Application of Functionalized Iron Magnetic Nanoparticles (γFe₂O₃) by Humic Acid for Elimination of Anionic and Cationic Pollutants from Wastewater

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ABSTRACT
Due to expensive costs in wastewater treatment, humic acid (HA) functionalized onto Fe₃O₄ magnetic nanoparticles (FeMNPs-HA) was synthesized in this study to remove Cr⁶⁺ and Pb²⁺ from wastewater. FeMNPs-HA was synthesized by the co-precipitation method for cheap and eco-friendly materials. FTIR and TGA were used for the characterization of FeMNPs-HA. FTIR showed similar bands for both HA and MNPs-HA and this indicated that HA was successively functionalized at FeMNPs. Moreover, TGA analysis showed high stability of material synthesized, since loss of weight began over 600 °C. Batch adsorption experiment was conducted to state the optimum conditions for removal of positive and negative ions (Pb⁺² and Cr⁶⁺) from the aqueous solution using FeMNPs-HA. Adsorption of the studied metals onto FeMNPs-HA reached equilibrium in less than 5 minutes, whereas the adsorption process wasn't affected by pollutants concentrations. Langmuir adsorption model was suitable to explain the sorption process of Pb⁺² and Cr⁶⁺ onto MNPs-HA with maximum adsorption capacities reached 99.99 mg g⁻¹. The FeMNPs-HA proved to ha the capability for elimination more than 99% of Cr⁶⁺ and Pb⁺² from the wastewater at optimized pH. Synthesized material was applied for toxic metals elimination from industrial wastewater (JWW). FeMNPs-HA showed high removal efficiency for Cd, Cr and Ni. Based on the adsorption data; FeMNPs-HA could be considered as an efficient material for wastewater purification from heavy metals regardless their charge.

Keywords: Magnetic Nanoparticles; Humic Acid; Water Purification; Heavy Metals; Isotherm Study.

INTRODUCTION
Due to industrial activities such as tanneries, textiles, ceramics, photography, plating …etc, different metals were discharged into wastewater and cause hazard impacts on the ecosystem, since many of these industries aren't connected with sewerage system (Li et al., 2014). Consequently, they discharge their effluents directly to nearest water bodies, which resulted in risks to aquatic organisms, soils and plants irrigated with this kind of water and finally for humans consume on these plants (Sharma et al., 2009). Many technologies was successfully used for elimination of toxic metals from wastewater such as precipitation, electrochemical reduction, ion exchange, electrodeposition, membrane technology, and adsorption.

Adsorption is considered as most common and effective technique for elimination of different toxic metals from wastewater for economic reasons. There are many adsorbent materials were used for metal removal from wastewater such as adsorption onto activated carbon (Khezami and Capart, 2005), hydrotalcite (Lazaridis and Asouhidou, 2003), coconut husk (Tan et al., 1993), maple sawdust (Yu et al., 2003), biogas residual slurry (Namasivayam and Yamuna, 1995), sugarcane pulp residue (Yang et al., 2009), cellulose graft copolymers (Eromoselle and Bayero, 2000), cross-linked chitosan (Rojas et al. 2004), lignin (Yun et al., 2008), red mud (Pradhan et al., 1999) andSuper-Amphiphilic Silica-Nanogel Composites (Atta et al., 2016). Many scientists had developed novel methods for production and employment of iron magnetic nanomaterials (FeMNPs) with marked characteristics and utilities, due to their diameter in nano size, large surface area to volume ratios and super-magnetism properties (McHenry and Laughlin, 2000; Afkhami et al., 2010 and Pan et al., 2010). Many scientists stated that FeMNPs can adsorb different kinds of pollutants from wastewater (Hu et al., 2005; Mayoet al., 2007; Yean et al., 2005 and Yavuz et al., 2006).

Humic acid has brilliant binding characteristics and electrostatic contacts with toxic metals, leading to metal-organic complexes (Sounthararajah et al., 2015). These complexes can improve the sorption of toxic metals onto iron magnetic nanoparticles. We aim in this study to functionalize γFe₂O₃ nanoparticles with humic acid to improve its ability for removal of cationic and anionic pollutants (Cr⁶⁺ and Pb²⁺). Also to study some factors (pH, pollutant concentration and time) that can change removal efficiency of γFe₂O₃ nanoparticles. Moreover, the adsorption mechanism of Cr⁶⁺ and Pb²⁺ onto adsorbent materials was evaluated during application of Langmuir and freundlich isotherms.

