HYBRID COMPOSITE BASED ON MAGNETITE/CHITOSAN FOR 2,4-D AND CHRYSOIDINE REMOVAL

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ABSTRACT

In this study, magnetite nanoparticles, chitosan, and a hybrid composite of magnetite/ chitosan were prepared through a simple method. The prepared materials were characterized via Fourier transform infrared spectroscopy, X-ray diffraction, Vibrating sample magnetometer, Laser diffraction particle size analyzer, and Zeta potential. Then, the adsorption capacity of these materials for 2,4-Dichlorophenoxyacetic acid (2,4-D) and chrysoidine removal were also determined in the same condition. Prepared materials have the ability to adsorb selectivity with 2,4-D and chrysoidine. There results show the potential application of hybrid composite magnetite/chitosan in developing efficient adsorbent in low cost in the field of environmental treatment.

Keywords: magnetite nanoparticle, chitosan, hybrid composite, 2,4-D, Chrysoidine.

1. INTRODUCTION

Nowadays, magnetic nanoparticles are of interest to researchers due to their wide range of applications as pigments, lithium-ion batteries, and cell separation [1]. On this basis, iron oxide nanoparticles such as magnetite and maghemite are the most studied magnetic materials, which can be easily synthesized in the laboratory [2]. Furthermore, iron oxide nanoparticles have been proved to have low toxicity and biocompatibility, so it is mainly studied in the field of medicine as a drug delivery agent [3, 4], and in the field of environmental remediation as a photocatalyst for degradation of dyes [5] or as a nano-adsorbent for the arsenic removal [6]. However, iron oxide nanoparticles also have limitations as it is susceptible to oxidation under environmental conditions, small specific surface area and it is not effective with organic contamination. Therefore, iron oxide nanoparticles can be combined with the suitable material such as silica, graphene, etc. to produce the hybrid composite materials. These hybrid materials also provide a

functional group on the particles surface, large specific area, as the result of this enhancing adsorption efficiency [7, 8].

Chitosan is a natural polysaccharide obtained by the partial alkaline deacetylation of chitin, the main component of the exoskeleton of crustacean, arthropod, and fungi. Chitosan structure is similar to cellulose. Chitosan is also non-toxic, hydrophilic, biocompatible, biodegradable and anti-bacterial, and can be considered as promising cost-effective adsorbents for the removal of hazardous anions in industrial wastewater [9]. Previous studies showed that chitosan acts as efficient adsorption to remove organic pollutants [10-12]. El Harmoudi *et al.,* studied the adsorption of 2,4-dichlorophenoxyacetic acid (2,4-D) by using two biopolymers based on chitin/chitosan and demonstrated the adsorption ability of 2,4-D onto chitosan due to the interaction between the amino group of chitosan and the carboxyl group of 2,4-D [11]. However, chitosan has unexpected properties such as low specific gravity, easy agglomeration, etc., that makes itself limited to use for pollutant removal applications. The combination of chitosan and magnetite nanoparticles creates a novel composite that ameliorates both properties and makes it become widely used as an adsorbent for removal of organic pollutants such as methyl orange, methylene blue [13, 14] and/or heavy metals [15].

Based on this purpose, we focus on the preparation of magnetite nanoparticles via a hydrothermal method, chitosan and the hybrid composite of magnetite/chitosan through a simple method. Then the adsorption efficiency of the prepared materials in the removal of 2,4-Dichlorophenoxyacetic and chrysoidine dye from aqueous solution is investigated.

2. MATERIALS AND METHODS

2.1. Materials

Iron (III) chloride (FeCl$_3$, Fisher Chemical), ferrous sulfate heptahydrate (FeSO$_4$.7H$_2$O, Merck), potassium hydroxide (KOH, Merck), acetic acid (CH$_3$COOH, Merck), chitosan low molecular weight (deacetylation degree > 60 %, Viet Nam), 2,4-Dichlorophenoxyacetic acid (C$_8$H$_6$Cl$_2$O$_3$, 2,4-D, Merck), chrysoidine crystal (C$_{12}$H$_{13}$ClN$_4$, China). Distilled water was used as the solvent throughout the experiment.

