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A comparison investigation on photocatalytic activity performance and adsorption efficiency for the removal of cationic dye: Quantum dots *vs.* magnetic nanoparticles

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ABSTRACT

In this research, the efficiencies of two methods, including quantum dots (QDs) based photocatalysis and magnetic nanoparticles (MNPs) based adsorption for the decolorization of Victoria blue R (VBR) were investigated and compared, experimentally. Synthesis of functionalized zinc sulfide (ZnS) QDs and iron oxide (Fe_3O_4) MNPs was carried out by a simple chemical precipitation method. 2-mercaptoethanol (ME) and sodium dodecyl sulfate (SDS) were applied for capping and surface modification of ZnS QDs and Fe_3O_4 MNPs, respectively. The prepared nanoparticles have been characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), transmission electron microscopy (TEM). The mean particle size of ZnS QDs and Fe_3O_4 MNPs were approximated to be 1–3 nm and 50–80 nm, respectively. In the photocatalytic and adsorption investigations, influence of affecting parameters on the removal efficiencies was studied and optimized. According to the results, both methods can be considered as green, simple and efficient strategies for the removal of organic dyes. However, comparative investigation of the characteristics of the methods demonstrated that the efficiency of the QDs based photodegradation method for the removal of VBR is higher than MNPs based adsorption process. It was also found that the maximum decolorization of 95% and 65% can be achieved after 20 and 45 min at optimum pH 10, 7.5, in the presence of 8 and 10 mg of QDs and MNPs for 30 mg/L of VBR, respectively. Finally, isotherm adsorption model and photodegradation mechanism were discussed, too.

1. Introduction

Pollution is an environmental problem of worldwide concern. Organic pollutants contamination is known to be a significant problem, which threatens the environment and human life [1]. Water pollution due to color dyestuff industries is topics of major concern today [2]. Many industries use dyes extensively in different operation such as textile, paper, plastic, leather, tanning, *etc*. An estimated 10–15% of the synthetic dyes are discharged into wastewater as effluent which carries the potential to cause environmental damage [3].

Moreover, color interferes with light penetration, reducing photosynthesis in aquatic plants and therefore destroying aquatic ecosystems. Also, dyes can be toxic, carcinogenic and mutagenic, which is a serious hazard to aquatic organisms as well as human health [4]. Victoria blue R (VBR) is a photosensitizer, which induce a cytotoxic response in several mammalian cell lines, though some dark toxicity observed, which it causes eye irritation and on ingestion and inhalation shows hazardous effects [5].

Till now, many conventional methods (chemical, physical, biological) have been developed to overcome this problem [6]. Some of the methods for removal of pollutants from wastewater are adsorption [7] membrane separation [8], catalytic ozonation [9], Fenton [10], electro-Fenton [11], advanced oxidation process [12,13], electrochemical degradation [14], photocatalytic degradation [15–17] biodegradation [18], and ultrasonic irradiation [19]. These methods have their own advantages and disadvantages.

In this work, among of the methods, quantum dot (QD) based photodegradation and magnetic nanoparticles based adsorption methods were applied as two experimental approaches for the removal of cationic dyes. Photocatalysis has received considerable attention in recent years as an alternate for treating water polluted with heavy metal ions, dyes and other pollutants [20]. In heterogeneous photocatalytic processes, the main reactions

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primarily take place on the surface of photocatalyst; thus, the effective adsorption of objective pollutants on the surface of photocatalyst was favorable for pollutant degradation by hydroxyl radicals, which was confirmed by electron spin resonance spin-trapping technique [21–23]. In the QD-based photodegradation process, quantum dots (QDs), zero-dimensional inorganic semiconductor nanocrystals, was used as nanophotocatalysts in a UV or visible driven photoactivation process to remove the pollutant dyes [16]. Moreover, this method is supported by some advantages such as high degradation efficiency, requirement of low amount of QDs, fast degradation, applicable for high concentration, and very low concentration of residual dye [24]. Due to the absence of the toxic elements in zinc-based QDs, and high surface area at compared to their bulk counterparts zinc sulfide (ZnS) QDs has been considered as the most popular choice for photocatalytic applications [25,26]. Moreover, semiconductors with wide gap such as ZnS, with band gap energy of 3.67 eV, are ideal for use as a host material for a large variety of metal impurities as a dopant in photocatalytic experiments due to rapid electron-hole pair generation by photo-excitation [27,28]. Today, the doping of ZnS with transition metal ions is of interest for investigation of the effects of dopants on the photoactivity properties of QD semiconductors. The impurities can either be unintentional due to lack of control during the growth of the semiconductor or they can be added on purpose to provide free carriers in the semiconductor [29].