MATERIALS AND METHODS
Materials
Stock solution (1000 mg Cr(VI) L⁻¹ and 1000 mg Pb²⁺ L⁻¹) were produced by dissolving 2.83, 3.97 g of potassium di-chromate and lead acetate, respectively in 1
Liter of deionized water. Desired concentrations of the adsorption experimental solutions were obtained by dilution of stock solution with deionized water. Humic acid was purchased from Canada humic company, Egypt. All chemicals employed in this study were analytical grade.

**Synthesis of MNPs (γFeO₃)**

A magnetic nanoparticle was synthesized by co-precipitation method described by Jeon et al. (2009). Briefly, dissolving a molar ratio of Fe (Cl)₃ and Fe SO₄ using ultrasonic waves. NaOH (6.5 M) was drop-wise into the previous solution under stirring to precipitate magnetic nanoparticles (FeO₃) with diameter around 10 nm. The black precipitate was collected by magnetic field and heated at muffle (300 °C) to produce γFeO₃ nanoparticles. FeMNPs were grinded and kept in desiccator for HA immobilization.

**Functionalyze FeMNPs with humic acid.**

To functionalize γFeO₃ nanoparticles with humic acid, 1 g of humic acid was dissolved in 100 ml NaOH (0.1 N) using ultra-sonication for 1 h. Then the solution was added to 100 ml of n-heptane and stirred for 1 h using magnetic stirrer. Thereafter, 1 g of γFeO₃ nanoparticles was added to the solution and stirred magnetically under heating for 48 h. The supernatant was poured and the precipitate was washed with methanol and several times with deionized water until the solution was neutralized. γFeO₃-HA (FeMNPs-HA) was oven dried at 70°C and pulverized using a milling process.

**Characterization of studied materials.**

Functional groups initiated onto both materials synthesized were checked using Fourier transform infrared spectroscopy (FT-IR), data were got from the diffuse reflectance style by employing Bruker Vertex 80 joined with Ram-FT module (RAM II) spectrometer. Thermo-gravimetric analysis (TGA) of FeMNPs-HA made by TA equipment SDTQ600 from ambient temperature to 1000 °C at a speed of 10 °C min⁻¹ at nitrogen atmosphere with gas flow at 20 ml/min.

**Batch adsorption experiment.**

Batch adsorption study was carried out to conduct the optimum conditions of Cr (VI) and Pb⁺² adsorption onto the studied materials at room temperature (30±1 °C). 0.1 g of studied materials was employed in a flask (250 mL) having 50 mL of pollutant solution (100 mg L⁻¹) at optimum pH. To state the efficacy of time on the optimum reaction time, the reaction solution was then subjected to agitation (200 rpm) by employing a horizontal shaker for different time intervals. Similar investigations were done to study the efficacy of pollutant concentrations (10–100mg L⁻¹) under pH values of (2, 5, 7 and 9) for aqueous phase on the adsorption capacity. Wastewater was filtered and stored at 4 °C until analysis. Chemical analysis of elements under study was carried out using inductively coupled plasma (ICP-AES) with low detection limits of Cd (5.0 μg L⁻¹), Cr (5.0 μg L⁻¹), Pb (50.0 μg L⁻¹) and Ni (5.0 μg L⁻¹). The samples were diluted before ICP measurement where necessary.

**Real industrial wastewater purification.**

A real industrial wastewater (IWW) collected from industrial wastewater treatment plant (employed for El-Rubiky town city) was employed for static adsorption experiment. Wastewater samples were collected using glass bottles (4 L) as reported by Ahrer et al. (2001). Samples were kept in an ice box until it brought back to the laboratory. Thereafter, samples were filtered and stored at 4 °C till adsorption study was done. Elemental analysis of collected wastewater (Table 1) showed that it contains higher amounts of Cr³⁺ and Ni²⁺, while it showed trace concentrations of other elements. Batch adsorption study was carried out to conduct the capability of studied material for removal of Cd²⁺, Cr³⁺ and Ni²⁺ at room temperature (30±1 °C). 0.1 g of studied materials was placed in a 250 mL glass bottle containing 50 mL of IWW (0.09, 4.9 and 62.3 mg L⁻¹ for Cd²⁺, Cr³⁺ and Ni²⁺ respectively) at actual pH (8.3).

