



# A novel adsorbent of $\text{Na}_2\text{Ta}_2\text{O}_6$ porous microspheres with $\text{F}^-$ gradient concentration distribution: High cationic selectivity and well-regulated recycling



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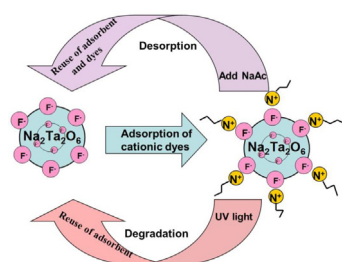
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## HIGHLIGHTS

- Pyrochlore  $\text{Na}_2\text{Ta}_2\text{O}_6$  porous microspheres with  $\text{F}^-$  gradient distribution were first prepared.
- $\text{F}^-$ - $\text{Na}_2\text{Ta}_2\text{O}_6$  microspheres as an adsorbent showed an excellent selectivity toward cationic dyes.
- The adsorption kinetics and isotherm of the adsorbents were investigated.
- The adsorbents were regenerated rapidly by adding to NaAc solution.
- The adsorbents' recycling was achieved by UV light illumination free from environmental secondary contamination.

## GRAPHICAL ABSTRACT

Pyrochlore-type  $\text{Na}_2\text{Ta}_2\text{O}_6$  porous microspheres with  $\text{F}^-$  gradient distribution were discovered to be a novel cationic selective adsorbent that show excellent adsorption and superior regeneration capability.



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## ABSTRACT

Pyrochlore  $\text{Na}_2\text{Ta}_2\text{O}_6$  porous microspheres with  $\text{F}^-$  gradient concentration distribution were first prepared, which showed an excellent selectivity toward cationic dyes as an adsorbent. These dyes were regenerated rapidly by adding to NaAc solution. After then, the adsorbent still showed a high adsorption capacity. Optionally, the effective recycling of the adsorbents was achieved by UV light illumination, free of secondary environmental contamination. The rate of adsorption reaction followed the pseudo second-order kinetics, and the sorption isotherm well fitted to the Freundlich isotherm model. Eventually, the adsorption reaction for the adsorbents was found to be a spontaneous and endothermic process.

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## 1. Introduction

Water contamination has become one of the main threats to human beings due to the discharge of hazard chemicals from many chemical-intensive industries such as textiles, plastics, tanneries,

pharmaceuticals, packed food, pulp and paper, painting, and electroplating industries [1,2]. For some toxic pollutants, even at trace level, exposure to them is believed to be a risk for the lives of human [3]. Thus, how to effectively and deeply remove undesirable toxic pollutants from water systems is very important, but still challenging. Numerous methods have been adopted to remove pollutants from aqueous environment, which include chemical precipitation, ion exchange, membrane filtration, adsorption, photocatalysis, and electrochemical technologies [4]. Among these

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methods, adsorption is highly economical and efficient. Comparing to the traditional adsorbents such as silica gels, polymeric materials, organobentonites, and activated carbons, nanosized metal oxides with large surface areas and high activities usually show the merits of very fast kinetics and favorable sorption to low-concentration pollutants in terms of the superior adsorption capacity [5–11]. Moreover, the selectivity of nanosized metal oxides could be significantly improved simply through surface modification with different functional groups [12–14]. Though there are extensive reports on effective adsorption and high selectivity for removal of toxic pollutants, very few have put forward on preferable reuse of the adsorbents as well as the dyes [15]. It is well known that the efficacy and utility of adsorbents greatly depend on the affinity of target contaminants toward adsorbents. Thus, the increase of adsorption capacity may also lead to difficulties in eluting dyes. Conventionally, large amounts of alkaline or acidic eluants are applied to wash and recover adsorbents for recycle use. In this regard, two distinct shortcomings are recognized: The first one is that the active site of adsorbent is easily corrupted and consequently the ability of adsorbent recycle is decreased greatly. In particular, some groups wrapped on the surfaces of adsorbents, for the purpose to promoting adsorptive capacity and improving selectivity, might be eluted together with dyes, causing a decrease of the active site. The second one is that the generated waste eluent usually requires further treatment to avoid a secondary pollution.

Tantalate is a kind of semiconductor photocatalyst with a wide-band gap. In this work, we report on a new methodology to prepare pyrochlore-type  $\text{Na}_2\text{Ta}_2\text{O}_6$  porous microspheres with a  $\text{F}^-$  gradient concentration distribution, which were found to be a novel cationic selective adsorbent with an excellent adsorption capacity. The rapid removal of the toxic pollutants can be reached through strong electrostatic interaction of superficial  $\text{F}^-$  with the cationic dyes. The regeneration relies on the suitable desorption processes which were realized by ions exchange. Especially the effective pollution-free recycling of adsorbents can be achieved by photocatalytic oxidation followed by a complete degradation of dyes.

