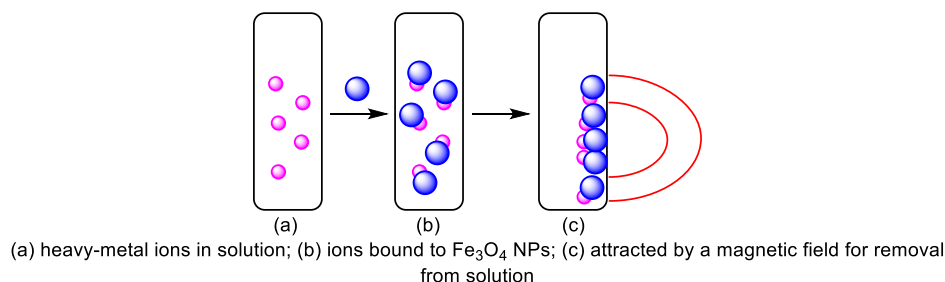# The efficacy of water-soluble Fe_3O_4 nanoparticles in the removal of heavy-metal ions from contaminated water.

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ABSTRACT: As overpopulation and industrial activity continue to increase at a rapid rate, heavy-metal contamination of our water supplies is becoming a more pressing issue. Wang et al. hypothesized that water-soluble Fe_3O_4 nanoparticles (NPs) with high stability and magnetic properties would rapidly absorb Pb^{2+} and Cr^{6+}, and then be magnetically separated from wastewater after complete adsorption. It was found that Fe_3O_4 nanoparticles with high solubility and high saturation magnetization use an electrostatic attraction adsorption mechanism to remove heavy metals from wastewater exceptionally well. Molecular orbital theory can explain the magnetic properties of these NPs and will be discussed.

(a) heavy-metal ions in solution; (b) ions bound to Fe_3O_4 NPs; (c) attracted by a magnetic field for removal from solution

Introduction

Wastewater contamination is emerging as a pressing environmental and public health issue, because metal pollution does not undergo biodegradation and consequently remains in waterways for extended periods of time. Pb^{2+}, a common metal pollutant, is known to affect protein synthesis by interacting with nucleic acids and tRNA and can hinder heme biosynthesis. Another heavy-metal pollutant, Cr^{6+}, is a known carcinogen that can be absorbed through the digestive system, respiratory tract and skin.[1] Contaminated wastewater also has negative effects on soil and seed germination, as well as larvae and embryo growth of aquatic species.[7]

Many methods, including chemical precipitation, ion exchange, liquid-liquid extraction, resins, cementation, and electrodialysis, have been used previously to remove heavy-metal ions from wastewaters.[2] A recurring challenge of these strategies, however, is the ability of magnetic powders to disperse in wastewater without use of external force; this property is called dispersibility. Particles with high dispersibility are more time and cost effective for wastewater collection and treatment facilities, as no additional resources are required to diffuse them throughout the wastewater. Wang et al. suggest a method that will address this challenge.

They propose the use of water-soluble Fe_3O_4 NPs that can be easily dissolved in wastewater, complete their adsorption of heavy-metal ions, and be removed from the system by magnetic separation. The goal of Wang et al. is to explore the solubility and magnetic properties of Fe_3O_4 NPs, as well as the kinetics and the mechanism of adsorption.

Molecular Orbital Theory

Fe_3O_4 is commonly known as magnetite and has magnetic properties that are suitable to remove heavy-metal ions. The magnetism of the particles can be explained by molecular orbital (MO) theory. In MO theory, symmetry properties and relative energies determine how atomic orbitals (AOs) interact to form MOs. The resulting MOs are occupied by the total number of electrons from each AO.[3] In MO theory, electrons are delocalized, or spread throughout the entire molecule, not just localized in the atom from which they originate.