**RESULTS AND DISCUSSION**

**Characterization of studied material.**

Humic acid was chosen due to its brilliant binding characteristics and electrostatic interactions with different metals, resulted to make metal-organic complexes. These complexes have an efficacy on the adsorption of different metals onto sorbent material (Sounthrarajah, et al., 2015). Being the products of stochastic synthesis, HA has an elemental composition that is non-stoichiometric, and structure which is irregular and heterogeneous (Hayes et al., 1989). FTIR was made and showed bands at 3400 cm⁻¹ belonging to H, bounded OH groups and might including those of COOH (Stevenson and Goh, 1971). Absorption in 2920 and 2850 cm⁻¹ region refers to aliphatic C-H stretching, while 2337 cm⁻¹ refers to extended C-H stretch groups (Reddy et al., 2018). MNPs-HA showed similar bands indicating successful coating of HA onto surface of MNPs. In the IR spectrum of FeMNPs-HA, the C=O extension were found at 1461 and 1630 cm⁻¹ indicating the carboxylateanion interacting with the Fe-O surface (Yantasee et al., 2007). S-H extension were found at 2329 cm⁻¹, which are characteristically very weak and rolled up by pollution of the C=O extension bands from the background (Jun et al., 2005). Moreover, bands of carboxylate stretches at 1600 and 1400 cm⁻¹ is harmonious with the carboxylate anion reacting with the Fe-O surface since the free carboxylic acid would have a C=O stretch above 1700 cm⁻¹ (Silverstein et al., 1974).

The thermo-gravimetric analysis (TGA) was done to state the amount of weight loss of synthesized material (FeMNPs-HA), either as a mission of increasing temperature, or isothermally as a mission of time and is shown at Fig 1(b). Approximately 38% weight loss was observed in the synthesized material (FeMNPs-HA) above 650 °C. This was attributed to the combustible HA present in synthesized material. However, no significant weight loss was showed between 946 °C to 1000 °C (Fig. 1b).
This reflected the stability of synthesized material. These results are in accordance with those reported by Lassoued et al., (2017) who stated that After 660°C, the curve of TGA became parallel to the temperature axis, which emphasized high stability of α-Fe₂O₃ nanoparticles.

Fig. 1. Different characteristics of synthesized material (a) FTIR spectra of HA, MNP-HA and (b) TGA of FeMNP-HA.

Batch adsorption experiment.

The removal of different chargeable pollutants to synthesized material is largely organized by the source and concentration of HA, metal ion concentration, pH, and other parameters (Hankins et al., 2006; Liu et al., 2004). Therefore, it is essential to state if the variance of these factors in the environmentally relevant range would effect on the removal of studied metals by FeMNP-HA.

Influence of pH

pH considered an essential parameter in the adsorption capacity of studied material. Different pH ranges were affected the ionization grade and solubility of the solute as the surface charge of the adsorbent (Noh and Schwarz 1989; Nandi et al., 2009). To study the impact of initial pH on elimination of studied contaminants using FeMNP-HA from aqueous solution, sorption study were achieved at different pH values (2, 5, 7 and 9) and observance all other study conditions constant (100 mgPb²⁺ or Cr (VI) L⁻¹; temperature, 30 ± °C; agitation, 200 rpm; studied material, 1 g L⁻¹; contact time, 300 min). From the results got shown in Fig. (2), we state that the pH of the adsorption solution significantly influence the adsorption capacity of studied material. Thus, as pH changes from acidic to basic states, Cr (VI) was less efficiently eliminated due to excess of hydroxyl ions resulted in the creation of aqua-complexes thereby delaying the sorption (Venkata et al., 2007a, b) and/or competing with Cr (VI) ions on the adsorbent material surface. Moreover, negative functional groups functionalized on adsorbent material considered a limited role in Cr (VI) adsorption, especially at basic conditions. Yoon et al. (2005) and Gao and Pedersen (2005) reported that pH of the solution influence on the amount adsorptive due to the spreading of surface charge of the adsorbent that could be changed (because of the formation of raw materials and the performance of activation), thus the amount of adsorption changeable consistent with the adsorbate functional groups. In general, FeMNP-HA has the ability to remove more than 99% of Cr (VI) from aqueous solution at low pH. These results are in accordance with those obtained by Ferreira et al. (2017) who reported that the adsorption capacity of Cr(VI) using magnetic coated polymers was dependent on pH values, and it decreases as the pH increases as a consequence of the charge repulsion between the surfaces of the solid negatively-charged and the anionic species chromium(VI) CrO₄²⁻. Adsorption exhibited a dependence on the electrostatic interactions. Also Hu et al., (2007) studied the elimination of Cr(VI) on different magnetic particles and concluded that the maximum adsorption of Cr(VI) was obtained at pH 2.0.