## 2. Materials and methods

### 2.1. Sample preparation

All chemicals were of analytical grade and used without further purification. A soluble precursor of  $\text{H}_2\text{TaF}_7$  was formed by dissolving metal tantalum in hydrofluoric acid at the sealed autoclave, maintaining at  $80^\circ\text{C}$  for 12 h. Then, a white precipitate was obtained after adjusting the pH value of the precursor solution to 13 using a given concentration of NaOH solution. When the reaction ended, the precipitate was transferred to a Teflon-lined autoclave, which was sealed and maintained at  $150^\circ\text{C}$  for 3 h. After cooling to room temperature naturally, the product was washed several times and then dried at  $80^\circ\text{C}$  for 12 h. A white crystalline powder was obtained, which was named as  $\text{F}^-$ - $\text{Na}_2\text{Ta}_2\text{O}_6$ .

### 2.2. Sample characterization

Phase purities of the samples were characterized by X-ray power diffraction (XRD) on Rigaku DMAX2500 X-ray diffractometer using a copper target. Particle sizes and morphologies of the samples were determined using scanning electron micrographs (SEM) (HITACHI S-4800 with an acceleration voltage of 20.0 kV) and transmission electron microscopy (TEM) (FEI Tecnai F20 S-Twin with an acceleration voltage of 200 kV). Energy-dispersive spectroscopy (EDS) was observed using Bruker-QUANTAX 200 detector. Zeta potentials of the samples were measured at  $25^\circ\text{C}$  using a Zetasizer Nano-Zs (Malvern Instruments, UK). The

specific surface areas of the samples were determined from nitrogen absorption data at liquid nitrogen temperature using Barrett–Emmett–Teller (BET) technique on a Micromeritics ASAP 2000 Surface Area and Porosity Analyzer. XPS measurements were performed on a Thermo ESCALAB 250 with a monochromatic Al K $\alpha$  (1486.6 eV) and charge neutralizer. The deconvolution software program was provided by Kratos. All binding energies were referred to the C1s peak at 284.60 eV. Dye concentration in the aqueous solution was measured at room temperature on a UV–vis spectrophotometer.

### 2.3. Adsorption properties test

Four kinds of adsorbates, methylene blue (MB), methyl orange (MO), safranin T, and azophloxine, were chosen to study the selective adsorption of microspheres  $\text{F}^-$ - $\text{Na}_2\text{Ta}_2\text{O}_6$ . Typically, 25 mg of  $\text{F}^-$ - $\text{Na}_2\text{Ta}_2\text{O}_6$  microspheres was mixed with a 50 mL dye solution at a concentration of  $20\ \mu\text{mol/L}$ . The suspension was magnetically stirred for certain time, and the adsorption capacities of the adsorbents were obtained by determining the absorbance of dyes in supernatant volumetrically at regular time intervals with a UV–vis spectrometer.

The amount of MB adsorbed by the adsorbent ( $q_t$ ) at each time interval  $t$ , was calculated using the mass balance equation:

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

where  $q_t$  is the amount of MB adsorbed per unit weight of the adsorbent at any time  $t$  (mg/g);  $C_0$  and  $C_t$  are the initial and liquid-phase concentrations of MB solution at any time  $t$  (mg/L), respectively;  $V$  is the volume of MB solution (ca. 0.05 L); and  $m$  is the amount of the adsorbent used.

### 2.4. Regeneration experiment

For dye desorption, 25 mg  $\text{F}^-$ - $\text{Na}_2\text{Ta}_2\text{O}_6$  fully adsorbed by MB were added into 50 mL of 0.1 M HCl or 0.2 M NaAc aqueous solution, and the suspension was then stirred for 10 min. When the desorption was completed, the adsorbent was then collected by centrifugation and reused for adsorption again. The supernatant solutions were analyzed by UV–vis spectra. The cycles of desorption–adsorption processes were repeatedly conducted 5 times. The percentage of MB adsorption in regeneration experiment is calculated as:

$$\text{Adsorption ratio (\%)} = \left( \frac{\text{Mass of dye adsorbed}}{\text{Mass of dye initial}} \right) \times 100 \quad (2)$$

## 3. Results and discussion

### 3.1. Structure and morphology of the porous microspheres

XRD diffraction peaks for the as-synthesized samples were well indexed to a pure cubic phase  $\text{Na}_2\text{Ta}_2\text{O}_6$  (Joint Committee for Powder Diffractions Standards, JCPDS card No. 70-1155) (Fig. 1a). Based on the half height width of (1 1 1) peak, the crystallite size was calculated to be around 6.7 nm for the primary particles, which differs from the porous microspheres with an average diameter of about 50 nm, as observed by SEM images in Fig. 2a. Further TEM image (inset of Fig. 2a) indicates that these porous microspheres were constructed by aggregation of tiny particles with an average diameter of about 7 nm, closer to that calculated by XRD. The existence of fluorine was detected in EDS spectrum of the as-prepared  $\text{F}^-$ - $\text{Na}_2\text{Ta}_2\text{O}_6$  (Fig. S1†). Furthermore, as shown in Fig. 2c, the XPS signal for F1s appeared at 684.5 eV, nearly equal to the reference data of 684–687 eV for fluoride [16]. Therefore, fluorine ions were

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