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# Adsorption of Ni(II) Ions from Aqueous Solution on the DMSA Functionalized Magnetic Nanoadsorbents

V.P. Kothavale[1], V. D. Chavan[2], S. R. Shingte[3], Subasa C. Sahoo[4], P.S. Patil[2,5], and P.B. Patil[3,a)]

[1]Department of Physics, BhogawatiMahavidyalaya, Kurukali, Shivaji University Kolhapur- 416001, India.
[2]School of Nanoscience and Technology, Shivaji University, Kolhapur-416004, India.
[3]Department of Physics, The New College,Shivaji University, Kolhapur, Maharashtra -416012, India.
[4]Department of Physics, Central University of Kerala, Kasaragod-671316, India.
[5]Department of Physics, Shivaji University, Kolhapur, Maharashtra -416004, India.

[a)]Corresponding author: prashantphy@gmail.com

**Abstract.** The magnetic nanoparticles (MNPs) were synthesized by the thermal decomposition method and functionalized with meso-2,3-dimercaptosuccinic acid (DMSA). The MNP-DMSA were used as a nanoadsorbents for the removal of Ni(II) ions from aqueous solution. MNPs were characterized by X-ray diffraction (XRD), field emissionscanning electron microscopy (FESEM), and vibrating sample magnetometer (VSM). The MNPs have magnetite phase with a particle size around 25 nm.The magnetic measurement showed that MNPs exhibits superparamagnetic nature with a saturation magnetization of 44 emu/g. The batch adsorption experiments were carried out to remove Ni(II) by optimizing the contact time and initial Ni(II) concentration. The maximum 60 % efficiency was achieved for Ni(II) metal ions removal from the aqueous solution.

## 1. INTRODUCTION

Industries like a metallurgical, tannery, chemical manufacturing, mining, pesticides, and battery manufacturing have been releasing enormous heavy metals into water resources. Water contamination by heavy metals is harmful to human health and also to the ecological system. Therefore it is necessary to remove the heavy metals from polluted water efficiently[1]. There are various physiochemical methods such as ion exchange, solvent extraction, coagulation, chemical precipitation, adsorption, membrane separation, ultrafiltration, etc. for the removal of heavy metals from wastewater. Among these methods, adsorption is the most common method due to its low operating cost, high-efficiency, and easy operational conditions[2]. Several adsorbents like carbon nanotubes, activated carbon, silica gel, clay minerals, magnetic nanoparticles (MNPs), graphene oxide, etc. have been developed for heavy metal removal[3]. Among these adsorbents, MNPs have a high surface to volume ratio, good colloidal stability, and superparamagnetism withhigher magnetization[4]. In addition to this, after adsorption of metal contaminants, MNPs can be easily separated from wastewater by an external magnetic field. To prevent the oxidation of nanoparticles and to improve the heavy metal adsorption capacity, MNPs can be functionalized with compounds, such as chitosan, EGTA-modified chitosan, humic acid, valine, meso-2,3-dimercaptosuccinic acid (DMSA) etc[2,5]. Functionalized MNPs provides specific functional groups like -COOH, $-NH_2$, -OH, -SH, etc. for heavy metal adsorption and thus it may increase the removal efficiency[6].

In this work, $Fe_3O_4$ MNPs were prepared by a thermal decomposition method and functionalized by DMSA. The nanoadsorbents MNP-DMSA was employed for the removal of Ni(II) from aqueous solution.

## 2. EXPERIMENTAL

### 2.1 Materials

All the chemicals used were of analytical grade and used without further purification. Ferric acetyl-acetonate $(Fe(acac)_3)$, phenyl ether, meso-2,3-dimercaptosuccinic acid (DMSA), and 1-2 octanediol were purchased from Sigma Aldrich. Oleic acid, oleylamine, dimethyl sulfoxide (DMSO), hexane, and ethanol were purchased from S.D. fine-chem India. Nickel sulfate pentahydrate was purchased from Fisher Scientific.

### 2.2 Characterizations

X-ray diffraction (XRD) measurements were performed on Bruker AXC D2- phaser diffractometer using Cu $K_\alpha$ radiation ($\lambda$ =1.5406Å). The field emission scanning electron microscope (FE-SEM) JEOL JSM-7100Fwas used to investigate the size of particles.Magnetization measurement was carried out using the vibrating sample magnetometer attached to Physical Property Measurements Systems (PPMS) of Quantum Design, Inc. Magnetization loop was measured at 300 K in magnetic fields up to 30 kOe. The absorbance was measured using a visible spectrophotometer visiscan-167 of Systronics India.