While adsorption of Pb²⁺ onto studied material wasn't affected by pH value. Since the removal of Pb²⁺ recorded > 99% at different pH levels (Fig. 2). This might be attributed to excess of negative chargeable ions (at higher pH) on the adsorbent material which can hold positive chargeable ions (Pb⁺²). In addition to, brilliant binding characteristics and electrostatic interactions of HA with studied metals leading to metal-organic complexes at low pH. These complexes have an efficacy on the adsorption of studied metals on FeMNP-HA. Also, hydroxyl groups functionalized onto synthesized material due to coated HA (fig. 1a) play an important role with adsorption of positive ions (Pb⁺²) at low pH.

Fig. 2. Influence of pH on the removal of Cr (VI) and Pb²⁺ by nano FeMNP-HA.

Influence of pollutant concentration

To state the effect of pollutant concentration on the adsorption capacity of studied material, batch adsorption experiment was employed using different pollutant concentrations varying from 0 to 100 mg Cr (VI) and Pb⁺² L⁻¹. Other operational conditions were stabilized at adsorbent dose 1 g L⁻¹, contact time 3h, optimum pH, temperature 30 ±1 °C and agitating at 200 rpm. Fig. 3 illustrates the influence of different pollutants
concentrations on to removal efficiency of studied material. The results revealed that the removal of studied pollutant using FeMNPs-HA weren't affected by initial concentration. This was attributed to high adsorption capacity of synthesized material due to high surface area (Jeon et al., 2009). Moreover, humic acid functionalized has different kinds of functional groups as listed before in section 3.2.1 (see fig 1). This increase the chance of synthesized material to adsorb both kinds of chargeable pollutants (Cr\(^6\) and Pb\(^2+\)) especially at neutralization. This study revealed that compared to other adsorbent materials (Liu et al., 2008; Salem et al., 2014), the prepared MNP-HA exhibited remarkable enhancement in different chargeable heavy metals. In addition to, the synthesized material (FeMNPs-HA) with adsorbed different chargeable pollutants could be easily desorbed from water with magnetic separations at very low magnetic field gradients (Liu et al., 2008), which can confidently decrease water treatment costs. It is estimated that the synthesized material FeMNPs-HA has wide applicability in the elimination of chargeable metals from wastewater.

**Influence of contact time**

Efficacy of contact time on the adsorption of studied pollutants was studied by changing contact time of the adsorption reaction from 10 to 600 minutes, and uniforms other operational conditions (optimum pH, pollutant concentration 100 mg L\(^{-1}\), adsorbent dose 1 g L\(^{-1}\), temperature 30 ± 1 °C and agitating 200 rpm). The results revealed that contact time didn't affect significantly on the adsorption of studied pollutants, since optimum adsorption capacity was achieved in >99% removal during 5 minutes (Fig. 4). This implies that studies pollutants (Pb\(^{2+}\) and Cr\(^6\)) can interact easily with the active sites of FeMNPs-HA and the adsorption process happened at monolayer, since the adsorption rate was independent on time. Davis and Bhatnagar (1995) stated that in the existence of HA, the oxidation of heavy metals to hydrous metal oxides is a comprehensive result of numerous interactions. If the oxide using the same sites for binding HA and metals, the binding of HA directly on the oxide surface may reduce the metal adsorption due to the sites blockage and competition. On the other hand, the binding of HA to oxide may prefer the uptake of metals because of the complexation between HA and metals, whereas the HA in solution could stop the fraction of metal from adsorbing to the oxide (Liu et al., 2008). The adsorption reached to equilibrium during first 5 minutes, this gives the synthesized materials a preferable choice for wastewater treatment especially resulted from industrial activities.

![Graph](attachment:image.png)

**Fig. 4. Influence of time on the removal of Pb\(^{2+}\) and Cr\(^6\) (VI) using FeMNPs-HA**

**Isotherm study**

Isotherm study was employed to explain the nature of adsorption onto studied material. Langmuir and Freundlich isotherms equation were studied for describing adsorption capacity data.

