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Potential of cobalt ferrite nanoparticles ($CoFe_2O_4$) for remediation of hexavalent chromium from synthetic and printing press wastewater

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ABSTRACT

Cobalt ferrite ($CoFe_2O_4$) nanoparticles were successfully synthesized, characterized and utilized for the treatment of chromium containing synthetic wastewater and printing press wastewater. Characterization of $CoFe_2O_4$ nanoparticles was carried out by XRD, TEM, SEM, AFM, VSM and BET surface area analysis. TEM analysis confirmed the formation of nanoparticles in the range of approximate 12–21 nm having the surface area of 41.31 $m^2 g^{-1}$. The saturation magnetization of nanoparticles was determined to be 50.8 $Am^2 kg^{-1}$. Langmuir adsorption capacity of $CoFe_2O_4$ nanoparticles was calculated to be 16.73 $mg g^{-1}$. Kinetic study revealed that the Cr(VI) removal on $CoFe_2O_4$ nanoparticles followed the pseudo-second-order kinetic model. Further, the temperature study revealed the endothermic nature of Cr(VI) adsorption. Thermodynamic study revealed the feasibility of Cr(VI) adsorption on $CoFe_2O_4$ nanoparticles. Desorption study suggested that nanoparticles could be efficiently reused up to three cycles. The present study demonstrated that synthesized nanoparticles were quite efficient for the treatment of chromium ions and other metallic ions from printing press wastewater which further suggested that $CoFe_2O_4$ nanoparticles could be successfully used for the treatment of metal- rich industrial effluents.

1. Introduction

Recently, the application of nanoparticles in numerous areas is attracting more and more attention due to unusual physical and chemical properties exhibited by them such as high surface area-to-volume ratio and catalytic potential which makes them better in comparison to their bulk materials [1,2]. Among various nanoparticles, magnetic nanoparticles especially nanosized ferrite materials have been frequently used in variety of fields such as biosensors, gas sensors, magnetic catalysis, transformer core drug delivery, magnetic resonance imaging (MRI), lithium ion batteries, magnetic materials and microwave devices [3–5]. Cobalt ferrite ($CoFe_2O_4$) is one of the most widely used ferrites because of its high coercivity, chemical stability, mechanical hardness, moderate saturation magnetization and photo-induced magnetic effects [1,6–9]. Though variety of applications of cobalt ferrite have been investigated, but its application as an adsorbent material for the treatment of metallic pollutants is not yet much explored. Some studies regarding the application of nanosized cobalt ferrite in the treatment of metals and dyes from simulated samples are available, but those regarding its application for industrial effluents are very rare [8,10–12].

The present manuscript deals with the investigation of the efficiency of $CoFe_2O_4$ nanoparticles for the adsorption of Cr(VI) ions from synthetic wastewater as well as printing press wastewater. A simple method was opted for the synthesis of cobalt ferrite nanoparticles to make the treatment process cost effective. Chromium is one of the most widely used metals in different industries resulting in its excessive concentration in wastewater stream. Cr(VI) is known to be carcinogenic and teratogenic [13]. Cr(VI) may pose several health problems such as ulceration, dermatitis and allergy. The United States Environmental Protection Agency (USEPA) has set the maximum permissible level for discharge of Cr (VI) into inland surface waters and in domestic water supplies as 0.1 $mg L^{-1}$ and 0.05 $mg L^{-1}$ respectively [14]. Though the application of Cr(VI) in various industries cannot be reduced but still, the harmful effects generated by hexavalent chromium can be reduced by proper treatment of chromium containing wastewater with efficient techniques before it gets discharged into the water streams. So, chromium metal has been selected for the present study. Effects of various important parameters viz. pH, initial concentration, adsorbent dose and

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temperature which can affect the removal of Cr(VI) ions were studied for optimization of process parameters for maximum removal of metal ions. Several kinetic models were applied to investigate the mechanism of removal process. Isotherm and thermodynamic studies were also performed. Efficiency of synthesized $CoFe_2O_4$ nanoparticles was also investigated for the treatment of metal-rich wastewater of a printing press collected from a local printing press HELPRINT Mikkeli, Finland.

2. Experimental

2.1. Synthesis of $CoFe_2O_4$ nanoparticles

Nanoparticles of $CoFe_2O_4$ were synthesized by the previously reported method with slight modifications [3,15]. For synthesis of nanoparticles, the molar concentrations of Fe^{3+} and Co^{2+} were taken in 2:1 ratio into the solution which was prepared by dissolving $FeCl_3{\cdot}6H_2O$ and $CoCl_2{\cdot}6H_2O$ in deionized water. Fe^{3+} and Co^{2+} solutions were mixed and stirred on the magnetic stirrer (IKA-RH Basic KT/C) at 100 rpm for their proper mixing. After stirring, the mixture solution (Fe^{3+} and Co^{2+}) was added into 3 M NaOH solution at high stirring speed. After completion of precipitation reaction, a black coloured solution was obtained which was further stirred for 30 mins with the addition of linseed oil (surfactant) and then the temperature of mixture solution was maintained at 80 °C and the solution was stirred for more 2 h. $CoFe_2O_4$ nanoparticles were separated by centrifugation to remove water and surfactant and then washed with deionized water until pH of filtrate became 7.0. Finally, the precipitate was washed with ethyl alcohol and then kept in an Oven (TERMAKS) for 36 h at 60 °C for drying. $CoFe_2O_4$ nanoparticles were characterized by X-ray diffraction (XRD) model, transmission electron microscopy (TEM), scanning electron microscopy (SEM), Energy-dispersive X-ray spectrometry (EDX), Atomic force microscopy (AFM), Brunauer, Emmett and Teller surface area analysis, and Vibrating Sample Magnetometer (VSM) analysis. pH_{zpc} of $CoFe_2O_4$ nanoparticles was determined by the earlier reported method [16].