MO diagrams illustrate the theory and can be used to determine the bond order of a molecule, as well as its relative stability by energetic comparisons. If the total energy of the delocalized electrons in the MOs is less than in the AOs, the molecule is more stable than the separate atoms. If the energy is higher, the molecule is predicted not to form because it is un-

stable. MO diagrams can also tell something about the magnetic properties of the molecule. A molecule is diamagnetic if all the electrons in its MOs are paired, and it is slightly repelled a magnetic field. A paramagnetic molecule has at least one unpaired electron in its MOs. The unpaired electrons act as tiny magnets, so the molecule is consequently attracted by an external magnetic field.[3]

The AOs of an iron atom has 6 valence electrons in the 3d orbital, 4 of which are unpaired. Fe is therefore paramagnetic and has a strong magnetic moment, which is generated by the spinning motion of unpaired electrons. The Fe ions, Fe^{2+} and Fe^{3+}, have 4 and 5 unpaired electrons in the 3d orbital, respectively. For this reason, they too are paramagnetic and thus are attracted by magnetic fields. These ions have experimentally observed magnetic moments of 5.1-5.5 and 5.9, respectively.[3]
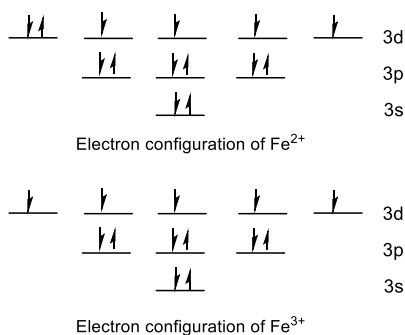
Figure 1 Electron configurations of Fe^{2+} and Fe^{3+} show paramagnetism due to unpaired electrons in the 3d orbital.

When small enough in size (<20 nm), a particle can be affected by thermal fluctuations that have the ability to change the direction of the magnetization of the entire crystal. In a bigger particle, thermal fluctuations may only change the magnetization of some of the crystal. A material comprised of many NPs with fluctuating magnetizations behaves like a paramagnet. However, the entire crystal, not just the atom, has fluctuating magnetization (Figure 2). In this experiment, Fe_3O_4 NPs behave like good paramagnets, and can be removed by a magnetic field even when attached to heavy-metal ions.
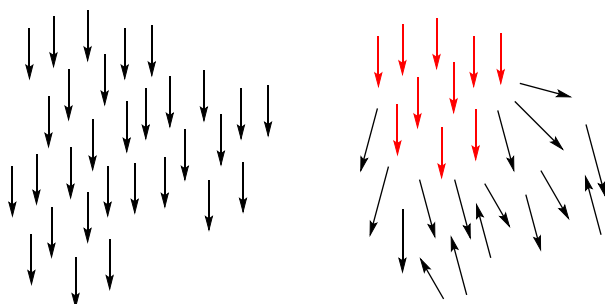
Figure 2 On the left, the entire Fe_3O_4 NP is affected by thermal fluctuations. On the right, only the larger part of the particle (in red) is affected.

Once adsorption of the heavy-metal ions occurs, an external magnetic field is introduced to remove the Fe_3O_4 NPs from water. Three solutions of Fe_3O_4 NPs were synthesized to compare the adsorption capacities of water-soluble and insoluble particles. Two varieties of water-soluble NPs were prepared and characterized as S1 and S2; water-insoluble NPs of a comparable size were characterized as S3. Batch adsorption experiments were then conducted with each type of NPs and varying concentrations of the heavy-metal ions, Cr^{6+} and Pb^{2+}.

In a batch adsorption experiment, the adsorbent is stirred in wastewater in a mixing vessel for a set period of time until equilibrium is attained. After the process is complete, the adsorbent bound to the adsorbate is removed from the system through the introduction of a magnetic field.[4]
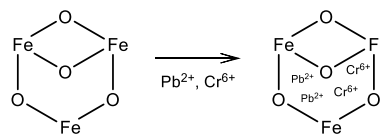
Figure 3 Fe_3O_4 NPs absorb Pb^{2+} and Cr^{6+} ions before magnetic removal from the system.

