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# Preparation of clay/alumina and clay/alumina/Ag nanoparticle composites for chemical and bacterial treatment of waste water

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## HIGHLIGHTS

- The clay/Alum and clay/Alum/Ag composites have been synthesized for the first time.
- Both composites have high adsorption capacity of anionic and cationic dyes.
- The synthesized composites can remove dye pollutants from aqueous solution quickly.
- The clay/Alum/Ag nanocomposite exhibits very good antibacterial activity.

## ARTICLE INFO

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## ABSTRACT

The pollution of water resources with chemical and biological pollutants is the serious problem of the present century. So synthesis of new adsorbents which can remove both types of pollutants is necessary. In the present study a novel clay/mesoporous alumina composite has been synthesized in order to remove both cationic and anionic dye pollutants and their binary mixtures from aqueous solutions. Also the clay/mesoporous alumina/Ag nanoparticle composite has been synthesized for the first time by the new combined method and used for both chemical and biological treatment of aqueous solution. The characterization of the prepared nanocomposite has been performed by TEM and EDS techniques. The results show that the synthesized materials are good adsorbents for effective removal of both cationic and anionic dye pollutants. Also the nanocomposite shows very good antibacterial activity against both Gram negative and Gram positive bacteria.



## 1. Introduction

Clay is a general term including many combination of one or more clay minerals with trace of metal oxides and organic matter [1]. The high surface area, chemical and mechanical stabilities and versatility of structural properties and functional surface groups, candidate it as proper adsorbent [2–4], catalyst [5,6], enhancer for paper properties [7], etc. Different kinds of clay nanocomposites have been used to remove chemical pollutants from aqueous solutions. For example Urbano et al. [8] synthesized water-insoluble polymer–clay nanocomposite ion exchange resin based on N-methyl-D-glucamine ligand groups and used it to remove arsenic from aqueous solution [8]. The exfoliated polypyrrole-organically modified montmorillonite clay nanocomposite which is synthesized by Setshedi et al. [9] used as an effective adsorbent to remove Cr(VI) from aqueous solution [9].

Since adsorption is the most effective method for purification of water than the other methods, the synthesis of cheap and efficient adsorbent with appropriate adsorption properties is desirable. Although clay is an excellent adsorbent to remove cationic dyes from aqueous medium [10,11] but it cannot remove anionic dye effectively from aqueous solutions. Recently we have reported that ordered mesoporous alumina (OMA) is the adsorbent with high adsorption capacity and very high rate of adsorption which is able to remove anionic dyes selectively from aqueous solution [12]. So the combination of clay and mesoporous alumina can produce an applicable adsorbent to remove both anionic and cationic dye pollutants from aqueous solutions which are present in real waste water. In the present study the clay/mesoporous alumina composite (clay/Alum) has been synthesized and used to remove reactive blue (cationic dye) and reactive yellow (anionic dye) from aqueous medium. The adsorption processes of both dyes onto the prepared composite were studied from both kinetic and equilibrium points of view. The adsorption of both dyes onto the clay has also been studies.

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As industrial waste water such as textile waste water usually contains a mixture of dye pollutants, development of an adsorbent which is capable to remove the mixture of dye pollutants from aqueous solution is favorable. The competitive adsorption has been studied from equilibrium [13,14] and kinetic [15] points of view. In the present study the ability of synthesized clay/Alum composite to remove a mixture of cationic (reactive blue) and anionic (reactive yellow) dye pollutants from the aqueous solution has been investigated.

The presence of pathogens in the drinking water is the serious danger for the human health. Therefore the synthesis of multifunctional material which can remove both chemical and biological pollutants from water is so desirable in a practical point of view. So in the present study the clay/mesoporous alumina/Ag nanoparticle composite (clay/Alum/Ag) has been synthesized by combination of sol–gel method (for the synthesis of mesoporous alumina) [16] and photogeneration method (for the formation of silver nanoparticles) [17,18]. The prepared nanocomposite has been used for removal of dye pollutants from aqueous solution and also for biocidal action against two model bacteria. The physical and chemical properties of clay/Alum/Ag nanocomposite have been determined by TEM and EDS techniques.

## 2. Experimental

### 2.1. Materials

Pluronic F127 (MW = 12,600) was purchased from Sigma–Aldrich. Aluminium iso-propoxide (for synthesis), ethanol (99.8%), nitric acid (65%) and silver nitrate (extra pure) were purchased from Merck Co. Reactive yellow (RY) and reactive blue (RB) were gained from Alvan Sabet Co. (Iran).

