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Application of Modified Silica Coated Magnetite Nanoparticles for Removal of Iodine from Water Samples

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Abstract: The adsorption of iodine onto silica coated magnetite nanoparticles (im-SCMNPs) that modified with imidazole was investigated for removal of high concentrations of iodine from wastewater. Modified silica magnetite nanoparticles showed high efficiency in removing iodine from wastewater samples. The optimum pH for iodine removal was 7.0-8.0. The adsorption capacity was evaluated using both the Langmuir and Freundlich adsorption isotherm models. The size of the produced magnetite nanoparticles was determined by X-ray diffraction analysis and scanning electron microscopy. Synthesized magnetite nanoparticles showed the high adsorption capacity and would be a good method to increase adsorption efficiency for the removal of iodine in a wastewater treatment process. The Langmuir adsorption capacity (q_{max}) was found to be 140.84 mg/g of the adsorbent.

Keywords: Modified silica magnetite nanoparticles; Iodine; Imidazole; Water samples

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Introduction

It was found that iodine shows low affinity toward subsurface sediment, except illite [1], and iodine is weakly adsorbed on sediment materials [2]. The weak adsorption capabilities of clays for iodine can be enhanced by exchanging the cations in the natural inorganic interlayer with certain organic cations [3]. Activated aerogels impregnated with silver ion can enhance the iodine adsorption due to an increase in electrostatic attraction [4].

Molecular iodine is one of the major species of iodine that may be present in food, drinking water and seawater [5]. Molecular iodine is an important bactericide and is added to drinking water as a disinfectant [6]. Iodine is one of the fission products generated in a nuclear reactor and can enter into the reactor water [7]. The I_2 is also an important reactant or product in many chemical reactions that are used for analytical applications [8]. Thus, development of reliable methods for the removal of molecular iodine in different matrices is of considerable importance.

The presence of iodine in environmental samples is relatively low. The main source of contamination of the environment by iodine is thin film transistor liquid crystal displays, TFT-LCD [9]. In the TFT-LCD, wastewater is detrimental to the proper operation of the wastewater treatment facility due to its potential biocidal effect toward microorganisms; and zero-valent iron has been proved effective in removing iodine from the wastewater [10]. Several reports have been published on the removal of iodine from water samples. It was found that iodine shows low affinity toward subsurface sediments, except illite [11]. Um et al. reported that iodine is weakly adsorbed on sediment materials [12]. The weak adsorption capabilities of clays for iodine were en-

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hanced by exchanging the cations in the natural inorganic interlayer with certain organic cations [13]. Activated aerogels impregnated with silver ion enhanced the iodine adsorption due to an increase in electrostatic attraction [14]. Curtius and Kattilparampil [15] reported that adsorption of iodine on Mg-Al layered double hydroxide (LDH)is an anion-exchange process. Kentjono et al. used synthesized Mg-Al (NO_3) LDH and used to remove boron and iodine from polarizer manufacturing wastewater [9].

Nanometer-sized materials have attracted substantial interest in the scientific community because of their special properties [16]. The size range of nanoparticles is from 1 to almost 100 nm, which falls between the classical fields of chemistry and solid state physics. The relatively large surface area and highly active surface sites of nanoparticles enables them to have a wide range of potential applications, including shape-selective catalysis [17], chromatographic separations [18], sorption of metal ions [19], enzyme encapsulation [20] DNA transfection [21], and drug delivery [22].

The synthesis of magnetite nanoparticles has been intensively developed not only for its great fundamental scientific interest but also for many technological applications in biology [23], medical applications [24], bioseparation [25]; and separation and preconcentration of various anions and cations [26,27], due to their novel structural, electronic, magnetic and catalytic properties.

In the present paper modified magnetite nanoparticles was employed for removal of iodine and used as an effective adsorbent in the wastewater treatment. The technique was found to be very useful and cost-effective for a better removal of iodine.

