Adsorption of nickel ions by surface modified magnetite nanoparticles: Kinetics study

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Authors Info

Carlin Geor Malar¹,
M. Seenuvasan^{2,*} and
K. Sathishkumar⁴,

¹Department of Biotechnology,
Rajalakshmi Engineering College,
Chennai-602 105, India

²Department of Petrochemical
Engineering, SVS College of
Engineering, Coimbatore-642 109,
India

³Department of Chemical
Engineering, Hindusthan College
of Engineering and Technology,
Coimbatore-641 032, India

⁴Department of Chemical
Engineering, SSN College of
Engineering, Chennai-603 110,
India

*Corresponding Author Email :
msvasan.chem@gmail.com

Edited by

Professor G. Manjula

Reviewed by

Dr. M. Anil Kumar
Dr. S. Subhagar

Abstract

Aim: In this study, the adsorption ability of surface modified magnetite nanoparticles was investigated.

Methodology: Magnetite nanoparticles (MNs) were prepared by solvothermal method and the surface was modified by 3-(2-Aminoethylamino) propyldimethoxymethylsilane (AEAPS) and utilized as an adsorbent against nickel ions in aqueous solution. Characteristic studies were performed to study the various properties of MNs before and after surface modification. Ni_2^+ adsorption was studied as a function of contact time, initial concentration and adsorbent dosage at neutral pH and constant temperature (100 °C).

Results: Presence of required characteristic peaks in IR spectrum and X-ray diffraction (XRD) patterns revealed formation of magnetite and surface modification. Spherical and defined morphology of surface modified MNs (aMNs) was studied through electron micrographs. The kinetic data obeyed the first-order equation.

Interpretation: Surface modified MNs can be used for the efficient removal of Ni_2^+ from aqueous solution. Also, the kinetics study revealed the adsorption capacity of MNs against nickel ions.

Key words: Adsorption, Kinetics, Magnetite, Nanoparticles, Nickel ions

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Introduction

Release of organic and inorganic compounds into the environment tremendously pollutes the aquatic ecosystem. Effluents released by the human activities turn toxic over prolonged accumulation (El-Shahawi *et al.*, 2010; Andreu *et al.*, 2016; Li *et al.*, 2015; Luna-Acosta *et al.*, 2015). Metallic compounds used for various industrial processes are carried as trace elements in the waste water.

It becomes important to remove these toxic heavy metals from the waste water by an efficient method. Recently, nanoparticles are effectively involved in the heavy metal adsorption because of their higher surface area property (Seenuvasan *et al.*, 2013). Amongst various nanoparticles, magnetite (MNs) outstand in their versatile physical and chemical properties (Seenuvasan *et al.*, 2014; Keyhanian *et al.*, 2016; Balaji *et al.*, 2016) that makes them suitable to be used as an adsorbent. Also, uniformly sized monodisperse MNs serve as an excellent adsorbent are widely synthesized by simple solvothermal method (Yanez-vilar *et al.*, 2009; Sahoo *et al.*, 2012; Zhang *et al.*, 2013; Wang *et al.*, 2013) due to its additional benefits of hydrothermal synthesis (Chaisri *et al.*, 2015; Dar *et al.*, 2015).

The objective of the study was to assess the suitability of surface modified MNs for effective elimination of Ni^{2+} from aqueous solution. Solvothermally synthesized MNs were modified using AEAPS and the properties were studied using various characterization analysis. Then, the adsorption of nickel on the surface modified MNs was studied as a function of contact time, initial concentration and adsorbent dosage.

Materials and Methods

Magnetite nanoparticles was synthesized by following a modified solvothermal method (Li *et al.*, 2016). Briefly, 18.5 mM of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 3mM of sodium acetate was mixed with ethylene glycol and ethylene diamine to form a homogeneous mixture. It was then kept at 200 °C for 8 hr in a Teflon lined autoclave and the formed dark colored MNs were decanted magnetically and vacuum dried at 60 °C.

Typical surface modification of MNs involved treatment with the silanizing agent (Deng *et al.*, 2013). AEAPS (3 mM) in toluene/methanol mixture (1:1 v/v) was added to the MNs suspension and kept at 80 °C for 6hr under vigorous stirring. The surface modified MNs (aMNs) were decanted magnetically and stored for future use.

Characterization of MNs and aMNs was performed using FT-IR (Perkin Elmer FTIRC 100566) in 4000-400 cm^{-1} range, X-ray diffractometer (XRD, X'Pert3 Powder X-ray Diffractometer) with Cu K α radiation at 30 kV and 30 mA, FESEM (FEI quanta FEG 200, Operating voltage 30 kV) and BET (Quantachrome ASiQwin) analysis.

Adsorption was performed as batch experiments by mixing 10 ml nanoparticles suspension and 10 ml of nickel solution of varying concentration (10 to 50 mg l^{-1}). The reaction was performed in shaker with continuous mixing at 100 rpm for 24 hr (room temperature). Nanoparticles were then removed by centrifugation and the nickel left in the supernatant was measured in Atomic Absorption Spectroscopy (AAS). The nickel concentration in the solution was then calculated by the following equation:

$$C = \frac{(C_i - C_e)V}{m} \quad (1)$$

Where, C , C_i and C_e are Ni^{2+} concentration adsorbed on a MNs (mg g^{-1}), initial and equilibrium (mg l^{-1}), respectively; V is the volume (l) and m is the mass (mg) of the adsorbent.

