Synthesis of dimercaptosuccinic acid (DMSA) coated magnetic nanoparticles: feasibility on dye decolorization and heavy metal adsorption

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Abstract. As highlighted in UN sustainable development goals 2030 report, one of the important challenge in future is to provide clean water. Thus, enormous efforts have been made to improve water quality from recalcitrant pollutants such as organic dyes, heavy metal and others. Magnetic nanoparticles is one of viable candidate to degrade the above pollutants due to its unique properties such bifunctional (catalytic and adsorption) capability & ease for magnetic separation. However, one of the main challenge is to maintain its colloidal stability to exploit its advantages for water remediation. Thus, this work explored its colloidal stability by coating it with heavy metal chelating agent namely Dimercaptosuccinic Acid (DMSA). The resultant clustered magnetic nanoparticles were evaluated its feasibility by using Rhodamine B dye and lead (Pb) heavy metal as model system. It is revealed that DMSA-coated magnetic nanoparticles is a viable candidate for this model system.

1. Introduction

Due to emerging concern in protecting the public health sustainability, water security is crucial towards achieving this goal. Enormous efforts have been made to ensure water cleanliness via various technologies. In the effort to mitigate water contamination issues, there is a growing interest on using magnetic nanoparticles (MNPs) as an adsorbent and/or catalyst for pollutant removal [1]. Magnetite (Fe3O4), maghemite (γ-Fe2O3), hematite (α-Fe2O3), and goethite (α-FeOOH) [2-3] are some of the most commonly used MNPs. On top to the exceptionally high surface to volume ratio that provides large area of loading sites for pollutant removal, their intrinsic magnetic property allows further separation of this nanoagent from the treated water.

The most significant challenge related to the formulation of MNP suspension is the occurrence of particle agglomeration. Agglomeration is a process in which the individually dispersed particles are clumped into a single cluster [1]. Agglomeration starts with the formation of doublets, which later on grow into triplets, quartet, and so forth. Therefore, the number concentration of the primary particles decreased accompanying with the increase in the number concentration of larger agglomerates, as the time progresses [6]. One of the strategies to enhance their colloidal stability is by functionalized with polymer so that the MNPs is been clustered to ensure their collective forces intact.

Among the functionalized IONP, those coated with meso-2,3- dimercaptosuccinic acid (DMSA, Figure 1A) present great potential in both target-drug delivery and remediation of heavy metal...
pollution [4]. DMSA, a dithiol, is a derivative and an analogue of dimercaprol that contains two sulfhydryl groups (–SH) [7]. Oxidation of DMSA molecules around IONP generates a cage of disulfide-cross-linked DMSA molecules around the IONP core, which establishes a negative surface charge of the particles due to an excess of carboxylate groups17 (Figure 1B). The ability of sulfhydryl-containing compounds to chelate metals, e.g. lead, mercury, arsenic, and cadmium, has been well studied. DMSA is not toxic to humans and has been approved for clinical use for chelation therapy [4].

![Figure 1. A. Structural formula of meso-2,3-dimercaptosuccinic acid (DMSA); B. DMSA-MNPs: DMSA molecules bind to MNPs surface via their carboxylate groups and form a cage by disulfide bridges.][4]

2. Methodology

2.1. Materials

For the preparation of bare iron oxide nanoparticles, chemicals used were Iron (II) Chloride Tetrahydrate (Merck), Iron (III) Chloride 6-Hydrate (HmbG Chemicals). In order to bind this magnetic nanoparticles, meso-2,3 Dimercaptosuccinic Acid (Sigma Aldrich) used. For heavy metal adsorption, lead nitrate Pb (NO₃)₂ (Sigma Aldrich) was used while for dye degradation, Rhodamine B Base (Sigma Aldrich), Sodium Hydroxide (Sigma Aldrich) and Hydrogen Peroxide (Systerm) were used as it is.

2.2. Synthetic procedures of MNPs

MNPs were synthesized by using co-precipitation method to obtain the magnetic iron oxide nanoparticles [4]. The preparation steps of iron oxide nanoparticles is by mixing the ferric chloride and ferrous chloride all together with the molar ratio of 2:1. Then the distilled water added to the solutions containing both Fe²⁺ and Fe³⁺ and heat up to 50°C for 10 min. After heating, the solutions precipitated by ammonia. In this moment, black color particles being precipitated which denoted iron oxide nanoparticles. These particles separated by using a strong magnet and then wash with distilled water for a few times. The particles is left in the water in order to make it in the state of colloidal.

2.3. Synthesis of MNPs-DMSA

The MNPs were coated with DMSA. For this 0.13 g (0.7 mM) of DMSA were dissolved in 150 mL double-distilled water by stirring at 50 °C and then added to 100 mL 40 mM iron in form of MNPs during vigorous stirring. After 30 min at room temperature, the particulate content was separated by centrifugation at 800g for 5 min. After the removal of the supernatant the particles were resuspended in 80 mL double-distilled water. The pH of the dispersion was adjusted to 10 with NaOH and then to 7.4 with HCl. The resulting dispersion was finally filtered through a 0.2 μm filter [4].

