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A comprehensive study on the uptake of dyes, Cu(II) and radioactive ^{137}Cs(I) by sonochemically synthesized strontium/yttrium tungstate and molybdate nanoparticles

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ABSTRACT

$SrWO_4$, $SrMoO_4$, Y_2WO_6 and $Y_2Mo_3O_{12}$ nanoparticles has been synthesized via a facile sonochemical route. The samples obtained have been characterized using powder XRD and TEM. The surface area and surface charge of the nanoparticles have been determined from BET adsorption isotherm of N_2 and zeta potential studies, respectively. Sorption characteristics of all the samples have been analyzed for cationic dye (Rhodamine B, Methylene blue), heavy metal Cu(II) ion and radioactive ^{137}Cs(I) uptake. The effect of pH, concentration of dye and loading of sorbent on the process of adsorption has been analyzed. $SrWO_4$ could be used for the selective removal of RhB from a mixture of RhB and MB dyes. The dye sorption process for all samples has been discussed using Langmuir and Freundlich models. Kinetic studies indicate that the adsorption behavior obey the pseudo second order rate law. The rate determining step has been elucidated from the Webber Morris and Boyd plots. Thermal regeneration of the dye loaded sorbents is easily possible and similar adsorption efficiency upto six consecutive cycles has been demonstrated. For the Cu(II)/Cs(I) loaded samples, pH variation leads to efficient regeneration of the sorbents. A comparative study on the uptake properties of all four sorbents for dyes and toxic heavy metal ions indicates that the efficiency of the sorption process depends on the surface charge as well the inherent crystal structures of the materials. It could be inferred that sonochemically synthesized $Y_2Mo_3O_{12}$ nanoparticles exhibits superior sorption characteristics for uptake of dyes, heavy-metal ions like Cu(II) and radioactive ^{137}Cs(I) ions.

1. Introduction

Environmental pollution is considered to be the biggest bane of rapid urbanization and industrialisation in recent years [1]. The detrimental effects are generally manifested in the form of increased air and water pollution. Untreated sewage and effluents from various industries contaminate the water bodies creating a huge pressure in effectively managing this life saving resource [2]. Wastewater containing dye residues and toxic heavy metal ions are quite common in effluents from textile, leather, food, cosmetics, battery manufacturing units as well as electronics industries. Various methods have been tested through the passage of time to remove such pollutants from wastewater and adsorption is considered to be a forerunner amongst them [3–7]. In this technique, preferential partitioning of pollutants occurs from the gaseous or liquid phase onto the surface of a solid substrate [8]. It is a simple, efficient and fast technique with comparatively low cost in terms of system design, initial investment and land requirement [9]. One of the most widely investigated adsorbent in water treatment process is activated carbon but the commercially available form is expensive with poor regeneration efficiency [10]. Consequently there has been an upsurge in developing low cost adsorbents from industrial as well as agricultural wastes such fly ash, bentonite, peat, red mud, rice husk, etc. [11,12]. However, the sorption capacities of these materials vary considerably depending on their method of production and origin and acts as a deterrent for deployment in large scale wastewater treatment [13]. The sorption properties of various synthetic adsorbents like activated alumina, zeolites, silica gel, etc have also been studied thoroughly. However, the poor sorption kinetics of these materials

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due to slow intraparticle diffusion of the solute, prove to be a hindrance [14]. Recently, nanomaterials are being explored as new generation sorbents for wastewater treatment due to their small size and high surface areas [15]. Consequently, ZnO, TiO_2, Al_2O_3, SnO_2, ZnS, Fe_3O_4, CuO, metallic iron nanoparticles and their composites with activated carbon have been synthesized and their applicability in wastewater treatment has been documented [16–20]. However, the quest for novel adsorbents continues unabated since it is difficult to find a single adsorbent that can be equally effective for different types of pollutants.

Contributing to this search of novel adsorbents, we have recently reported the superior sorption properties of sonochemically synthesized barium/manganese/copper tungstate and molybdate nanoparticles [21–23]. The metal tungstates and molybdates are two important classes of inorganic materials finding application in the area of optoelectronics, luminescence, magnetic materials, scintillating materials, catalysis, etc. [24–28]. However, the sorption properties of this series of materials have been explored recently by our group [21–23]. The efficiency of the sorption process is dependent on the surface charge as well as inherent crystal structure of the various metal tungstates and molybdates. The metal atoms attached to the tungstate/molybdate tetrahedra via the oxygen atoms play a crucial role in the resultant crystal structure and can affect the sorption properties. Recently, the photocatalytic activity for degradation of various pollutants have been studied for $SrWO_4$ and $SrMoO_4$ which belongs to this class of materials [24,29]. However, there are no reports on their sorption properties. Hence it was of interest to study the sorption properties of tungstates and molybdates with divalent strontium ions and compare it with tungstates and molybdates of trivalent yttrium ions.