Many possible models were investigated to understand the kinetics mechanism involved in the Ni^{2+} adsorption. First-order, pseudo-first-order and pseudo-second-order models. On the basis of the experimental data and model, the correlation coefficient (R^2) exhibited the predicted values. Higher R^2 values were chosen and that model was known to describe the kinetics successfully. Equation (2) gives the first-order rate kinetics.

$$\log C_e = \frac{k_1}{2.303} t + \log C_0 \quad (2)$$

Where, C_0 and C_e are Ni^{2+} concentration at initial and at time t (mg l^{-1}) respectively, and k_1 is the first-order rate constant (min^{-1}).

Pseudo-first-order kinetics in linear form can be expressed as:

$$\log (q_0 - q_e) = \log (q_0) - \frac{k_1}{2.303} t \quad (3)$$

Where, q_0 and q_e are Ni^{2+} concentration at time ' t ' and at equilibrium (mg g^{-1}) and k_1 is the rate constant for pseudo-first-order kinetics (min^{-1}).

Pseudo-second-order kinetics can be expressed as

$$\frac{t}{q_e} = \frac{k_1}{k_2 q_0^2} + \frac{t}{q_0} \quad (4)$$

Where k_2 is the rate constant for second-order kinetics (g mg min^{-1}) (Kumar *et al.*, 2009)

Results and Discussion

Fig. 1 depicts the FTIR spectrum of MNs and aMNs. The characteristic peak present at 570 cm^{-1} corresponds stretching Fe-O vibrations (Seenuvasan *et al.*, 2013a). Bands around 3200 cm^{-1} and at 1624 cm^{-1} was due to the presence of hydroxyl groups on the surface of MNs (Seenuvasan *et al.*, 2013a) and the surface modification was observed by peak shift of Fe-O to 556 cm^{-1} . Amino group from AEAPS was evident from the peak at 3112 cm^{-1} in aMNs (Malar *et al.*, 2018). The FTIR peaks confirmed the formation of MNs and the surface modification of MNS by AEAPS.

Fig.1 : FT-IR Spectrum of (a) MNs (b) aMNs.

Fig. 2 : XRD pattern of (a) MNs and (b) aMNs.

Fig. 3 : FESEM micrograph of aMNs.

Diffraction patterns (Fig. 2) of MNs and aMNs show the characteristic peaks at 31.2° , 35.5° , 43.1° , 57° and 62.9° with indices (2 2 0), (3 1 1), (4 0 0), (5 1 1) and (4 4 1) to reveal the inverse spinel structure. Smaller sized crystalline structured MNs are obvious from the sharp broadened peaks. With the help of

Fig. 4 : Kinetic models (a) first-order, (b) pseudo-first-order and (c) pseudo-second-order and their parameters.

Table 1 : Kinetic models and their parameters

Kinetics Model	Parameters	
First-order equation	R^2	0.974
	k_1	0.0094
Pseudo-first-order equation	R^2	0.704
	k_1	0.0281
Pseudo-second-order equation	R^2	0.7636
	k_2	0.0226

Debye-Scherrer equation ($d = 0.9 \lambda / \beta \cos \theta$; β is the full width at half maximum) on the intense peak, the size was calculated to be 11.53 nm and 12.22 nm for MNs and aMNs, respectively.

Irregular and defined spherical morphological appearance was observed from the electron micrographs (Fig. 3) of MNs and aMNs respectively. It was very clear that the surface modification of MNs resulted in uniform distribution of amino groups.

High surface area and porous structure of MNs ease the adsorption capacity. The sorption activity determines the physico-chemical properties of the adsorbent. The specific surface areas were found to be $94.32 \text{ m}^2 \text{ g}^{-1}$ and $93.15 \text{ m}^2 \text{ g}^{-1}$ for MNs and aMNs, respectively. Reduction in the surface area by surface modification did not affect the adsorption capacity at a notable extent.

For constant initial concentration of metal ions, the rate constant and correlation coefficient were determined using the plot $\log C_e$ Vs t (Fig. 4a) that showed a linear fit with highest R^2 value (0.974). Hence, first-order model can be considered as best fit to describe the adsorption kinetics and the Ni^{2+} adsorption follows first-order kinetics (Seenuvasan *et al.*, 2018).

Fig. 4c illustrates the plot of t/q_e Vs t that explains the pseudo-second-order kinetics. Pseudo-second-order kinetics failed to explain the adsorption mechanism due to the deviation. Table 1 gives the comparison of kinetic parameters of all the kinetics models.

The study revealed that surface modified MNs can be an effective adsorbent for the removal of Ni^{2+} from aqueous solutions. The formation of MNs and surface modification were confirmed by the presence of all the characteristic peaks in FTIR spectrum. Also, nanosized crystalline structure and mesoporous morphology were clear from the XRD patterns and FESEM images respectively. With an insight knowledge on the properties of the aMNs, the adsorption mechanism of Ni^{2+} from the aqueous solutions were described by the kinetics study. Adsorption of Ni^{2+} obeys the first-order equation with good relation.

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