2.2. Preparation of materials

Preparation of magnetite nanoparticles (IONPs): Magnetite nanoparticles (Fe$_3$O$_4$) were prepared by hydrothermal method following process [2, 3]: A mixture of FeCl$_3$ and FeSO$_4$.7H$_2$O was dissolved in a beaker containing 100 mL distilled water under continuous stirring. Then, KOH was added into the solution with continuous stirring at room temperature until the precipitate occurred (pH ~ 12). The obtained solutions were transferred into Teflon lined steel autoclaves, and the hydrothermal synthesis was carried out at 150 °C for 5 h. After the reaction, the solid was taken out of the Teflon lined steel autoclaves; then, washed several times with distilled water and ethanol. After that, dry at 80 °C for 12 h in an oven.

Preparation of chitosan microparticles (CI): Chitosan microparticles were prepared following process: 2.00 g Chitosan was dissolved in 100 mL of 4 % acetic acid solution at room temperature under continuous stirring for overnight. Chitosan solution obtained was doped into 1 M KOH solution under vigorous stirring. The synthesis products were washed with distilled water then dry at 50 °C for 24 h.

Preparation of hybrid composite of magnetite/chitosan (IONPs-CI): The simple method is carried out in distilled water by a similar process of synthesizing chitosan. However, 0.50 g IONPs are dispersed in chitosan solution by ultrasound and shaken before doped into 1 M KOH solution.

2.3. Characterization method

Powder X-ray diffraction (XRD) patterns were measured on a Bruker D8 Advance diffractometer with CuK$_\alpha$ radiation ($\lambda = 1.5418$ Å, 2θ/steps = 0.03°/step). Fourier transform infrared spectroscopy (FT-IR) using a FTIR Jasco-6000 spectrophotometer (wavenumber range of 4000-400 cm^{-1}). The morphology and particles size distribution of IONPs powders, CI, and its hybrid composite were recorded on a Scanning electron microscopy (Hitachi S-4800) and Laser diffraction particle size analyzer (Shimadzu SALD-2101). The surface charge of those particles was examined using a Zeta phoremeter IV (CAD Instrumentation) under the following conditions: room temperature, pH = 5.5, 10^{-3} M KCl solution was used to set the ionic strength. The magnetic properties of the material are characterized by Saturation Magnetization (M_S), which value was measured by VSM (Vibrating Sample Magnetometer).

2.4. Removal of 2,4-Dichlorophenoxyacetic and chrysoidine in aqueous solution

Removal of 2,4-Dichlorophenoxyacetic: Amount of 0.1000 g adsorbent material was dispersed in a beaker containing 100 mL of 2,4-D solution had known concentration by ultrasound for 5 min; then the beaker was shaken in a thermostat shaker for 30 min. In order to study the adsorption isotherms, 24 h of contact was applied at room temperature. After that, the samples from suspension were separated by centrifugation, and the remaining 2,4-D was analyzed on Agilent 6430 triple-quad LC/MS system. Conducted five experiments with 2,4-D concentrations are: 1.0; 5.0; 10.0; 15.0 and 20.0 mg/L.

Removal of Chrysoidine: Amount of 0.1000 g adsorbent material was dispersed in a beaker containing 60 mL of 400 mg/L Chrysoidine solution by ultrasound for 5 min., then the beaker was shaken in a thermostat shaker. In order to study the adsorption isotherms, 12 h of contact was applied at room temperature. After that, the samples from suspension were separated by centrifugation. The remaining chrysoidine after adsorption process was determined using a UV-vis spectrophotometer at $\lambda = 450$ nm [16].