Langmuir isotherm is a theoretical isotherm developed in 1916; the Langmuir isotherm is expressed as the following equation (Balasubramaniam et al., 2009).

\[
\frac{Ce}{q_e} = \frac{1}{q_{max}b} + \frac{1}{q_{max}C_e}
\]

Where \(q_e\) is the amount (mg g\(^{-1}\)) of pollutant adsorbed at equilibrium, \(C_e\) is the equilibrium pollutant concentration (mg L\(^{-1}\)) in-water samples, \(q_{max}\) (maximum adsorption capability) are the Langmuir constants of adsorption. A plot of \(Ce/q_e\) versus \(Ce\) for the adsorption of Pb\(^{2+}\) and Cr\(^6\) ions onto FeMNPs-HA gives a straight line of the slope \(1/q_{max}\) and intercept \(1/(q_{max}b)\) as shown in Fig. (5).

Freundlich isotherm is commonly used to describe adsorption characteristics for heterogeneous surface. Freundlich isotherm can be expressed as the following equation:

\[
\ln q_e = \ln K_f + \frac{1}{n} \ln C_e
\]

Where \(K_f\) is the constant related to overall adsorption capacity (mg g\(^{-1}\)); \(C_e\) is the constant related to surface heterogeneity (dimensionless).

The applicability of these two isotherm models was quantified by the square of the correlation coefficient \(r^2\). The adsorption of Pb\(^{2+}\) an Cr\(^6\) onto FeMNPs were fitted well with Langmuir isotherm model, since the \(R^2\) were close to unit using Langmuir equation than Freundlich equation. This implies that the adsorbent material has smooth surface and that all sites are identical and energetically equivalent, thermodynamically this implies that each site can hold one adsorbate molecule, adsorption can't proceed beyond monolayer; the ability of a molecule to be adsorbed at a given site is independent of the occupation of neighboring sites, which mean there will be no interactions between adjacent molecules on the surface and immobile adsorption (Coulson et al., 1991).
IWW experiment.
Effluents of IWW located at El-Rubiky industrial city (Cairo, Egypt) was employed for this experiment. Efficacy of FeMNPs -HA for removal of different metals from real IWW was tested during batch adsorption experiment (Table 1). The results showed that FeMNPs - HA has the ability to adsorb much amounts of chargeable elements from real environment without adjusting optimum pH. This was attributed to high adsorption capacity of MNPs-HA beside low concentration values of metals at tested real IWW. Moreover, checked elements were positively charged ions which are preferably adsorbed at higher pH. Synthesized material proved to has the ability to purify IWW to meet the legislation of irrigation water (FAO, 2007).

CONCLUSION
FeMNPs was synthesized and successfully embedded with HA by agitating with n-heptane and HA for 48 hours to increase its removal efficiency for anionic (Cr\(^{6+}\)) and cationic (Pb\(^{2+}\)) pollutants. Material synthesized was characterized by FTIR and TGA equipment. TGA results showed high stability for synthesized material. Batch adsorption experiment was employed to study the efficiency of studied material for removal of Cr (VI) and Pb\(^{2+}\). The pH of the adsorptive medium markedly influence on the removal efficiency of Cr (VI), while adsorption of Pb\(^{2+}\) onto studied material wasn't affected by pH value. Since the removal of Pb\(^{2+}\) recorded > 99% at different pH levels. Adsorption of cationic (Pb+2) and anionic (Cr-6) pollutants onto adsorbent material (FeMNPs -HA) weren't affected by pollutant concentrations or reaction time. Adsorption data was fitted well with Langmuir adsorption isotherm.

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تطبيق حبات أكسيد الحديد المغناطيسي المتناهية الصغر والمشبعة بحمض الهيوميك في إزالة المعادن من المياه العادمة. ومراجعة، تامر محمد سالم عطيه, معهد بحوث الأراضي والمياه والبيئة, مركز البحوث الزراعية بالجيزة, مصر.

العنوان: تأثير مادة حيدرالكرين المصنعة على إزالة cadmium ويون لمعادن أخرى من المياه العادمة.


النوعية: استخدام حيحيدرالكرين المصنعة من حبيبات أكسيد الحديد المغناطيسي المحملة بحمض الهيوميك لاستخدام حلول ملوثة بالميومنيتي." مادة حيدرالكرين المتاحة لعمليات الفصل.

اللعبة: FTIR


المراجعات: 