On the other hand, the adsorption process by solid adsorbents shows potential as one of the most efficient methods for the treatment and removal of organic contaminants in wastewater treatment [30]. Adsorption is a well-known equilibrium separation process and an effective method for water decontamination applications. Moreover, adsorption has been found to be superior to other techniques for water reuse in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants [31]. In the recent years, magnetic separation method has been widely used due to low cost, simplicity and being quick in separation and high efficiency. In this regard, application of iron oxide magnetic nanoparticles as green and efficient magnetic nanomaterials adsorbents for the removal of pollutants has been developed in the recent years, due to their unique properties, such as high surface area-to-volume ratio, surface modifiability, excellent magnetic properties, great biocompatibility, ease of separation using an external magnetic field, reusability and comparatively low cost [32]. Therefore, magnetic based adsorbents that facilitate separation by magnetic field have begun to be used in the field of environmental remediation [33].

The purpose of the present work is to investigate the capability of doped ZnS QDs and surfactant modified iron oxide nanoparticles, for the removal of VBR from aqueous solution. Water-based synthesis of ZnS QDs as pure and doped with nickel and cobalt metal ions was carried out by a simple, efficient and fast chemical precipitation method, in the presence of 2-ME as capping agent, at room temperature. Also, surfactant modified Fe_3O_4 MNPs were prepared by the chemical precipitation method. After characterizations, the effect of different experimental parameters on the performance of both methods was investigated according to their efficiencies for the removal of VBR cationic dye, as a model molecule.

2. Experimental

2.1. Materials

In the synthesis of ZnS QDs, 2-mercaptoethanol and chloride salts of zinc and iron ions (all from Merck) were of the highest purity available and used without any further purification. Victoria blue R (VBR) dye was purchased from Aldrich Company. Sodium sulfide ($Na_2S{\cdot}9H_2O$; 98%; w/w) and ammonia solution (25%; w/w) were purchased from Daejung Company (Korea). Aqueous solutions of hydrochloric acid and sodium hydroxide were used for pH adjustment of the solutions.

2.2. Apparatus

All UV–vis absorbance spectra were recorded with a UV–vis spectrometer (Perkin-Elmer UV–vis spectrophotometer LAMBDA-25). Transmission electron microscopic (TEM) images were obtained with a JEM-200CX transmission electron microscope. X-ray diffraction (XRD) patterns were obtained using German Bruker D8Advanced Diffractometer with Cu Kα source (λ = 1.5406 Å). The surface morphology of the particles was recorded on a Philips XL30 series instrument using a gold film for loading the dried particles on the instrument. Magnetic properties of the prepared MNPs were studied by a vibrating sample magnetometer (VSM; Kashan University, Kashan, Iran). The pH measurement of sample solutions was controlled with a Metrohm 692 pH-meter. A mercury lamp (36 W/m^2, Philips) was used as UV light irradiation source in photocatalytic studies.

2.3. Synthesis of pure and doped ZnS QDs

The ZnS QDs doped with transition metal ions (*i.e.* Ni^{2+} and Co^{2+}) were prepared based on a procedure previously reported [34,35]. Accordingly, for the synthesis of ZnS QDs doped with 3% of Ni and Co impurities, firstly, 250 mL aqueous solution of Zn^{2+} and dopant (0.1 $molL^{-1}$) was prepared with a mole ratio of 3.0 in doubly distillated water, and the solution was inserted in a three necked flask. Then, capping process was carried out by drop-wise adding 250 mL of 2-mercaptoethanol (0.1 mol L^{-1}) as capping agent, under nitrogen atmosphere and vigorous stirring. After it, precipitating agent (*i.e.* sulfide ions) was added drop-wise to the flask, under vigorous stirring. The precipitated nanoparticles were isolated by centrifugation, then washed with distillated water, and dried at 50 °C. Synthesis of pure ZnS QDs was also carried out by similar approach; but without the addition of dopant ions.

2.4. Synthesis of pure and modified Fe_3O_4 MNPs

The chemical co-precipitation method was used without using any surfactant for preparation of Fe_3O_4 NPs. For this purpose, $FeCl_3{\cdot}6H_2O$ and $FeCl_2{\cdot}4H_2O$ with a mole ratio of 2:1 were dissolved in 100 mL deionized water (degassed with nitrogen gas before use) to prepare a stock solution. The solution was heated to 85 °C, under nitrogen atmosphere. Subsequently, the ammonium hydroxide solution (10 mL, 25%; w/w) was added drop-wise to the reaction mixture and was allowed to continue about 1 h. After the reaction, the obtained Fe_3O_4 MNPs precipitate was separated from the reaction medium by a magnetic field, and washed four times with 100 mL of deionized water, to remove the impurities and unreacted materials [7].

In order to coat the Fe_3O_4 NPs with SDS, the prepared unmodified Fe_3O_4MNPs were ground into powder in an agate mortar and placed in a clean and dry round-bottom flask. To this, 20 mL of an aqueous solution of SDS surfactant (0.05 mol L^{-1}) was added, under nitrogen atmosphere and the mixture placed in a sonic bath for 60 min. The mixture was stirred at 80 °C for 12 h, after which the mixture was cooled down. The SDS-modified Fe_3O_4 MNPs was separated from the mixture by a magnet. After washing the particles with distilled water, the functionalized Fe_3O_4 MNPs were dried under vacuum for one day at ambient temperature.