The adsorption capacity of adsorbents for 2,4-D and chrysoidine were calculated using equation [7, 13]:

$$q_e = \frac{V(C_0 - C_t)}{W}$$

(1)

where C_0 (mg/L) and C_t (mg/L) are the initial and equilibrium of 2,4-D or chrysoidine concentrations respectively, W (g) is the weight of dried adsorbent used, and V (L) is the working volume of the solution.

3. RESULTS AND DISCUSSION

3.1. Characterization of the prepared materials

The structure of magnetite nanoparticles and the hybrid composite of magnetite/chitosan were analyzed by XRD as shown in Figure 1. XRD patterns results confirm that the prepared

magnetite nanoparticles and the crystal phase in hybrid material are composed of magnetite Fe_3O_4, as indicated by diffraction peaks at $2\theta(°) = 30.1, 35.5, 43.1, 53.1, 57.1$ and 62.5 from the (220), (311), (400), (422), (511) and (440) lattice planes [2, 7, 14, 15]. The rough baseline of hybrid material diffractogram due to chitosan largely exist in the sample.
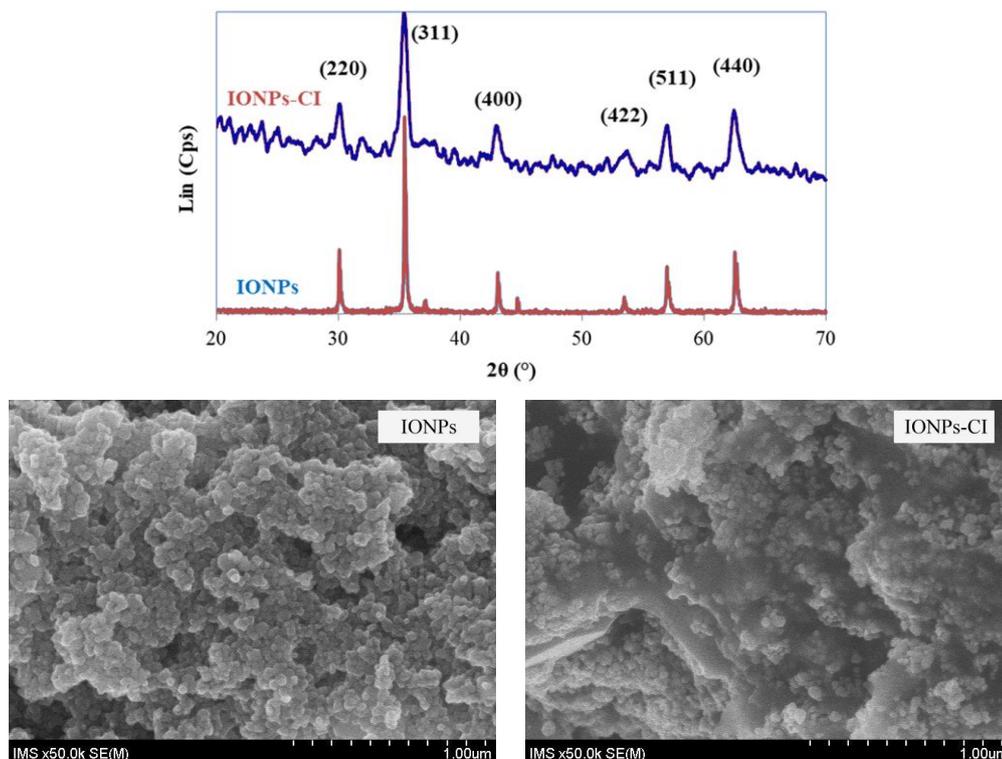

Figure 1. X-ray diffraction (XRD) patterns and SEM images of IONPs and IONPs-CI.

