

Highly Efficient Removal of Anionic Dyes from Water by Cationic Polymer Brush-Functionalized Magnetic Mesoporous Silica Nanoparticles

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Abstract

Methyl orange (MO) and bromothymol from contaminated water using magnetic mesoporous nanoparticles coated with a cationic polymer brush (poly(2-methacryloyloxy)ethyl]trimethylammonium chloride solution) (Fe₃O₄-MSNs-PMETAC). Efficient removal of blue (BT) dyes Atom transfer radical polymerization (ATRP) was used to grow polymer chains on magnetic mesoporous silica nanoparticles. Chemical surface modification was confirmed by IR, TGA, SEM and TEM. The results show that the obtained Fe₃O₄-MSNs-PMETAC material had a nearly spherical shape with a magnetic core of about 30 nm and a silica shell thickness ranging from 135 to 250 nm. The adsorption performance of the materials was found to be unaffected by the pH of the medium (3–9) with 100% removal efficiency for both dyes. The adsorption of BT and MO on the surface of Fe₃O₄-MSNs-PMETAC was found to follow the Freundlich and Langmuir models, respectively. The synthesized Nano composite materials exhibit enhanced properties such as large maximum adsorption capacity, rapid synthesis process, and easy separation from solution, thus avoiding potentially toxic anionic elements (arsenate and chromate) etc. can be effective sorbents for the removal of other contaminants from water and wastewater [1,2].

Keywords: Magnetic nanoparticles; Mesoporous silica nanoparticles; Cationic polymer brushes; Kinetic isotherm; Anionic dyes

Introduction

Increased population density leads to increased economic activity and manufacturing. As a result, the types and amounts of organic pollutants introduced into water sources are increasing. Some of these contaminants are poorly biodegradable or non-biodegradable. Continued exposure to such pollutants has detrimental effects on humans. Today, the most common industries such as textiles, plastics and paper rely on one of the most common contaminants, dyes [3,4]. Organic dyes have complex molecular structures, are highly toxic, highly stable, poorly biodegradable, and can combine with metal ions to form complex pollutants. Many methods have been used to remove organic pollutants from wastewater, such as photo catalysis sedimentation, reverse osmosis, ion exchange ozonolysis, electrolysis, membrane processes and adsorption technology has been used. Adsorption is one of the leading and most important techniques used for dye removal as it is an effective and economically acceptable process with reproducible and high retention efficiencies without generating secondary contamination. Used as adsorbents to remove dyes from aqueous solutions, including activated carbon metal-organic frameworks (MOFs), grapheme-based Nano composites and natural clays there are many traditional ingredients that are used. However, most of these materials are limited because they are difficult to manufacture and dispose of, have low selectivity, and are costly. In recent years, magnetic nanoparticles (MNPs) have received much attention in wastewater treatment due to their magnetic properties that allow them to be easily removed from the system. MNPs include nickel, cobalt, iron and their oxides. Due to their high surface energy, aggregation occurs and affects adsorption capacity they. Iron nanoparticles synthesized for water treatment to remove metal ions they found that the removal efficiency of such nanoparticles was high despite their chemical instability. To improve chemical stability (rust) and prevent aggregation, MNPs can be coated with a protective layer Protective layers can be organic (self-assembled monolayers and polymers) or inorganic (eg silica shells). Mesoporous silica nanoparticles (MSNs) are the most widely used adsorbents in water treatment due to their stability, affordability, resistance to various environments, low toxicity,

[5,6] large surface area, large pore size, and pore volume. It is one of the most sensitive nanomaterial's Coating MNPs with a mesoporous silica shell can prevent MNPs from agglomerating, protect against rusting, and improve impurity selectivity and adsorption capacity. Elmo Barak et al. We prepared his MNPs covered with silica shells of different thicknesses (5, 8, 10, and 15 nm) to recover oil from oil-in-water emulsions. They found that the best results were obtained when the thickness of the silica layer was 5 nm. Huang et al. Synthetic Magnetic Silica Nanoparticles Coated with Diethylenetriamine Pent acetate (DTPA)-Modified Chitosan Select Pb(II) and Methylene Blue Dye (MB) from Polymetallic Effluent Based on Anion Synergy increases viral adsorption The amount of Pb(II) adsorbed in the presence of MB increased from 111.71 to 268.01 mg g⁻¹, synergistically increasing the MB removal efficiency in the presence of lead.

To the best of our knowledge, few studies have used magnetic mesoporous nanoparticles coated with polymer brushes as adsorbents. This study demonstrated the synthesis of magnetic mesoporous nanoparticles modified with a cationic polymer brush (poly (2-(methacryloyloxy) ethyl trimethylammonium chloride solution) using atom transfer radical polymerization (ATRP) to remove the anionic dye. We investigated the anionic dyes methyl orange (MO) and bromothymol blue (BT) from aqueous solutions. Techniques such as FTIR, SEM, and TEMP [7-9].