Experiments and Data

The solutions of heavy-metals were prepared using stock solutions of each ion and deionized water, and the concentrations of each ion in solution were then measured using atomic absorption spectroscopy (AAS). AAS is a spectroscopic method of measuring the concentrations of elements in solution. It is extremely sensitive, and can measure particles as small as parts per billion of a gram in a sample. This technique is element-specific, meaning it uses wavelengths of light specifically absorbed by an element. In this experiment, for example, a lamp containing chromium or lead emitted light from excited chromium or lead atoms; this process is called atomization. The light has the specific wavelength to be absorbed by any particles of the corresponding ion in solution. The higher the concentration of particles in solution, the greater the absorbance.[5]

After preparing the calibration curves of each species, Wang et al. added the adsorbent, Fe_3O_4 NPs, to each solution. Calibration curves are used to determine an unknown concentration of an element, like Cr^{6+} or Pb^{2+}, in solution. Several known concentrations are used to calibrate the spectrometer and generate a calibration curve of concentration vs. absorbance.[5] The concentration of the unknown sample is then determined by where its absorbance falls on the calibration curve.

When adsorption equilibrium was reached, the NPs were magnetically separated from the solution. To measure the efficacy of the NPs, AAS was used again to determine the residual concentrations of metal ions in solution. The amount of heavy-metal ions adsorbed per unit mass of adsorption, q_e, was calculated using an equation that depends on the initial concentration of the metal ion, C_0, the equilibrium concentration, C_e, the total volume of the solution, V, and the dry-weight of the hydrogel beads, W. The units of q_e are mg g^{-1}.

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

Wang et al. discovered that the adsorption of Pb^{2+} at varying concentrations increased as the length of contact time with the NPs increased. As the concentration of metal ion was increased, the adsorption capacity of the NPs also increased.[1] Figures 4-6 show the adsorption capacity of the water-soluble and insoluble particles over time as a function of ion concentration.
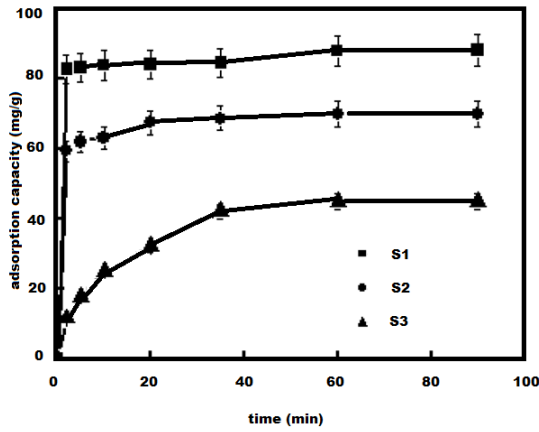
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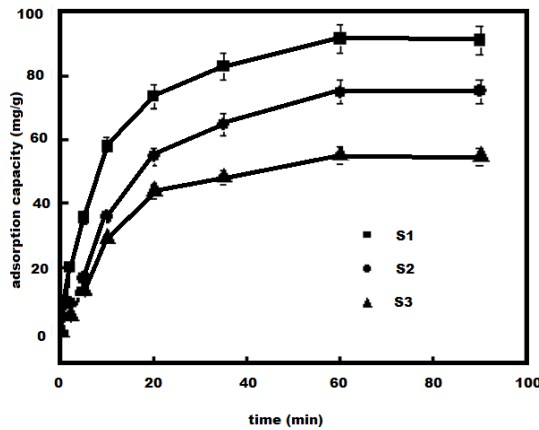**Figure 4** Plot of the adsorption capacity of S1, S2 and S3 for 10 mg L^{-1} of Pb^{2+}