Experimental

Instrumentation

A Metrohm model 713 pH-meter was used for pH measurements. A single beam UV-mini-WPA spectrophotometer was used for determination of iodine concentration in the solutions. The size, morphology and structure of the nanoparticles were characterized by transmission electronic microscopy (TEM, Philips, CM10, 100 KV) and scanning electron microscope (SEM, SEM-EDX, XL30 Philips Netherland). The crystal structure of synthesized materials was determined by an X-ray diffractometer (XRD, 38066 RIVA, d/G.Via M. Misone, 11/D (TN) ITALY) at ambient temperature. A 40±5% kHz ultrasonic water bath (DSA 100-SKr-Korea) was used was used.

The mid-infrared spectra of Fe_3O_4, silica coated and imidazole loaded on silica coated magnetite nanoparticles in the region (4000-400 cm^{-1}) were recorded by Perkin-Elmer FT-IR spectrometer (KBr pellets) Model spectrum GX.

Reagents and materials

All the chemicals and reagents used in this work were of analytical grade and purchased from Merck (Merck, Darmstadt, Germany). A stock solution (1000 mg/l) of iodine was prepared in deionized distilled water, and experimental solutions of desired iodine concentrations were obtained by successive dilutions of the stock solution with deionized distilled water. The concentration of iodine in the experimental solution was determined from the calibration curve prepared by measuring absorbance of different predetermined concentrations of iodine solutions at 460 nm ($\lambda_{\max}$).

Preparation of nanostructured silica-coated magnetite

The magnetite nanoparticles were synthesized according to a co-precipitation method followed by aeration oxidation proposed elsewhere [28,29]. Then, the magnetitesuspension prepared above (20 ml) was placed in a 250 mlround-bottom flask and allowed to settle. The supernatant wasremoved, and an aqueous solution of tetraethoxysilane (TEOS,10% (v/v), 80 ml) was added, followed by glycerol (60 ml). The pH of the suspension was adjusted at 4.6 using glacial aceticacid, and the mixture was then stirred and heated at 90°C for 2 hunder a nitrogen atmosphere. After cooling to room temperature,the suspension was washed sequentially with deionized distilled water (3×500 ml), methanol (3 × 500 ml), and deionized distilled water (5×500 ml).

Loading of imidazole onto silica coated nanomagnetite with imidazole

The silica coated magnetite nanoparticles derivative moiety was prepared by reaction with 3-chloropropyltrimethoxysilane (CPTS) as silylation agent [30]. A sample of 10.0 g of silica coated magnetite nanoparticles was suspended in 50 mL of dry toluene and 10.66 mmol of CPTS was added to this suspension. The mixture was refluxed for 48 h, and the modified silica was filtered off, washed twice with toluene, and dried under vacuum at room temperature. In order to prepare immidazol modified magnetite nanoparticles (im-SCMNPs), 5.0 g silica coated magnetite nanoparticles was added to 50 ml of dry toluene and 5.0 g imidazole. Then a few drops of triethylamine were then added to favor the reaction equilibrium [31]. Triethylamine was used as disprotonant agent to increase the efficiency of the reaction. The reaction mixture was refluxed with stirring for 72 h. The solid phase was filtered, washed with toluene and ethanol, and dried under vacuum at room temperature for 24 h (Fig. 1)

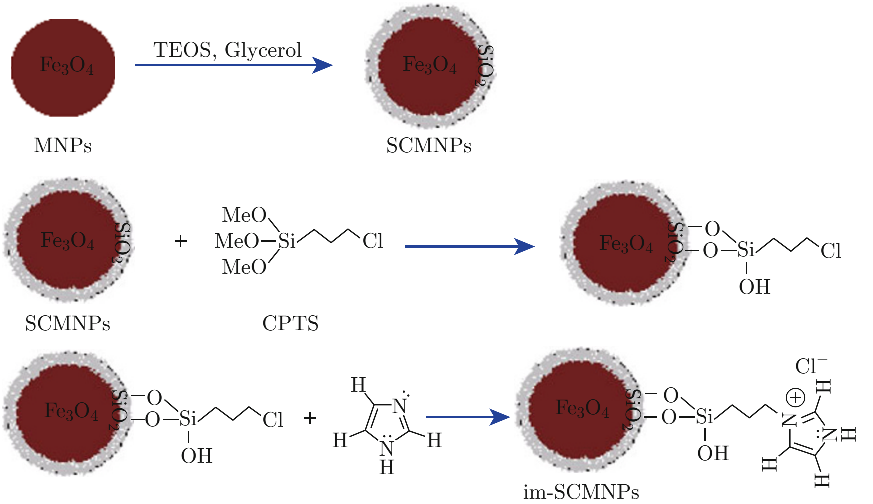

Fig. 1 Reaction schematic diagram for the modification of magnetic nanoparticles with imidazole.