The SEM images show the morphologies of IONPs and hybrid composite IONPs-CI materials. It can be seen that the magnetite nanoparticles were coated well dispersed by chitosan. The average grain size of magnetite nanoparticles was obtained at about 77 ± 5 nm from SEM images by manually counting the populations of 100 particles using *MeasureIT software* (Olympus). Otherwise, the particles size of IONPs-CI and CI were 89.86 ± 0.25 and 166.71 ± 0.29 µm respectively, which recorded from the laser diffraction particle size measurement.

FTIR spectra of magnetite nanoparticles, chitosan, and the hybrid composite of magnetite/chitosan are compared in Fig. 2. In the FTIR spectra, typical bands of chitosan are present: the band at 3403 cm^{-1} corresponds to the O–H stretching overlapping the N–H stretching, while the band at 2875 cm^{-1} is attributed to the C–H stretching. The sharp bands at $1423, 1382$ cm^{-1} are attributed to the CH_2 bending, the asymmetrical C–H bending of the CH_2 group, and the amide III band, respectively. The peak at 1601 cm^{-1} could be based on to the stretching of C–N vibration. The peak at 1651 cm^{-1} was due to C=O stretching (amide I) and at 1082 cm^{-1} show C–O stretching [3, 11-13]. The bands related to the C–O–C bridge are located at 1151 cm^{-1} (anti-symmetric stretching of C–O–C bridge), and 897 cm^{-1} (C–O–C stretching of the glycosidic linkage). The FTIR spectrum of IONPs-CI is very similar to the chitosan spectrum except for the absorption band at 581 cm^{-1} indicated the presence of IONPs in the material [3].

The magnetic properties of the pure magnetite and hybrid composite of magnetite/chitosan were recorded at room temperature. Hysteresis loops of IONPs and IONPs-CI are shown in Fig. 3. The IONPs had high saturation magnetization M_S = 77.20 emu/g. The saturation magnetization of IONPs-CI was decreased to 30.24 emu/g. The results showed that the saturated magnetization of IONPs is much higher than that of hybrid composite IONPs-CI due to the influence of the large content of chitosan which is not a magnetic material.
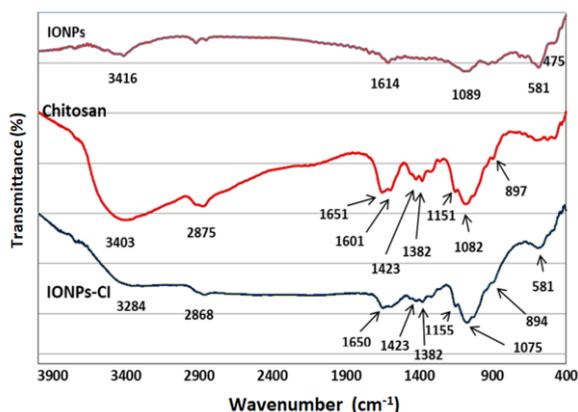

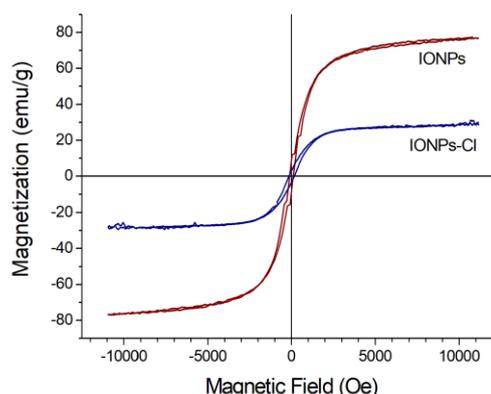*Figure 2.* The FTIR spectra of IONPs, CI and IONPs-CI.

Figure 3. Magnetizations curves of IONPs and IONPs-CI.

From the plot of magnetization curves, it can be suggested that the IONPs and IONPs-CI are superparamagnetic [2, 14]. Then, magnetic composite adsorbents could be quickly collected by applying an external magnet after adsorption. So the magnetic properties of the magnetic composite particles are strong enough to apply in the field of environmental remediation [15].