### 2.3 Synthesis and functionalization of $Fe_3O_4$ MNPs

MNPs were synthesized by thermal decomposition method[7]. For the synthesis of MNPs, 2 mmol $Fe(acac)_3$, 6 mmol oleic acid, and 4 mmololeylamine was dissolved in 20 ml phenyl ethersolvent.10 mmol 1-2 octanediol was mixed to the above solution with vigorous stirring under argon atmosphere. The final homogeneous solution was heated to 200 °C for 30 min and refluxed at 260 °C for 2 hin a 100 mL three-neck flask. The reaction mixture was then naturally cooled. The MNPs thus obtained were washed by ethanol and separated by an external magnetic.

To prepare DMSA modified MNPs, the ligand-exchange protocol was used[8].For this, 50 mg MNPs were washed by and centrifuged in ethanol and hexane mixture (1:1). Then MNPs were re-dispersed in toluene and added to the solution of 90 mg DMSA in 5 ml DMSO followed by sonication. The reaction mixture was then incubated at room temperature for 48h in a mechanical shaker. After this, MNP-DMSA were washed by ethanol and dispersed in the doubled distilled water, basified at pH 10 and dialyzed against doubled distilled water for 24h. MNP-DMSA particles were re-dispersed in the aqueous solution of pH 7. Finally, functionalized MNPs were magnetically separated from the solution and dried in vacuum[9].

### 2.4 Adsorption experiments

The adsorption of Ni(II) on MNP-DMSA was studied in aqueous solution by batch experiments at room temperature. The contact time was optimized by adding 50 mg MNP-DMSA in 10 ml of 500 mg/L Ni(II) solution. The solution was shaken in an incubator shaker at 125 rpm to reach adsorption equilibrium. The adsorbents were then separated from the solution by an external magnet. Similar batch experiments were carried out to optimize initial Ni(II) concentration (300-1000 mg/L). The concentration of Ni(II) before and after adsorption was analyzed spectrophotometrically at 384 nm. The removal efficiency (E) of Ni(II) was calculated by the equation,

$$E\,(\%) = \frac{c_0 - c_e}{c_0} \times 100 \qquad (1)$$

where $C_0$ and $C_e$ are the initial and equilibrium concentration of Ni(II) solution (mg /L).

## 3. RESULTS AND DISCUSSION

The XRD pattern of the MNPs is shown in Fig. 1(a). All peaks in the XRD pattern corroborates with the inverse spinel structure of the magnetite (JCPDS No. 00-001-1111 ). The absence of impurity peak in the pattern shows that the sample is pure magnetite. The average crystallite size calculated by the Debye-Scherrer formula was found to be 14 nm. The FESEM micrograph is shown in Fig. 1(b).The FESEM analysis shows, the MNPs are roughly spherical

and having average particle size ~25 nm. Figure 2 shows the room temperature magnetization curve of the MNPs. The MNPs have44 emu/g saturation magnetization. The non-saturating magnetization, along with zero coercivity and remanence, indicates that the MNPsare superparamagnetic[10].
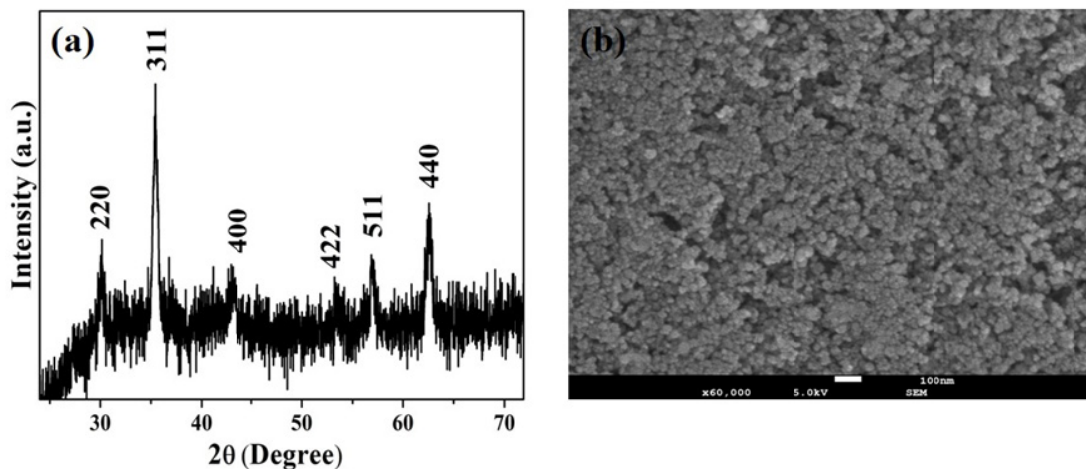