Adsorption behavior of iodine

Adsorption studies were performed by adding 0.05 g im-SCMNPs to the 50 mL solution of different concentrations of iodine in a 250 ml beaker. The pH of the iodine solution was adjusted at 7.0 using 0.1 mol/l HCl and/or 0.1 mol/l NaOH and the solution was stirred for 40 min. Then iodine loaded magnetite nanoparticles were separated with magnetic decantation. The concentration of iodine in the solution was measured spectrophotometrically at 460 nm. The concentration of iodine decreased with time due to its adsorption by magnetite.

Characterization

An infrared spectrum was obtained in the 400-4000 cm^{-1} range, by a Perkin-Elmer FTIR spectrometer. KBr pellets were used for solid samples. The infrared spectroscopy presents a useful tool to initially detect the success of the immobilization process. This proposal can be clarified by comparing the precursor and modified surfaces. The IR spectra of magnetite nanoparticles, Fe_3O_4, (MNPs), silica coated magnetite nanoparticles (SCMNPs) and imidazole loaded on SCMNPs (im-SCMNPs) are presented in Fig. 2. As can be seen, after silica coated on the Fe_3O_4, a new peak at 1044 cm^{-1} was appeared that indicated the Si-O band on the Fe_3O_4. At 2933 and 2864 cm^{-1} wavenumbers the C-H stretching of aliphatic groups and at 3128 cm^{-1} the N-H stretching of imidazole was observed and emphasized the modified silica coated was synthesized.

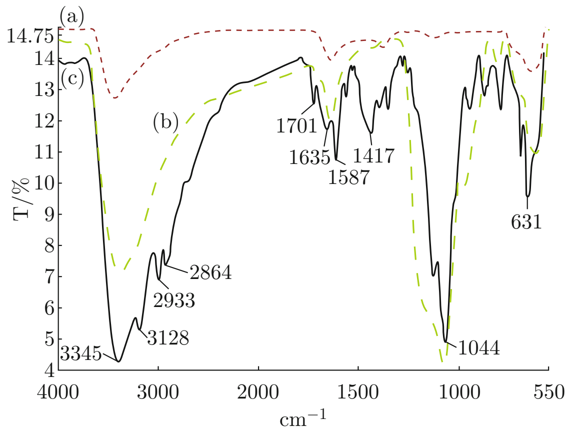

Fig. 2 The IR spectra of (a) MNPs (. . .); (b) SCMNPs (- - -); and (c) im-SCMNPs(_).

Results and discussion

The imidazole (1,3-diazole)–diiodine complex has been experimentally investigated in some instances and n–σ complexes were formed, i.e., they involved electron transfer from the N atom at position 3 of the imidazole ring to the antibonding molecular orbital σ^* of I_2. The monomer and charge-transfer complexes of imidazole with I_2 was investigated and clearly revealed that a suitable interaction occurred between the σ^* orbital of I_2 and the N lone pair in the imidazole at position 3 [32-34]. Therefore the chemical reaction of charge-transfer complexation of imidazole and iodine can be written as equation (1) [35,36]:

$$\text{Imidazole} + I_3^- \rightarrow \text{Imidazole} - I_2 + I^- \qquad (1)$$

When iodine is added to water, the following reaction takes place:

$$I_2(1) + H_2O(1) \rightarrow OI^-(aq) + 2H^+(aq) + I^-(aq)$$
$$(K = 2.0 \times 10^{-13}) \qquad (2)$$

I_2 molecules and water molecules react to substances such as hypoiodite (OI^-) and I^-. The formation of the hypohalite ion (IO^-) in neutral aqueous solutions of iodine is negligible. In basic solutions, iodine converts in a two stage reaction to iodide and iodate [37].