The average surface charge of the prepared IONPs, CI, and hybrid IONPs-CI materials is equal to –36.61; –7.76 and –10.02 mV, respectively (obtained from Zeta potential characterization). The IONPs have a large negative surface charge and nano-grains size, then IONPs are well dispersed and stable in the aqueous solution [2]. On the other hand, CI and IONPs-CI materials have a lower negative surface charge values; thus their particles are easy to agglomerate and/or flocculate in the aqueous solution, which may lead to decrease in the adsorption capacity of the adsorbent materials.

3.2. The efficiency in removing 2,4-D and Chrysoidine

Figure 4 (a,b) show the LC-MS spectra of 2,4-D and the relationship between the concentration of 2,4-D in the solution versus the adsorption capacity of adsorbent materials. The IONPs adsorption capacity increases as the concentration of the solution increase from 1 to 10 mg/L, then become saturated. Otherwise, the adsorption capacity of CI and hybrid material IONPs-CI were increased by increasing the concentration of 2,4-D and seems to have not reached saturation at 20 mg/L. The 2,4-D removal efficiency was found to be of 39.0 % and 32.5 % at the initial 2,4-D concentration of 15 mg/L for CI and IONPs-CI, respectively. The Langmuir isotherm model was used to determine the maximum adsorption capacity of 2,4-D on the adsorbent materials [11, 13, 14]. The Langmuir isotherm can be expressed by:

$$C_t / q_e = 1 / (K_L \, q_{max}) + C_t / q_{max} \qquad (2)$$

where C_t, K_L, and q_{max} are the equilibrium concentration of 2,4-D solution (mg/L), Langmuir constant (L/mg), and the maximum adsorption capacity (mg/g), respectively.

Based on the experimental results, the data of the adsorption of 2,4-D at equilibrium (q_e) and equilibrium 2,4-D concentration (C_t) were fitted to the form of Langmuir adsorption model. The obtained results of the Langmuir coefficients for 2,4-D adsorption were summarized in Table 1.
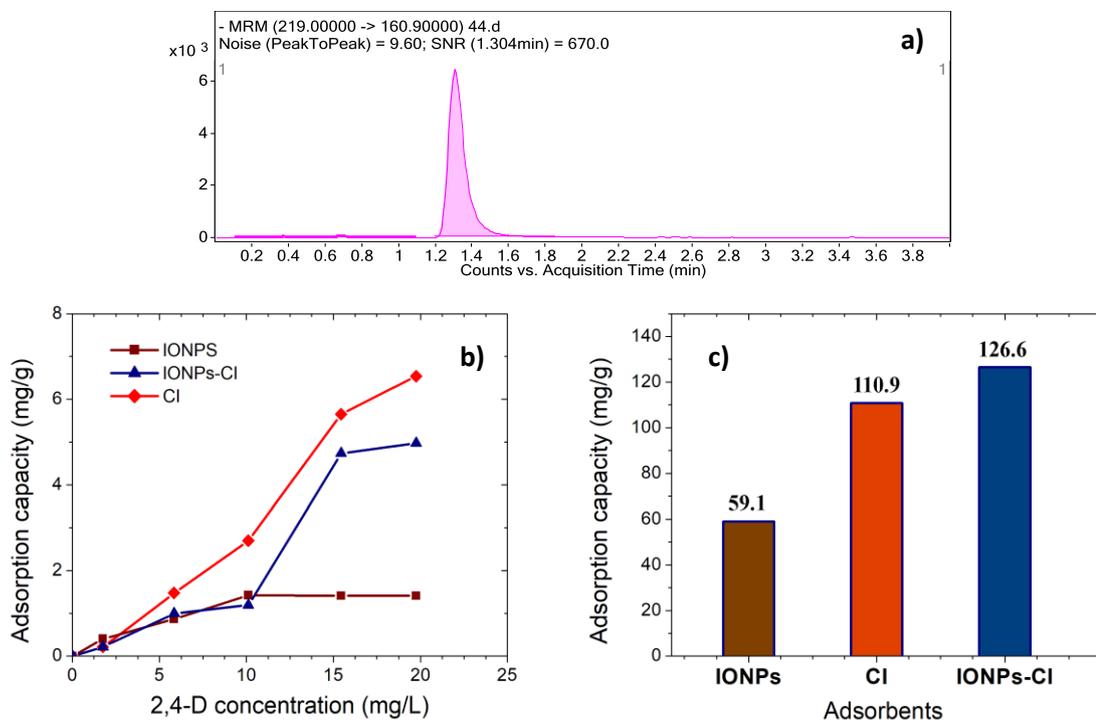
Figure 4. (a) LC-MS spectra of 2,4-D; (b) the relationship between the concentration of 2,4-D in the solution and the adsorption capacity; (c) the adsorption capacity of chrysoidine onto adsorbent materials.

