Application of Iron Oxide Nanomaterials for the Removal of Heavy Metal

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Abstract
This paper describes the adsorption of heavy metal ions from aqueous solutions by nanoparticles iron oxide. Scanning Electron Microscopes (SEM) and transmission electron microscope (TEM) results showed the successful synthesis. Moreover, adsorption studies were conducted under the different experimental conditions such as pH=6, contact time of 0-60 min, initial concentrations of 2-500 mg/L for used pesticides and adsorbent weights of 0.1 – 0.3 gr. Our study tested the removal of heavy metal cadmium . The optimum contact time, and adsorbent mass, were 60 min and 0.3gr. Experimental equilibrium adsorption data was studied using Langmuir model and Freundlich model. According to the obtained results, Freundlich model was the best adsorption isotherm.

Introduction
The iron oxide nanoparticles have been utilized in various promising applications, such as catalysis, electronic devices, information storage, sensors, and drug-delivery technology, biomedicine, magnetic recording devices, and environmental remediation. Magnetic nanoparticles have large surface areas relative to their volume and can easily bind with chemicals and then they be removed using a magnet. This principal way nanotechnologies might help alleviate water problems is by removing water contaminants including bacteria, viruses, pesticides and hazardous heavy metals like arsenic, chromium, Nickel , etc., Heavy metals contaminated waste water from industrial activities such as electroplating, textile dyeing; tanneries etc reach the surface or ground water sources if it is inadequately treated[1-2]. In addition leaching from solid waste dumps also contributes towards heavy metal accumulation. Polluted water is often treated by conventional or pressure-driven membrane processes to make it comply with drinking water standards. Conventional water treatment process consists of several stages. These include pre-treatment, coagulation, flocculation, sedimentation, disinfection, aeration, and filtration. One of the disadvantages of the conventional water treatment method is that it cannot remove dissolved salts and some soluble inorganic and organic substances. This article analysis the some of low cost, non toxic and sustainable approach for the remediation of waste water released from electroplating industries, palanisamy et al.,[3] studied superparamagnetic iron oxide nanoparticles (SPIONs) were synthesized via a co-precipitation technique using ferrous salts with a Fe²⁺/Fe³⁺. Carrier oils such as olive oil, and flaxseed oil have been used as the coating material, owing to their benefits to the environment. This paper is concerned with the removing a heavy metal, copper, nickel and chromium, from its aqueous solution by carrier oils mediated iron oxide nanoparticles filtration. The prepared nanoparticles were studied in terms of size, morphology, magnetic behavior, structure, surface area including surface chemical structure and charges using different techniques such as XRD, FTIR and TEM.

Water is the most essential compound on the earth for the human activities. Proving clean water is the prime requirement of the human being for their better health. Water pollution is increasing worldwide due to rapid growth of industry, increase human population, and domestic and agricultural activities which leads to the life time threatening diseases [4]. Heavy metals pollution is becoming one of the most serious environment problems globally [5-8]. It is the most threat problem for population in dense countries particularly for China and India [9–14]. Its presence in low concentration of heavy metals in various water resources could be harmful to human health. The treatment of heavy metals is so important due to their persistence in the environment. In order to detoxify heavy metals, various techniques like photocatalytical oxidation, chemical coagulants, electrochemical, bioremediation, ion-exchange resins, reverse osmosis, and adsorption have been employed [15, 16]. Among these nano-based adsorbers are the more convenient technologies for removal of heavy metals from the aqueous system [17–18].

Experimental
Materials
The nanofluid used in the experiment was 99.0+% pure iron oxide, with an average particle size of 20 nm. Figure 1 represents the morphology of Fe₂O₃ nano-particles by using SEM, TEM.

Theory models
Langmuir model
In this model, adsorption occurs uniformly on the active sites of the adsorbent, and once the active sites are occupied by adsorbates, the adsorption is naturally terminated at this site. The non-linear Langmuir equation is [19-20]:

$$
\frac{C_e}{q_e} = \frac{1}{Q_m \cdot K_{L}} + \frac{C_e}{Q_m}
$$
where $q_e$ is the maximum adsorption capacity (mg g$^{-1}$) of adsorbent, $C_e$ is the equilibrium concentration (mg L$^{-1}$), $q_e$ is the amount of metals adsorbed at equilibrium (mg g$^{-1}$). The linear Langmuir model is given by following equation where $b$ is the saturated monolayer adsorption capacity and the adsorption equilibrium constant. A plot of $C_e/q_e$ versus $C_e$ would result in a straight line. From the slope and intercept, the maximum adsorption capacity and bond energy of adsorbates can be calculated.

**Freundlich adsorption isotherm**

The Freundlich equation is an empirical model allowing for multilayer adsorption on sorbent. The non-linear form of Freundlich model is [21]:

$$\log q_e = \log K_f + \frac{\log C_e}{n}$$  

(2)

where $q_e$ is loading of adsorbate on adsorbent at equilibrium (mgg$^{-1}$); $K_f$ is indicator of sorption capacity (mg$^{-1}$·L·mg$^{-1}$), n is adsorption energetics and $C_e$ is aqueous concentration of adsorbate at equilibrium (mg L$^{-1}$).

The amount of Cd ions adsorption at equilibrium $q_e$ (mg/g) was calculated from the following equation:
Effect of initial concentration

The absorption ratio of metal Cd by iron oxide nano particles was studied under the effect of metal ions initial concentration in the range of 2 to 500 mg/l and pH=6 and 0.1 gr absorbent amount. Based on the Fig. 4 the absorption ratio is increasing from 49 to 99 by increasing metal ions initial concentration from 2 to 500 mg/l. Increasing the metal ions initial concentration leads to increase in concentration gradient driving force and absorption capacity. In low concentrations all of the metal ions with active sites are reacted but yet there are still free absorption sites in the absorbent surface. So the absorption capacity is increased with more occupancy of absorption sites. The obtained results are consistent with Kantamatia et al. (2013) in this regard. They reported that the optimum amount of copper and Co(II) Ions at a constant initial concentration of 50 mg/l [22].

| Table 1: Adsorption equilibrium constants obtained from Langmuir and Freundlich isotherms for Cd adsorption onto iron oxide nano particles (T = 30°C, pH = 6, t = 40 min). |
|-----------------|-----|-----|-----------------|-----|-----|
| Langmuir model  | Freundlich model |
| q max (mg/g)    | b   | R²  | kf              | l/n | R²  |
| 96.35           | 0.943 | 0.9724 | 66.38          | 0.086 | 0.999 |

Conclusions

The results of this study showed that the iron oxide nano particles could be used effectively for the adsorption of cadmium ions from aqueous solutions.

1. The maximum cadmium ion adsorption capacity for the iron oxide nano particles reached 155.71 mg/g under an initial concentration, and adsorption time of 500 mg/L, and 60 min, respectively.

2. Experimental equilibrium adsorption data was studied using Longmuir model and Freundlich model. According to the obtained results, Freundlich model was the best adsorption isotherm.

References