$$I_2 + 2OH^- \rightarrow I^- + IO^- + H_2O \quad (K = 30) \qquad (3)$$

$$3OI^- \rightarrow 2I^- + IO_3^- \quad (K = 10^{20}) \qquad (4)$$

The reaction can move both ways of the equilibrium, depending on the pH of solution. The following reaction mechanism occurs:

$$I_2 + I^- \rightarrow I_3^- \qquad (5)$$

Figure 3 shows the spectra of iodine in solution before and after addition of im-SCMNPs to the solution. As the results show, iodine molecule in the solution with pH 7.0 showed three absorption bands at 460, 390 and 290 nm. After 5 min the absorbance of the iodine solution at 460 nm decreased while the absorbance at two wavelengths 360 and 290 nm increased. The decrease and increase in the absorbances is the result of the conversion of iodine to triiodide anion. Triiodide is produced by the reaction of iodine by iodide ion produced from Eq. (2). By addition of im-SCMNPs, the absorbance at all three absorption bands decreased. As Fig. 3 shows, both the I_2 and I_3^- species can become adsorbed on im-SCMNPs adsorbent. But the im-SCMNPs adsorbent showed higher affinity towards the I_3^-.

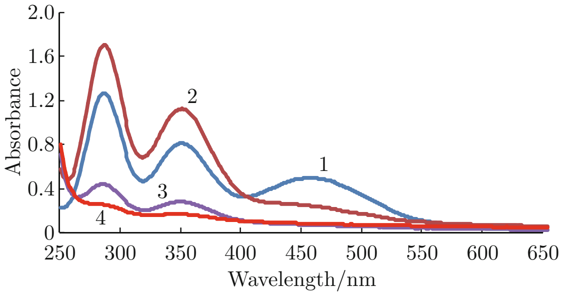

Fig. 3 The spectra of (1) iodine; (2) after 5 min in solution; (3) after 20 min; and (4) after 40 min in contact with im-SCMNPs.

Characterization of the adsorbent

The SEM and TEM images of the im-SCMNPs, as shown in Figs. 4 and 5, revealed the diameter of magnetite nanoparticles synthesized were around 38 nm from SEM image. The typical XRD profile of im-SCMNPs is shown in Fig. 6. The crystallite size was obtained around 27 nm from the XRD pattern according to Scherrer equation [26]. As the results show, the particle dimension obtained by SEM is higher than the corresponding crystallite size. This difference may be explained due to the presence of aggregates in SEM grain consisting of several crystallites and/or poor crystallinity [26].

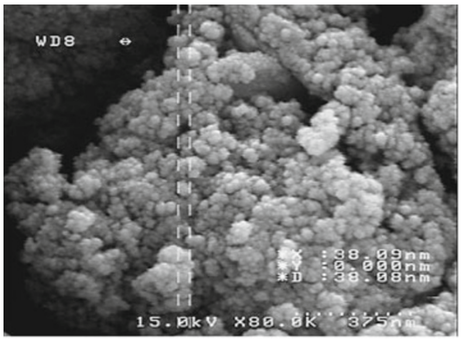

Fig. 4 The SEM patterns of im-SCMNPs.

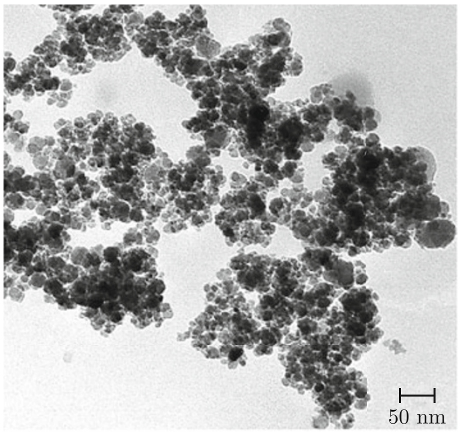

Fig. 5 The TEM patterns of im-SCMNPs.

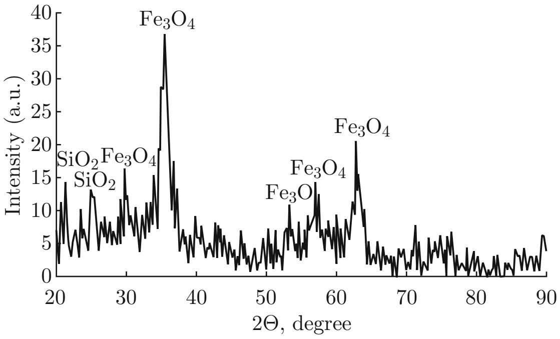

Fig. 6 The XRD patterns of im-SCMNPs.