Table 1. Adsorption constants and correlation coefficient (R^2) for 2,4-D adsorption fitting with a Langmuir isotherm model.

	q_{max} (mg/g)	K_L (L/mg)	R^2
IONPs	1.99	0.1641	0.9674
CI	17.14	0.0275	0.9346
IONPs-CI	16.92	0.0182	0.9027

The obtained correlation coefficients ($R^2 > 0.90$) showed that 2,4-D adsorption equilibrium data were fitted well with the Langmuir isotherm model. The maximum adsorption capacity of 2,4-D onto CI and/or IONPs-CI is attainted of 17.14 mg/g, and 16.92 mg/g; it is slightly larger than to the previously reported by El Harmoudi et al., (q_{max} = 11.157 mg/g on chitosan, and q_{max} = 6.079 mg/g onto chitin) [11]. The chitosan and hybrid composite of magnetite/chitosan have a better ability to remove 2,4-D in solution than bare IONPs, so the functional group on the surface of materials is supposed to be the main cause. The chitosan has a large amount of flexible group on the surface (amino and hydroxyl groups) [11, 12] compared with the bare IONPs (have only the hydroxyl groups) [2]; and those amino groups are thought to play an important role in the adsorption mechanism by electrostatic attraction and cation-dipole attraction between the chitosan and 2,4-D molecule [7, 11]. Besides, the chitosan and hybrid

material has a large specific surface area, which was another important factor that resulted in 2,4-D adsorption.

Additionally, the adsorption efficiency of those adsorbents for the chrysoidine solution also carried out in a "closed" condition with the initial chrysoidine concentration of 240 mg/g adsorbent, according to our previous research [16] by using the magnetite/carbon activated as the adsorbent for removal of chrysoidine dye. The results in Fig. 4c shows that the adsorption capacity of chitosan and a hybrid composite of magnetite/chitosan are equal to 110.9, and 126.6 mg/g, respectively and higher than that of IONPs (q_e = 59.1 mg/g). This expected result shows the potential application of chitosan and the hybrid composite of magnetite/chitosan in developing efficient adsorbent in low cost in the field of environmental treatment.

4. CONCLUSIONS

In the present work, magnetite nanoparticles, chitosan and the hybrid composite of magnetite/chitosan, were successfully prepared. The characterization results showed that the Fe_3O_4 nanoparticles has a homogeneous morphology, with the average sizes of 77 nm, the large negative of surface charge, and dispersed well in the hybrid composite of magnetite/chitosan material. Investigation the adsorption capacity of the material toward removing 2,4-D and chrysoidine in aqueous solution, the results indicated that the adsorption efficiency of the chitosan and hybrid material is better than bare magnetite nanoparticles. In the case of 2,4-D, the adsorption equilibrium data were fitted well according to the Langmuir isotherm model and the maximum adsorption capacity is attainted of 17.14 mg/g, and 16.92 mg/g on the chitosan and hybrid composite of magnetite/chitosan, respectively.

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