2.2. Adsorption experiments

Cr(VI) adsorption on $CoFe_2O_4$ nanoparticles was investigated by applying batch adsorption process. To prepare the synthetic wastewater of Cr(VI) ions, potassium dichromate salt was dissolved in distilled water to get 1000 mg L^{-1} stock solution of Cr(VI) ions which was further used to make different ranges of chromium solution from 75, 100, 125 and 150 mg L^{-1} by proper dilution. For adjustment of pH of the solution, 0.1 M HCl/0.1 M NaOH solution was added in chromium solution to get the required pH. For batch adsorption experiments, the appropriate amount of nanoparticles was added into the chromium solutions of different concentrations and agitated in a thermostat shaker for different time intervals to determine equilibrium time. After equilibrium time, the adsorbent was separated by using strong magnets. Analysis of residual concentration of Cr(VI) ions in aliquot was carried out by using ICP-OES (Model: iCAP 6300-Thermo Electron Corporation). Percentage removal of metal ions and amount of metal ions adsorbed on $CoFe_2O_4$ nanoparticles were determined by the following equations:

$$\mathrm{Cr(VI)removal}(\%) = \frac{(C_i - C_e)}{W} X100 \quad (1)$$

$$q_e = \left(\frac{C_i - C_e}{W}\right) * V \quad (2)$$

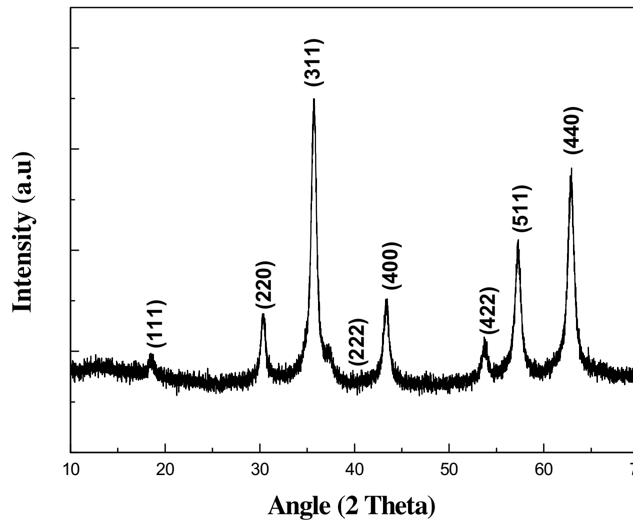

Fig. 1. XRD pattern of cobalt ferrite nanoparticles ($CoFe_2O_4$).

where C_i(mg L^{-1}) and C_e(mg L^{-1}) are the initial and equilibrium concentrations of Cr(VI) ions respectively. W(g) represents the weight of adsorbent, while V(L) is the volume of Cr(VI) solution. q_e(mg g^{-1}) is the amount adsorbed on per unit mass of the adsorbent. Batch adsorption experiments were also performed with collected printing press wastewater to observe the efficiency of $CoFe_2O_4$ nanoparticles for wastewater.

To make the treatment process cost effective, it is necessary to the evaluate regeneration and reuse capability of any adsorbent. In this point of view, for regeneration of metal loaded adsorbent, 10 g L^{-1} of loaded adsorbent was mixed with NaOH solution of different concentrations (0.01 M to 0.12 M) and agitated for 1 h. After 1 h agitation, the regenerated adsorbent was separated from

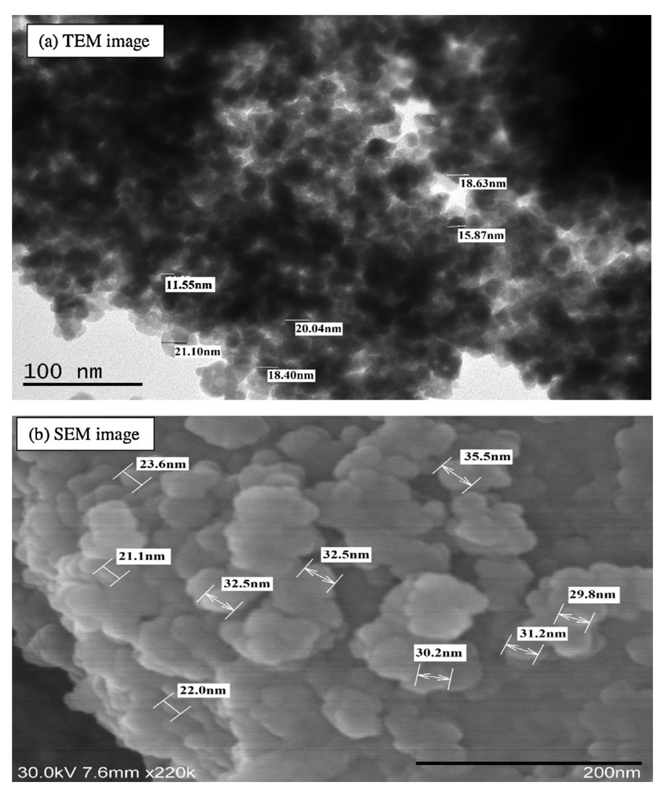

Fig. 2. (a) TEM image (b) SEM image of cobalt ferrite nanoparticles ($CoFe_2O_4$).