Effect of contact time

The effect of contact time on the adsorption of iodine was studied to determine the time taken by im-SCMNPs to remove 254 mg/l iodine solution at pH=7.0. A 0.05 g of im-SCMNPs was added into a 50 ml of iodine solution. Absorbance of the solution at 460 nm with time was determined to monitor the iodine concentration. The decrease in the concentration of iodine in the solution with time is due to its adsorption on magnetite nanoparticles. It can be seen that after about 40 min, almost all the iodine became adsorbed. Agitation time of 40 min was selected for further works.

Effect of pH

The effect of pH in the range 5.0-10.0 on the removal of iodine was investigated using 0.01 mol/l HCl or NaOH solutions for pH adjustment, with the initial iodine concentration fixed at 254 mg/l. As Fig. 7 shows, the percent adsorption increased by increasing pH and reached maximum at pH=7.0, remained nearly constant up to pH=9.0 and decreased at higher pHs. The high negatively charged adsorbent surface sites did not favor the adsorption of iodine at higher pHs due to electrostatic repulsion.

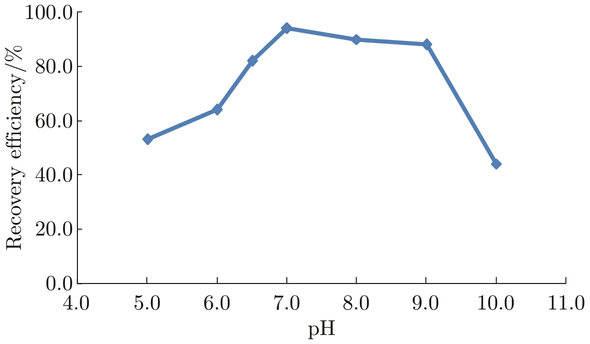

Fig. 7 Percentage of iodine removal at different pHs. Conditions: 0.05 g adsorbent, 20 ml of 254 mg/l of iodine and agitation time of 40 min.

Effect of the amount of adsorbent

The dependence of the adsorption of iodine to the amount of modified nanoparticles was studied at room temperature and at pH=7.0 by varying the adsorbent amount from 10 to 100 mg in contact with 20 mL solution of the mixture of 254 mg/l of iodine. The results are shown in Fig. 8. The percentage removal of iodine increased by increasing amount of im-SCMNPs due to the greater availability of the adsorbent. The adsorption reached a maximum with 50 mg of adsorbent that maximum percentage removal was about 98%.

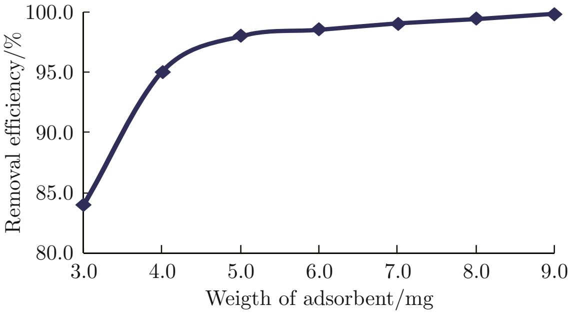

Fig. 8 Percentage removal of iodine at different amounts of adsorbent. Conditions: 20 ml of 254 mg/l of iodine, pH=7.0 and agitation time of 40 min.

Adsorption isotherms

The adsorption isotherm for iodine from water onto im-SCMNPs is shown in Fig. 9. The number of mg adsorbed per gram of adsorbent, (q_e), versus the equilibrium concentration of iodine is illustrated. The initial slope in Fig. 8 for adsorption of iodine on nanoparticles lies very close to the y-axis which shows that the affinity of iodine for this adsorbent is strong.