Figure 5 Plot of the adsorption capacity of S1, S2 and S3 for 50 mg L^{-1} of Pb^{2+}
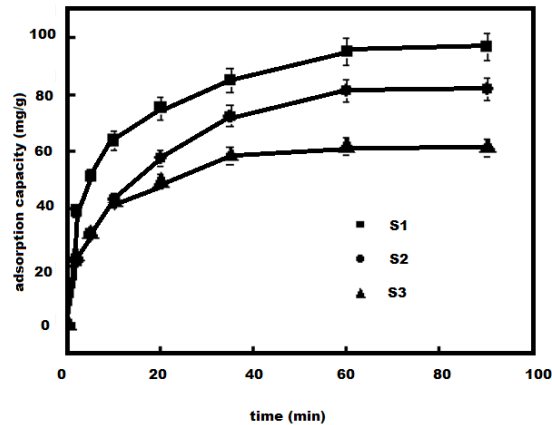

Figure 6 Plot of the adsorption capacity of S1, S2 and S3 for 100 mg L^{-1} of Pb^{2+}

Two models of adsorption isotherms were fitted to this data: the Langmuir isotherm model and the Freundlich isotherm model, which Wang et al. represent in Figure 4 of their article. In general, an adsorption isotherm is a curve that describes the retention or release of a particle from aqueous to solid phase at a constant temperature and pH.[6] The Freundlich and Langmuir isotherm models are both two parameter isotherms, meaning they are relatively simple.

The Langmuir isotherm was scientifically derived using statistical thermodynamics. It was originally developed to describe the adsorption of gases onto activated carbon, but is now used to describe a variety of adsorptions. It assumes adsorption onto a planar surface containing a finite number of uniform sites. Each site can only hold at most one molecule of adsorbate, a process known as monolayer adsorption. Additionally, the isotherm assumes no interactions between molecules of adsorbate once in the surface of the plane.[6] The Langmuir model can be expressed as:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{K_L q_{max}} \frac{1}{C_e}$$

In this equation, K_L is the Langmuir constant related to the energy of adsorption and q_{max} is the maximum amount of adsorption with monolayer coverage. The values of these constants can be determined from the linear plot of $1/C_e$ vs. $1/q_e$.[1]

The Freundlich isotherm is the oldest known relationship describing adsorption. Unlike the Langmuir isotherm, it is a purely empirical model and is not restricted to monolayer adsorption. However, a criticism of this model is that it lacks fundamental thermodynamic basis.[6] It relates the amount of adsorbate adsorbed per unit mass of adsorbent, q_e, to the solute equilibrium concentration, C_e, and the capacity of the adsorbent for the adsorbate (K_F). The Freundlich isotherm can be expressed as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

where $1/n$ and K_F values can be calculated from the slope and intercept of the linear plot of $\log C_e$ vs. $\log q_e$.[1]
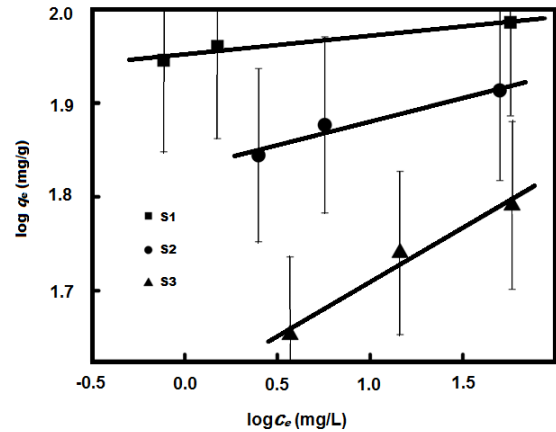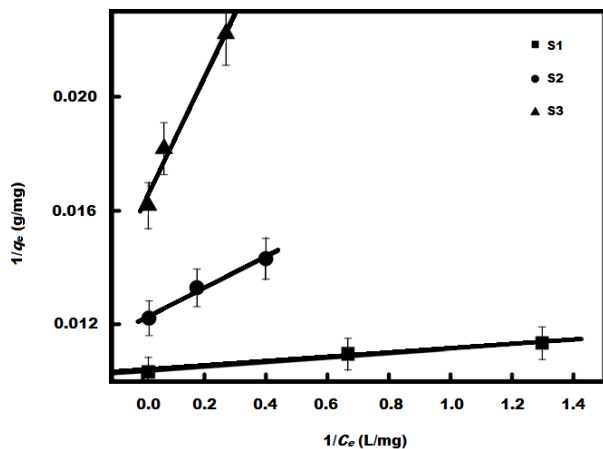

Figure 7 Freundlich adsorption isotherm for adsorption of Pb^{2+} on Fe$_3$O$_4$ NPs with 15 mg of adsorbent. S1 and S2 are water-soluble NPs of similar sizes. S3 is water-insoluble and of a similar size as S1 and S2.