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Materials and Methods

Ferric chloride (FeCl_2 , 99%) and ferric chloride (FeCl_3 , 99%) were purchased from Loba Chemise (Mumbai, India). Deionized water was obtained from an Elga Pure Nano pore system. Ammonium Hydroxide (NH_4OH , 28 wt%), Ammonium Nitrate (NH_4NO_3 , 99%), 3-Aminopropyltriethoxysilane (APTES, >98%), 2-Bromo-2-methylpropionyl Bromide (BIBB, 98%), N-2,2-bipyridyl (Bipy, 99%), cetyltrimethylammonium bromide (CTAB, 98%), copper (II) bromide (CuBr_2 , 99.9%), copper (I) chloride (CuCl , 99.9%), dichloromethane (DCM, HPLC grade), ethanol (HPLC grade), methanol (HPLC grade), hexane (HPLC grade), isopropanol (HPLC grade), tetraethylorthosilicate (TEOS, 98%) and [2-(methacryloyloxy) ethyl] trimethylammonium chloride solution (METAC, 75 wt% in HO) was obtained from Sigma-Aldrich (USA). Triethylamine (TEA, 99%) was purchased from Nexgen Chemicals (India). Hydrochloric acid (HCl, 36%) was purchased from Fisher Scientific (USA). Sodium hydroxide was purchased from BDH Chemicals (UK). All chemicals were used as received. Synthesis of magnetic nanoparticles (Fe_3O_4).

Magnetic nanoparticles (Fe_3O_4) were fabricated by co-precipitation method. Two separate aqueous solutions of ferric chloride (FeCl_2) and ferric chloride (FeCl_3) were prepared at concentrations of 0.1 M in 50 mL. The two solutions were mixed and then 25 mL of ammonium hydroxide (NH_4OH) was added with stirring at 70°C . for 20 minutes under a nitrogen atmosphere. The magnetic nanoparticles were collected by filtration, and he washed with water three times, followed by ethanol [10-12].

Magnetic Nanoparticles Embedded in Mesoporous Silica

Magnetic nanoparticles (0.5 g) were suspended in 180 mL of DI water. 1.0 g of CTAB ($\text{C}_{19}\text{H}_{42}\text{NBr}$) was added to this suspension, and 9 ml of aqueous ammonia (NH_4OH) was added while stirring at 40°C . A mixed solution of 16 ml of n-hexane (C_6H_{14})/4 ml of TEOS ($\text{Si}(\text{OC}_2\text{H}_5)_4$) was added drop wise to this suspension. After stirring for 12 hours, the solid product was obtained by filtration and then washed with water and ethanol three times. For template removal, the solid product was dispersed in a solution of ammonium nitrate (NH_4NO_3)/ethanol (10 mg/mL) and stirred at 80°C for 12 hours. Fe_3O_4 MSNs were collected by centrifugation and washed three times with ethanol [13-15].

Discussion and Conclusion

General Synthetic Procedure

Iron oxide nanoparticles (Fe_3O_4 NPs) were prepared by mixing ferrous and ferric salts in a basic medium. The mixture was heated at 70°C . for 20 minutes to complete the reduction reaction. Fe_3O_4 NPs were coated with a mesoporous silica shell using the Stöber method in the presence of a swelling agent (hexane) to increase the pore size. After removing the template using an ion-exchange method, the Fe_3O_4 -MSNs were coated with a thin layer of amine-terminated organic molecules (APTES). BIBB molecules were used to react with amine groups to generate ATRP initiator-capped Fe_3O_4 MSNs. Magnetic mesoporous nanoparticles were modified with a cationic polymer brush (poly(2-(methacryloyloxy)ethyl)trimethylammonium chloride solution) using the ATRP technique.

The effect of pH on the extraction efficiency of MO and BT at 350 ppm was investigated at various pH values from 3 to 9. The sorbent dose was (10 mg/10 ml) and the contact time was 3 hours at 25°C .

The extraction efficiency of both dyes on Fe_3O_4 -MSNs-PMETAC was observed to be approximately 100% at all pH values investigated. Furthermore, the effect of analytic concentration on the performance of Fe_3O_4 -MSNs-PMETAC was investigated using different dye concentrations (200, 300 and 500 ppm) at 25°C and pH 7.

MO uptake by Fe_3O_4 -MSNs-PMETAC gradually decreased as the dye concentration was increased from 300 ppm to 500 ppm. On the other hand, the extraction efficiency of the BT-removed material was slightly decreased.

In this study, we synthesized magnetic mesoporous nanoparticles and modified them with a cationic polymer brush (poly(2-(methacryloyloxy) ethyl trimethylammonium chloride solution). We then investigated the performance of the prepared materials by combining two kinds of ions. Dye removal was evaluated (MO and BT) and the effects of different parameters such as analytic dose, contact time and pH were investigated. This result confirms the ability of Fe_3O_4 -MSNs-PMETAC to remove MB and BT ions from contaminated water samples with 100% extraction efficiency. The values of the linear regression coefficients of the studied isotherms suggest that the adsorption behaviour of BT by Fe_3O_4 -MSNs-PMETAC is better approximated by the Freundlich isotherm, whereas for MO it follows the Langmuir isotherm. The kinetic behavior of both dyes was found to be secondary processes. These results indicate that the materials produced are molecularly it suggests that a new direction in the fabrication of engineered sorbents can be initiated.

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