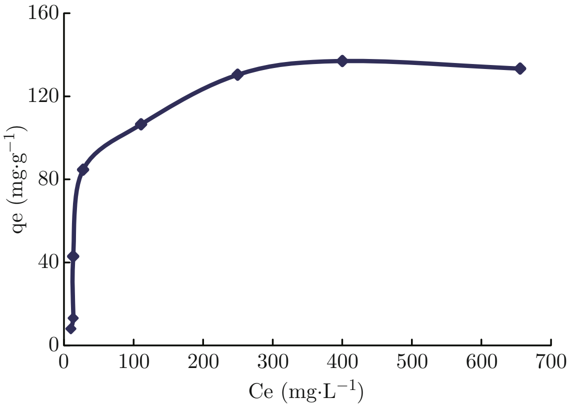

Fig. 9 Langmuir adsorption isotherm of iodine for modified im-SCNMPs.

Two models were tested to model the adsorption isotherms: Langmuir [38] and Freundlich [39] models. Langmuir model does not take into account the variation in adsorption energy, but it is the simplest description of the adsorption process. It is based on the physical hypothesis that the maximum adsorption capacity consists of a monolayer adsorption, that there are no interactions between adsorbed molecules, and that the adsorption energy is distributed homogeneously over the entire coverage surface.

The general form of the Langmuir isotherm is:

$$\frac{a_L q_e}{K_L} = \frac{K_L C_e}{(1 + K_L C_e)} \tag{6}$$

where C_e is the equilibrium concentration of the iodine in the solution (mg/l), q_e is the amount of iodine adsorbed per unit mass of adsorbent (mg/g), at equilibrium concentration, C_e, a_L (l/mg) and K_L (l/g) are the Langmuir constants with a_L related to the adsorption energy and $q_m[= K_L/a_L]$ signifies the maximum adsorption capacity (mg/g), which depends on the number of adsorption sites. The Langmuir isotherm shows that the amount of anion adsorbed increases as the concentration increases up to a saturation point. As long as there are available sites, adsorption will increase with increasing iodine concentrations, but as soon as all of the sites are occupied, a further increase in concentrations of iodine solutions does not increase the amount of iodine on adsorbents after linearization of the Langmuir isotherm, Eq. (6), we obtain:

$$\frac{C_e}{q_e} = C_e\left(\frac{a_L}{K_L}\right) + \left(\frac{1}{K_L}\right) \tag{7}$$

The parameters of this equation for iodine were calculated and are given in Table 1.

Table 1 Adsorption isotherms parameters of iodine onto im-SCMNPs.

Langmuir model				Freundlich model		
$q_{\max}$ (mg/g)	K_L	a_L	r	K_f	$1/n$	r
140.84	5.208	0.0369	0.997	5.44	0.5546	0.704

The Freundlich empirical model is represented by:

$$q_e = K_f C_e^{1/n} \tag{8}$$

where C_e is the equilibrium concentration (mmol/l), q_e is the amount adsorbed at equilibrium (mmol/g), and K_f ($\mathrm{mmol}^{1-1/n}\mathrm{L}^{1/n}$/g) and 1/n are Freundlich constants depending on the temperature and the given adsorbent-adsorbate couple. n is related to the adsorption energy distribution, and K_f indicates the adsorption capacity.

The linearized form of the Freundlich adsorption isotherm equation is

$$\ln q_e = \ln K_f + (1/n)\ln C_e \tag{9}$$

The parameters of this equation for iodine were calculated and are given in Table 1. The regression coefficients, r, for fitting the experimental data points to the linear forms of the Langmuir equations can be considered as a measure of goodness of fit and it is seen that Langmuir model is almost better successful in representing experimental isotherm data versus Freundlich model.

Conclusion

In this study new modified, nanometer-sized silica-magnetic sorbent has been prepared and indicated that the loaded surface with imidazole after CPTS, as precursor silylating agent, could be used as effective adsorbent material for the removing of iodine from water. The modified nanoparticles are highly monodisperse and magnetically separable, and they have high adsorptive capacities. The nanoparticles can rapidly and quantitatively adsorb iodine from water solutions. In acidic media, at pH<5, no sorption was detected due to the protonation of the functional groups. The im-$\mathrm{MMNP_s}$ may be used as an inexpensive, effective, and alternative sorbent for removal of iodine from water solutions. A comparison between the proposed sorbents with those reported for the adsorption of iodine [9-15] shows that it provides higher adsorption capacity and simpler separation of iodine loaded sorbent from water solutions.

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