Experimental section

2.1. Materials and chemicals

Excoecaria cochinchinensis Lour leaves were collected from Fujian Normal University's Cangshan campus. Chemicals, namely $CdCl_2 \cdot 2.5H_2O$, CH_3COONa, $FeCl_3 \cdot 6H_2O$, NaOH, HCl, CH_3CH_2OH and NaCl were analytical grade and used directly without further purification. Deionized water was used in all experiments.

2.2. Preparation of IONPs

Firstly, the leaf extract was prepared by heating 30.0 g dry *Excoecaria cochinchnensis Lour* leaves in 500 mL of distilled water at 80 °C. After boiling for 1 h, the extracts were vacuum-filtered and stored at 4 °C for further use. Secondly, 19.68 g of CH_3COONa and 6.48 g $FeCl_3 \cdot 6H_2O$ were dissolved in 120 mL of leaf extract and then the mixture was stirred vigorously at 70 °C for 2 h. After being cooled to room temperature, the products were filtered through a 0.45 mm membrane and washed three times with ethanol and distilled water. The products were vacuum-dried at 45 °C overnight and ground, and then passed through a 110-mesh sieve to obtain raw IONPs. These in turn were calcined at 300 °C for 4 h in a tube furnace under N_2 conditions.

2.3. Characterization analysis

Morphological characteristics and size of IONPs were established by transmission electron microscopy (TEM, FEI Tecnai G2 F20). The elemental mapping of IONPs was measured using an X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific Escalab 250Xi) with an Al Ka X-ray radiation (1486.6 eV) for excitation. The magnetic properties of the IONPs were recorded using a magnetometer (Quantum Design MPMS (SQUID) XL, USA) with a maximum magnetic field of 20,000 Oe in powder form at room temperature. IONPs was further characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray spectrometer (EDS). Further descriptions of these can be found in the Supplementary material (Fig. S1, Fig. S2, Fig. S3).

2.4. Adsorption experiments

1000 mg L^{-1} stock solutions of Cd (II) were prepared by dissolving 0.203 g of $CdCl_2 \cdot 2.5H_2O$ in deionized water. Adsorption experiments were carried out in 50 mL plastic centrifuge tubes containing 25 mL 10 mg L^{-1} Cd (II) solution and 1.0 g L^{-1} (0.025 g) of IONPs. The solutions were adjusted to pH 6.5 using 0.1 M HCl and agitated on a thermostatic shaker at 150 r min^{-1}, and a temperature of 25 °C. Individual tubes were sacrificed after specific time intervals (2 min, 4 min, 8 min, 10 min, 30 min, 60 min, 120 min, 240 min) and centrifuged at 4000 r min^{-1} for 5 min, and then filtered through a 0.45 μm membrane. The residual Cd (II) concentrations of the filtrate were determined by an atom adsorption spectrophotometer (AA240FS, Varian, USA). The adsorption and removal rates of Cd (II) were calculated as follows:

$$Q = (C_0 - C_t) \times V/m \quad (1)$$

$$W = [(C_0 - C_t)/C_0] \times 100\% \quad (2)$$

where Q is the adsorption capacity (mg g^{-1}), W is the removal rate (%), C_0 and C_t are the initial concentrations of Cd (II) in the solution and the concentration at time t (mg L^{-1}), V is the volume of solution (L), and m is the quality of IONPs (g).

2.5. Kinetics of Cd (II) adsorption

Pseudo-first order kinetics and pseudo-second order kinetics are utilized to fit the adsorption of Cd (II) in water by IONPs (Balarak et al., 2015; Jiang et al., 2010):

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (3)$$

$$t/Q_t = 1/\left(k_2 Q_e^2\right) + t/Q_e \quad (4)$$