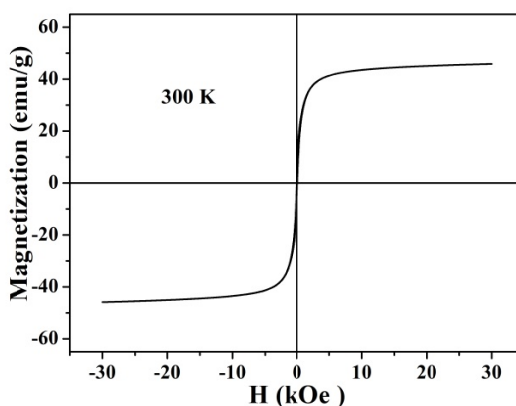**FIGURE 1.** (a) XRD pattern, and (b) FESEM micrograph of $Fe_3O_4$ MNPs



**FIGURE 2.** Magnetization curve of MNPs at room temperature.

The removal efficiency for Ni(II) metal ions was studied as a function of contact time, and initial concentration of Ni(II), and the results are shown in Fig. 3. Contact time is an important factor in the adsorption of metal ions. The effect of contact time for 500 mg/L Ni(II) ion concentration at adsorbent dose 5 g/L was evaluated, as shown in fig. 3(a). From fig. 3(a), it is seen that the removal efficiency for the Ni(II) metal ions rapidly increased with time due to the vacant adsorbent sites and reached 44 % at 135 min. After135 min., the adsorption of Ni(II) reaches equilibrium. This equilibrium condition was reached maybe because all the adsorption sites get occupied by Ni ions.

The effects of initial concentration on the removal of Ni(II) from aqueous solution was studied and is shown in Fig. 3(b). The percentage of Ni(II) removal efficiency was decreased with the increase in the initial concentration. This decrease in removal efficiency is due to the limited availability of adsorption sites because of the fixed adsorbent dose. As the concentration of Ni(II) was increased from 300 mg/L to 1000 mg/L, the removal efficiency decreased from 60 % to 12 % as shown in fig. 3(b). Maximum 60 % removal efficiency was achieved for 300 mg/L initial concentration of Ni(II) ions. To improve removal efficiency, the adsorbent dose, temperature, and pH of the solution needs to be optimized.
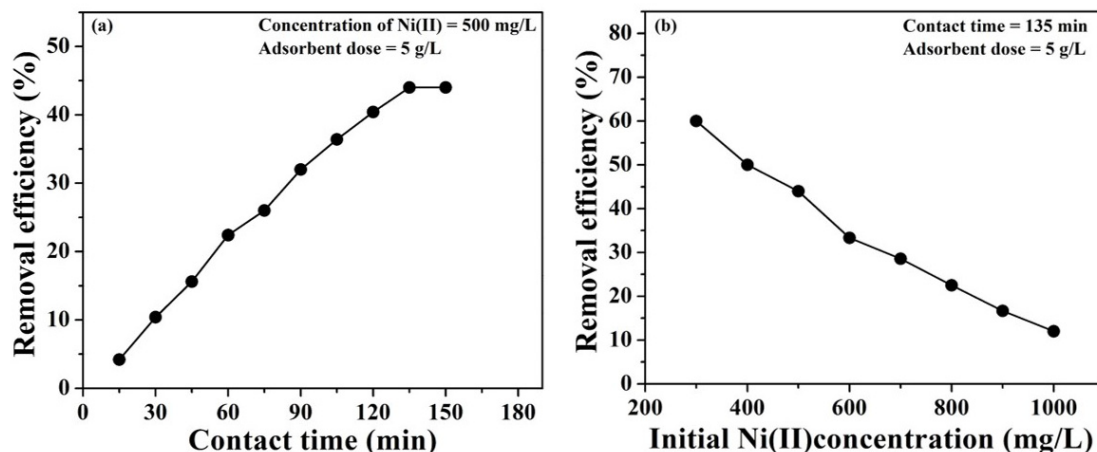
**FIGURE 3.** (a) Effect of contact time on removal efficiency of Ni(II) by MNP-DMSA nanoadsorbents, (b) Effect of Initial Ni(II) concentration on removal efficiency of Ni(II) by MNP-DMSA nanoadsorbents

# 4. CONCLUSIONS

The DMSA functionalized MNPs were effectively used as a nanoadsorbents forthe removal of Ni(II) from the aqueous solution. The XRD pattern shows the puremagnetite phase of the MNPs with an average size of25 nm. The magnetic measurements showed that MNPs are superparamagnetic at room temperature with 44 emu/g saturation magnetization.The MNP-DMSA nanoadsorbents showed 60 % removal efficiency in 135 min for 300 mg/L concentration of Ni(II) ions at 5g/L adsorbent dose. Although we have employed our nanoadsorbent for the removal of Ni(II), DMSA functionalized MNPs can become a potential candidate for the removal of various toxic metal ions in wastewater.

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