



Synthesis, characterization and application of a hexagonal mesoporous silica for pesticide removal from aqueous solution



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ABSTRACT

A hexagonal mesoporous silica (SiO_2) was hydrothermally synthesized in alkaline media by using mixed cationic cetyltrimethylammonium tosylate-non-ionic Pluronic F68 surfactants as template. After characterization by commonly used techniques, the solid was evaluated as adsorbent for the removal of dicationic herbicide paraquat (PQ^{2+}). The adsorption of the PQ^{2+} on SiO_2 has been studied in batch experiments by performing adsorption isotherms under different conditions of pH, supporting electrolyte concentration, and temperature. Adsorption kinetic on the studied material has also been carried out and discussed. The adsorption of PQ^{2+} on the studied material is strongly dependent on pH, increasing as pH increases. The adsorption seems to take place by direct binding of the cationic herbicide to SiO_2 active sites (e.g. surface and/or inside the mesopores) through electrostatic interactions and outer-sphere (or ionic pair) complexes formations, as deduce from adsorption experiments at several ionic strengths and temperatures. The analysis of thermodynamic parameters suggests that the adsorption of PQ^{2+} on the studied solid is exothermic and spontaneous in nature. Even after four regeneration cycles through acid washing, the mesoporous material has still a removal efficiency of ca. 75%, showing a promising application for the treatment of wastewater containing paraquat ions.

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1. Introduction

Use of agrochemicals constitutes an unpleasant task but absolutely necessary to tackle the multiple kind of adverse events that can irretrievably damage the quality of various crops. On the other hand, serious health effects may be promoted due to pesticide discharges from manufacturing plants, surface runoff, leaching accidental spills and other sources [1]. In fact, there are several papers that report pesticide concentrations in waste and surface waters higher than pollution threshold limit [2]. Harmfulness of agrochemicals is further enhanced by their mobility and persistence in the aqueous media [3].

Among the numerous agrochemicals in use today, the herbicide paraquat (1,1'-dimethyl-4,4'-dipyridinium chloride) is the most widely used in the world, although it has been forbidden in the European Union since 2007. Its popularity is related to its physical and chemical properties (e.g. high solubility in water, low vapor pressure and high binding potential) and to its quick and non-selective action to kill green plant tissue upon contact [4,5]. Paraquat (PQ^{2+}), also known under the name of methyl viologen, kills

green plants by inhibiting the conversion of nicotinamide adenine dinucleotide phosphate (NADP) to its hydrogen form NADPH during photosynthesis [6]. Additionally, some studies proved that this compound is one of the few herbicides capable of controlling the growth of weeds that became resistant as a result of over-use of non-selective glyphosate herbicides [7]. However, it is known that this herbicide is one of the most toxic poisons if deliberately or accidentally ingested. PQ^{2+} has toxic effects on the lungs, livers, and kidneys of mammals [6]. In recent years, investigations on PQ^{2+} toxicity have suggested that this herbicide might be an environmental factor contributing to a neurodegenerative disorder, such as Parkinson's disease [8]. World Health Organization (WHO) has reported this herbicide as the "major suicide agent" which killed several thousands of people in the past few years due to its acute toxicity, its relative cheap price and its lack of a known effective antidote [9]. Therefore, and as it has not yet been established an effective therapy for acute PQ^{2+} poisoning, it is of great interest the development of an effective adsorbent as antidote or filter for the removal of herbicides from poisoned circulation system or contaminated environment, mainly on solids with high surface area, pore size and catalytic activity.

Since 1990, mesoporous silica and silica-based materials have attracted considerable attention because of their high surface area ($>200 \text{ m}^2 \text{ g}^{-1}$), ordered pore distribution, narrow pore size

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distribution (2–>10 nm, higher than zeolites), high thermal stability and easy regeneration and reusability in comparison with several soils and soil components [10,11]. Due to these properties, they are ideal base materials for catalyst, catalyst support and adsorbent as well as template for other materials. Particularly, silica materials with two-dimensional (2D) hexagonal array of uniform cylindrical mesopores ($p6mm$ space group), like MCM-41, SBA-3 or SBA-15, have attracted considerable attention for possible application as adsorbents because their mesostructures provide the pore size required for the adsorption of large molecules of gas and liquid [12]. MCM-41 and SBA-3 are commonly synthesized by using a cationic surfactant of the family of quaternary ammonium salts as template (i.e., CTAX, where CTA^+ is the cetyltrimethylammonium ion and X^- is the Br^- or Cl^- counterion) [11, 13]. SBA-15, on the contrary, is frequently synthesized by using the non-ionic triblock poly(oxyethylene)–poly(oxypropylene)–poly(oxyethylene) copolymer Pluronic P123 [12]. Recently, several researchers have reported the formation of well-ordered and high thermally-stable mesostructures by using the dual template system CTAX-Pluronic, although the formation of either MCM- or SBA-type materials is strongly related to the experimental synthesis conditions, such as pH, temperature, surfactant concentration, $CTA^+/Pluronic$ molar ratio, type of X^- , calcination temperature, etc. [14,15].

There are several papers in literature related to the adsorption of PQ^{2+} on porous materials, especially concerning zeolites. On the one hand, Ibrahim and Jbara [16] reported that the adsorption of PQ^{2+} on a natural zeolitic material such as phillipsite–faujasite stuff strongly enhances when the adsorbent is thermally activated and/or modified with monovalent cations such as K^+ and Na^+ . Cation exchange was reported to play a key role on the adsorption process. Similar mechanism was reported by Zhang et al. [17] and later by Rongchapo et al. [18] on the adsorption of the pesticide on a surface-modified zeolite Y. On the other hand, Shieh et al. [19] showed that the adsorption of PQ^{2+} on amino acid-functionalized SBA-15 strongly depends on the time and pH of the solution, but not on the temperature. The adsorption mechanism was related to π – π stacking interactions between the adsorbent and the adsorbate.