2.4. Nanoparticles characterization and colloidal stability test

Nanoparticles structural investigation was carried out using a transmission electron microscopy (EFTEM, Libra 120 Carl Zeiss) operated at 100 kV. Micrographic grids were prepared by placing a drop of diluted sample dispersion in ethanol onto a carbon-coated copper grid and dried at room
temperature. On the other hand, Dynamic light scattering (DLS) method by using Malvern ZS were used to study the hydrodynamic diameter of the as-made nanoparticles.

2.5. Feasibility for the heavy metal adsorption and dye decolorization

Solutions containing Pb (II) were prepared at concentration 50 ppm. Then, 1 g/L of the MNPs coated DMSA was added to 50 mL lead aqueous solution under vigorous stirring of 250 rpm. The experiments were performed in triplicate. After a specified time, the MNPs coated DMSA were magnetic separated and the initial and residual concentrations of arsenic were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Perkin Elmer Optima DV 7000). The RHB degradation experiments were carried out by which the 1 g/L MNPs coated DMSA were added into 50 mL of a 100 mg/L RHB solution in the presence of H2O2 as electron donor, and the suspension was shaken in a thermostated shaker at stirring rate of 250 rpm under room temperature. The experiments were performed in triplicate. After the reaction, the microcapsules were separated using an external neodymium boron ferrite (NdBFe) cylindrical magnet. The concentration of RHB was monitored spectrophotometrically recorded using a Perkin Elmer Lambda 25 UV–vis spectrophotometer, with a maximum absorbance wavelength for RHB at 554 nm

3. Results and Discussion

3.1. Nanoparticles characterization & colloidal stability

Nanoparticles morphology were characterized by using TEM as shown in Figure 2 revealed that the MNPs coated DMSA were clustered into smaller groups. By rough dimension, the size of nanocluster MNPs-coated is approximately ~60nm. It was observed, nanocluster MNPs-coated were encapsulated by a layer of polymer indicating potential successful functionalization and stabilization of the nanoparticles. The potential mechanism for the colloidal stability is the steric repulsion in which DMSA inhibit attraction between the nanoparticles [1]. Further investigation using DLS measurement, further confirmed the hydrodynamic diameter of MNPs coated DMSA ~113.6 nm much smaller to as-made MNPs by 3-fold. This might be due to MNPs tendency to agglomerate due to high magnetic dipole moment between particles [1]. In addition, zeta potential value of -37.8 mV after 7 days indicated the stability of MNPs coated DMSA samples (Table 1). The agglomeration of as-made MNPs were confirmed by the incremental value of zeta potential after 7 days of synthesis.

Figure 2. TEM micrograph of MNPs coated DMSA. DMSA successfully clustered the MNPs
Table 1. DLS measurement of hydrodynamic size and zeta potential

| Sample            | Hydrodynamic size (nm) | Zeta Potential (mV) |
|-------------------|------------------------|---------------------|
|                   | 24 hours | 7 days | 24 hours | 7 days |
| Bare MNPs         | 327.5    | 548.8  | -25.8    | -18.4 |
| MNPs coated DMSA  | 113.6    | 208.1  | -41.7    | -37.6 |

3.2. Heavy metal adsorption feasibility

Heavy metal chelating capacity for the MNPs coated DMSA were investigated using lead (II) as model system. The adsorption process were performed for 6 hours experiment as presented in Figure 3. It was clearly observed the adsorption capacities of MNPs coated DMSA were at maximum around 130 mg/g after 3.5 hours adsorption time in comparison just 80 mg/g for as-made MNPs respectively. The sorption binding capacity of MNPs coated DMSA is far more superior might be due to additional availability of ligand shells from the DMSA [5]. The availability of active sites and its pH value are crucial in optimizing the process of the sorption. Furthermore, thiol group attached to DMSA is potentially have strong binding affinity with heavy metals. DMSA also is non-toxic for human being which make it an attractive candidate for MNPs surface functionalization and stabilization [5].

![Figure 3. Comparison of adsorption capacities (mg/g) between as-made MNPs and MNPs coated DMSA](image)

3.3. Dye degradation feasibility

One of the advantages of MNPs is their ability to perform bi-functional which is adsorptive and catalytic properties. With the introduction of hydrogen peroxide as oxidizing agent, MNPs will act as catalyst to degrade the organic contaminants such as dyes. From the experiment using RHB dye as model system as observed in Figure 4, clearly depicted the superiority of the MNPs coated DMSA compared to as-made MNPs to catalytically degrade the dye. This might be due to colloidal stability behavior MNPs-DMSA which render to availability of active sites for the oxidizing agent and pollutant to react onto surface of catalyst [1]. Interesting to point out, the improvement is not more than 0.1 of C/C₀ which potentially indicated inhibitory behavior of DMSA for the RHB dye to penetrate onto MNPs surfaces which explain less dramatic improvement of the degradation. However, this hypothesis need to be confirmed further.
4. Conclusions

From the research, we can conclude several conclusions which are;

i. Magnetic nanoparticles coated with DMSA were synthesized successfully by the electrostatic interaction technique

ii. The stability of clustered MNPs-coated DMSA were better compared to as-made MNPs in term of hydrodynamic diameter size after 7 days of synthesis (~208nm)

iii. As the result, lead (II) adsorption and RHB dye decolorization proof that statistically increment of performance were observed by using MNPs-coated DMSA model system.

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