In this work we have studied the sorption properties of sonochemically synthesized strontium and yttrium tungstates/molybdates for various pollutants like dyes, heavy metal ions and radioactive wastes. Rhodamine B (RhB) and methylene blue (MB) were chosen as model pollutants for the dye sorption studies. The choice was based on the fact that both of them find extensive application as colorants in textile and food industry and are known to be carcinogenic, neurotoxic and cause irritation in the eyes, skin and respiratory tract of animals and human [30,31]. Their slow kinetics makes them unsuitable for biological remediation and hence remediation by adsorption on nanoparticles appears to be a suitable alternative technique. Copper was chosen for the heavy metal sorption studies since copper toxicity is prevalent nowadays due to widespread use of copper in utensils, fungicides, hot water pipes, etc. [32]. Excess copper in the digestive tract causes gastrointestinal distress and its presence in water bodies is toxic to fish and algae [21]. The applicability of our sonochemically synthesized strontium and yttrium tungstates/molybdates in treating radioactive wastes was tested via ^{137}Cs sorption. This is one of the biotoxic radioactive fission product generated from the nuclear fuels in the reactors and have a long half life of 30 years. Hence, the safe removal of ^{137}Cs from aquatic environment attracts special attention, particularly after the Fukoshima Daiichi accident [33].

2. Experimental

2.1. Materials and method

The experiments were carried out in aqueous media under air at room temperature and pressure. AR grade strontium nitrate [$Sr(NO_3)_2$], yttrium nitrate [$Y(NO_3)_3{\cdot}6H_2O$], sodium tungstate [$Na_2WO_4{\cdot}2H_2O$] and sodium molybdate [$Na_2MoO_4{\cdot}2H_2O$] of high purity (≥99%) were obtained from commercial sources.

2.1.1. Synthesis of $SrWO_4$

To an aqueous solution (25 ml) of [$Sr(NO_3)_2$] (3.50 g, 16.54 mmol, 25 ml aqueous solution of [$Na_2WO_4{\cdot}2H_2O$] (5.46 g, 16.54 mmol) was added dropwise under pulse sonication. After the addition was complete, the reactants in the beaker was sonicated (100 W/cm^2) under air for 30 min. using an ultrasonicator (Oscar Ultrasonics) operating at 40 kHz. The resulting precipitate was washed with water repeatedly and centrifuged. The white precipitate obtained was dried in air.

2.1.2. Synthesis of $SrMoO_4$

An aqueous solution (25 ml) of [$Sr(NO_3)_2$] (3.01 g, 14.26 mmol) was pulse sonicated and 25 ml of [$Na_2MoO_4{\cdot}2H_2O$] (3.45 g, 14.26 mmol) was added to it dropwise. Immediate precipitation was observed. The ultrasonication was continued for 30 min and the resultant solution was centrifuged to separate the precipitate. The white precipitate was washed thrice with distilled water and air dried.

2.1.3. Synthesis of Y_2WO_6

[$Y(NO_3)_3{\cdot}6H_2O$] (2.26 g, 5.90 mmol) was dissolved in 20 ml of water. To it 25 ml of an aqueous solution of [$Na_2WO_4{\cdot}2H_2O$] (1.95 g, 5.90 mmol) was added under sonication (100 W/cm^2). The reactants were sonicated for 90 min.The white precipitate formed was centrifuged out and washed repeatedly. The product obtained was heated in a muffle furnace at 300 °C for 1 h.

2.1.4. Synthesis of $Y_2(MoO_4)_3$

[$Na_2MoO_4{\cdot}2H_2O$] (1.72 g, 7.10 mmol) solution in 25 ml of water was added slowly to a 20 ml solution of [$Y(NO_3)_3{\cdot}6H_2O$] (2.72 g, 7.10 mmol). The mixture was sonicated for 90 min using an ultrasonicator operating at 100 W/cm^2. The precipitate obtained was washed repeatedly with distilled water and centrifuged out. It was dried in air and heated in a muffle furnace at 750 °C for 1 h.

2.2. Dye sorption experiments

The sorption studies with our sonochemically synthesized $SrWO_4$, $SrMoO_4$, Y_2WO_6 and $Y_2Mo_3O_{12}$ samples for each individual dye viz. RhB and MB was carried out in the batch mode [21–23]. Each experiment was done thrice to ensure reproducibility and the average values of the readings have been used for further calculations. Since dye sorption is influenced by many factors like pH, amount of sorbent and initial dye concentration, the experimental conditions were varied accordingly to understand the sorption process. Broadly it can be stated that, an accurately weighed amount of the sorbent was equilibrated at room temperature with a known concentration of the dye maintained at a particular pH for a known period of time. The details are given later along with the discussion of each sorption experiment to avoid confusion. Once the equilibration was complete, the amount of dye left behind in solution was measured spectrophotometrically by checking the absorbance at 546 and 668 nm for RhB and MB, respectively.

2.3. Copper removal experiments

The uptake studies were carried at room temperature (25 °C) in batch mode using aqueous solutions containing copper ion. 10 ml of aqueous copper ion solution of known concentration (50 ppm, 100 ppm, 200 ppm) at a particular pH (2 and 7) was equilibrated with 10 mg of $SrWO_4$/$SrMoO_4$/Y_2WO_6/$Y_2(MoO_4)_3$ sample. The concentration of metal ion left behind in solution after equilibration was determined. The solution after equilibration was analyzed for the presence of copper ions by complexation with PAR