### 2.2. Instruments

The adsorption processes were followed by the UV–vis spectra which were obtained by a UV–vis spectrophotometer (PG T-80). The TEM images of the clay/Alum/Ag nanocomposite have been obtained by the transmission electron microscope Philips CM120 apparatus. A 6 W, column-lick, low pressure mercury lamp (Philips) at the wavelength 253.7 nm was used to form silver nanoparticles. $N_2$ adsorption–desorption isotherms of clay and clay/Alum composite have been gained by Quantachrome Nova Station A at 77.3 K. The samples were outgassed at 290 °C for 5 h, before nitrogen adsorption. The pore size distributions were calculated based on the DFT method. A VEGA/TESCAN-XMU instrument was used to obtain Energy dispersive X-ray spectroscopy (EDX) analysis of the synthesized clay/Alum/Ag nanocomposite.

### 2.3. Preparation of clay/Alum composite

The preparation of the ordered mesoporous alumina has been reported by Grant et al. [16]. In the present study clay/Alum composite was synthesized with slight modifications to the Grant method. Briefly, a solution of F127 (0.75 g) in ethanol (40 ml) was stirred for 4 h. Then 1.0213 g aluminium iso-propoxide and 0.85 ml $HNO_3$ 0.65% were added to above solution and stirred for another 5 h. After that 3 g clay was added to the obtained mixture and stirred for 5 min. The solvent has been slowly evaporated by oven at 60 °C during 48 h. Finally the obtained specimen was calcinated in a quartz tube furnace by heating at 1 °C/min to 400 °C and keeping at 400 °C for 4 h.

### 2.4. Preparation of clay/Alum/Ag nanocomposite

A green photogeneration method for the preparation of the Ag nanoparticles (Ag NPs) based on the UV irradiation of the ethanolic solution of F127 and $AgNO_3$ has been reported in our recent works [17,18]. Since F127 acts as a pore directing agent in the synthesis of mesoporous alumina and also the formation of Ag NPs depends on the presence of F127 and both synthesis occurring in ethanolic medium, the clay/Alum/Ag nanocomposite was synthesized for the first time by combination of the sol–gel method of the mesoporous alumina synthesis [16] and photogeneration method of the Ag NPs [17,18]. Briefly after stirring of the solution of 0.75 g F127 in 40 ml ethanol for 4 h, 0.003 g $AgNO_3$ was solved in the above solution and irradiated by UV lamp for 13 min. The UV–vis spectrum of the obtained dispersed Ag nanoparticles has been shown Fig. 1. The absorbance peak around the 400 nm (Fig. 1) proves the formation of Ag NPs [19]. Then 1.0213 g of aluminium iso-propoxide and 0.85 ml $HNO_3$ 65% were added to the solution of F127 and Ag NPs and stirred for 5 h. After that 3 g of clay was added to the obtained mixture and stirred for 5 min. The solvent evaporation was occurred at 60 °C during 48 h. The final specimen was calcinated in a quartz tube furnace by heating at 1 °C/min to 400 °C and keeping at 400 °C for 4 h.

### 2.5. Batch adsorption experiments

#### 2.5.1. Adsorption of single dye pollutants

In kinetic experiment 5 ml of a solution of 10 (mg/l) RB or RY with 5 mg of clay or clay/Alum composite was placed in a shaker (150 rpm, and 25 °C) and at the proper time intervals the residual RB and RY concentrations, $C_t$, was determined at 608 nm and 413 nm, respectively. Eq. (1) has been used to calculate the amount of adsorbed RB and RY per unit mass of the adsorbent at time $t$.

$$q_t = \frac{(C_0 - C_t)}{m} \times V \tag{1}$$

where $C_0$ and $C_t$ are the initial concentration of each dye and its concentration at any time, respectively. $V$ is the solution volume and $m$ is the mass of adsorbent.

For the equilibrium experiment a series of solution with the concentration between 10 and 120 (mg/l) was prepared and then a set of 5 ml of each solution with 5 mg of clay or clay/Alum composite were placed in a shaker (150 rpm and 25 °C) for 24 h. The amount of adsorbed dye per unit mass of the adsorbent at equilibrium, $q_e$, was calculated by following equation.

$$q_e = \frac{(C_0 - C_e)}{m} \times V \tag{2}$$

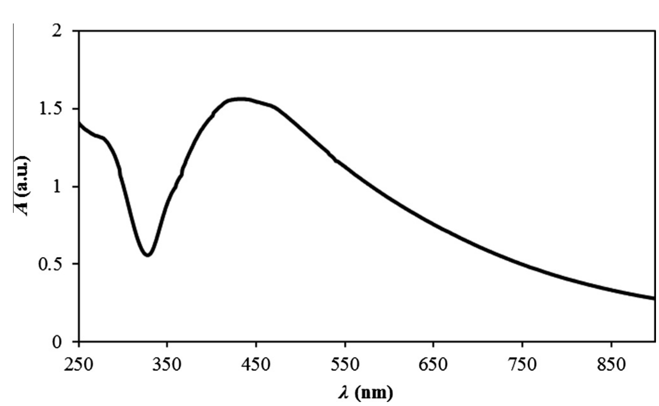


**Fig. 1.** UV–vis spectrum of the Ag NPs obtained by UV irradiation of the solution of F127 and $AgNO_3$ for 13 min.