The correlation coefficients of the linearized form of both equations show that the Langmuir model is a better fit for the experimental data for the adsorption of both Pb^{2+} and Cr^{6+}. As time increased, the adsorption capacity also increased.

Figure 8 Langmuir adsorption isotherm for adsorption of Pb^{2+} on Fe_3O_4 NPs with 15 mg of adsorbent. Error is significantly reduced from Freundlich model (see Figure 4).

The water-soluble particles (S1, S2) were found to be more effective adsorbents than the insoluble particles (S3). The smaller Fe_3O_4 water-soluble NPs were slightly more effective than their larger counterparts. The experiments with both Cr^{6+} and Pb^{2+} took place over a relatively short period of time. Both reached maximum adsorption in 90 minutes. This timeframe is practical for real-life application when it is important to clean up water contamination as quickly and effectively as possible. However, the experiment was conducted with volumes of 1 liter, which does not necessarily translate to the millions of gallons of water processed daily in some wastewater treatment plants.

Having explored the propensity for magnetite to adsorb heavy-metal ions in solution, Wang et al. were interested in identifying the mechanism of adsorption. The surface area of the particles plays a large part in the adsorption mechanism, and the surface charge of the NP is also important. Water-soluble magnetite NPs have a large number of carboxyl groups on their surfaces that are in part responsible for their solubility. These carboxyl groups give the magnetite a negative surface charge which Wang et al. assert implies that the main adsorption mechanism is electrostatic attraction. This hypothesis is supported by previous research, as well.

Conclusion

Overall, this experiment with water-soluble Fe_3O_4 NPs to remove heavy-metal ions from solution was successful. Wang et al. compare the maximum adsorption capacity (q_{max}) of the NPs with the literature values of q_{max} for other previously studied Cr^{6+} and Pb^{2+} adsorbents. The Fe_3O_4 NPs have a of q_{max} of 96.8 mg g^{-1}, which is higher than all other adsorbents except for magnetic carbonaceous NPs (123.1 mg g^{-1}) and chitosan modified Fe^0 nanowires (113.2 mg g^{-1}).[1]

The results of this experiment are exciting for a number of reasons. The simple method of preparation, water solubility and high magnetic response of the NPs are factors that make them more effective than other adsorbents. However, the question remains about their efficiency in real-world situations of contaminated wastewater. It would be beneficial to try this experiment with Fe_3O_4 NPs to see how and if they would still function on a large-scale in terms of dispersibility, as well as magnetic response.

It would also be worthwhile to explore any other possible effects of the NPs on the aquatic ecosystem. Research suggests that some nanoparticles can be toxic to humans, fish and bacteria either by themselves or as a result of transformations over time.[7] It would be interesting to explore the ability of water-soluble Fe_3O_4 NPs to adsorb other types of heavy-metal ions, such as Cu^{2+}, Cd^{2+} and Hg^{2+}.[8]

An additional challenge is that nanoparticles may become concentrated in wastewater sludge, which is the product of solids accumulated during the clarifying process. Nanoparticles bound to heavy-metals that fail to be magnetically separated from the system may settle in the sludge and consequently end up in landfills when it is removed from wastewater treatment plants. In this case, it is possible that both the metal pollutants and the NPs would be reintroduced to the waterways, creating a harmful cycle.[7]

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ABBREVIATIONS

NPs, nanoparticles; MO, molecular orbital; AO, atomic orbital; AAS, atomic absorption spectroscopy.

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