The aim of this article is to present a study of PQ^{2+} adsorption on a hexagonal mesoporous silica. The adsorbent was hydrothermally synthesized in alkaline media by using a mixed-surfactant template composed by the cationic surfactant cetyltrimethylammonium tosylate and the amphiphilic copolymer Pluronic F68. On the one hand, and as far as we know, there is no information in the literature on the silica synthesis by using this mixture since we have introduced it in 2012 [20]. On the other hand, the adsorption data obtained at a variety of pH, ionic strength, temperature, and reuse cycles are used to gain insights into the mechanisms that govern the adsorption process and into the factors that promote or prevent it. The obtained results will also serve as a basis for further synthesis of new materials for pollution control.

2. Materials and methods

2.1. Chemicals

Paraquat dichloride ($MW = 257.16 \text{ g mol}^{-1}$), cetyltrimethylammonium *p*-toluene sulfonate or tosylate (CTAT, $MW = 455.7 \text{ g mol}^{-1}$), Pluronic F68 ($PEO_{76}PPO_{29}PEO_{76}$, $MW = 8400 \text{ g mol}^{-1}$, and PEO and PPO being the poly(oxyethylene) and the poly(oxypropylene) chain units, respectively) and tetraethyl orthosilicate (TEOS, 99%) were purchased from Aldrich. Potassium hydroxide, potassium chloride, potassium nitrate, nitric acid, hydrochloric acid, sodium acetate, acetic acid, sodium carbonate, sodium hydroxide, sodium hydrogen carbonate, disodium phosphate

anhydrous, and monosodium phosphate anhydrous were obtained from Anedra.

All chemicals were of analytical grade and used as received. Double distilled water was used for the preparation of solutions.

2.2. Synthesis and characterization of mesoporous silica

Mesoporous silica (SiO_2) was prepared using a procedure similar to that described in an earlier work [20]. Briefly, 11.6 mL of TEOS were mixed with 2 mL of water and stirred in an autoclave flask for 10 min at 500 rpm. At the same time, 38 mL of Pluronic F68-CTAT mixed solution were prepared with a 1:3 M ratio by adding the desired amount of surfactants to water. This mixture was stirred in a conical flask at 35 °C to form a transparent template solution and then it was left at room temperature. To obtain the mesoporous material, 20 mL of a 1.43 M NaOH solution were added drop by drop to the TEOS solution under stirring and 2 min later the surfactant solution was incorporated. The final pH of the mixture was around 11.8. The resulting gel, whose composition was 1 TEOS:0.53 NaOH:0.011 CTAT:0.0037 F68, was stirred for 5 min and then left for 48 h in an autoclave at 100 °C. After this, the gel was filtered and washed with distilled water and dried at room temperature. Finally, it was calcined in an air flux by increasing the temperature from room temperature to 540 °C with a heating rate of 2 °C min^{-1} , and holding for 7 h at 540 °C.

The synthesized material was characterized by the techniques usually employed in porous materials, such as scanning and transmission electron microscopy (SEM and TEM); XRD; FT-IR spectroscopy; electrophoretic mobility measurements; and the N_2 -BET method for surface area, pore volume and pore diameter determination. SEM was performed using an EVO 40-XVP microscope. The sample was prepared on graphite stubs and coated with a ca. 300 Å gold layer in a PELCO 91000 sputter coater. TEM was performed using a JEOL 100 CX II transmission electron microscope, operated at 100 kV with magnification of 450,000 \times . Observations were made in a bright field. The powdered SiO_2 was placed on 2000 mesh copper supports. XRD patterns were obtained via a Philips PW 1710 diffractometer with $CuK\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) and graphite monochromator operated at 45 kV, 30 mA and 25 °C; the angle step and counting time were $0.02^\circ(2\theta)$ and 1 s, respectively. The electrophoretic mobility of SiO_2 was measured with a Zetasizer Nano Series instrument (Malvern Instruments Ltd.) at room temperature, and the Zeta potential was calculated using the Smoluchowski equation [21]. Stock suspensions containing 0.1 g L^{-1} of solid in 10^{-2} M KNO_3 were used for the measurements. The pH of the suspensions was adjusted to the desired value by adding small volumes of HNO_3 or KOH solutions. The N_2 adsorption isotherms at 77.6 K were measured with a Quantachrome Nova 1200e instrument. The sample was degassed at 373 K for 720 min at a pressure of 1×10^{-4} Pa. FT-IR experiments were recorded in a Nicolet FT-IR Nexus 470 Spectrophotometer. To avoid co-adsorbed water the sample was dried under vacuum until constant weight and then it was diluted with KBr powder before the FT-IR spectrum was recorded.

2.3. Adsorption experiments

Adsorption experiments (in darkness to avoid photodegradation) were obtained with a batch equilibration procedure using 15 mL polypropylene centrifuge tubes covered with polypropylene caps immersed in a thermostatic shaker bath. Before starting the experiment, a stock PQ^{2+} solution (2×10^{-3} M) was prepared by adding the corresponding solid to buffer solutions. The pHs investigated were 4.4 (0.1 M acetate/acetic acid), 7.0 (0.1 M $HPO_4^{2-}/H_2PO_4^-$), and 9.5 (0.1 M CO_3^{2-}/HCO_3^-). 50 mg of mesoporous material were introduced into the tubes and mixed with varying

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