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# Synthesis of hybrid hydrogel of poly(AM co DADMAC)/silica sol and removal of methyl orange from aqueous solutions

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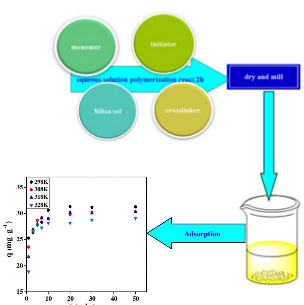
## HIGHLIGHTS

- ▶ Poly(AM co DADMAC)/silica sol is prepared by a simple one-step method.
- ▶ The removal % of dye reaches to 83% from 50% when silica sol is added.
- ▶ Strong acidic and basic conditions can greatly decrease the adsorption capacity.

## GRAPHICAL ABSTRACT

The hydrogel of poly(AM co DADMAC)/silica sol was prepared through a one-step solution polymerization method, which was used as an absorbent in the removal of methyl orange. The kinetics and isotherms of adsorption were also studied.

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## ABSTRACT

A hybrid hydrogel (poly(AM co DADMAC)/silica sol) from acrylamide (AM), diallyl dimethyl ammonium chloride (DADMAC) and silica sol was prepared by aqueous solution polymerization, using *N,N′*-methylenebisacrylamide (MBA) as crosslinker and ammonium persulfate (APS) as initiator. Its structure and characterization were determined by means of FTIR, SEM, TEM and TG; meanwhile, the effects of silica sol content, pH values and temperatures were studied on the adsorption of methyl orange onto (poly(AM co DADMAC)/silica sol (PAMDS). The adsorption rate data and adsorption equilibrium data were analyzed based on the pseudo-second-order model and four isotherm models respectively. Results obtained from this study indicated that the kinetic behavior accorded with the pseudo-second-order kinetic model. The isotherm behavior can be explained by the Langmuir, Freundluich and Generalized isotherm models. The activation energy was also evaluated for the removal of methyl orange onto PAMDS. This hybrid hydrogel may be used as good adsorbent for the adsorption of anionic dyes from effluents.



## 1. Introduction

Textile industry is one of the most important industrial sectors which needs the most water and discharges the most wastewater in the productive process in China. Even small traces of the non-biodegradable and highly toxic dyes can bring harmful to mankind [1]. Such wastewater with deep color, high content of organic pollutants, complex composition, high biological toxicity, is difficult to dispose with conventional methods and brings serious pollution. Over last one decade it has been established that the adsorption is now an effective and economical method for the removal of dyes from wastewater among many methods for removing dyes including coagulation and occultation [2], membrane separation [3], oxidation or coronation [4], electro-coagulation [5] and adsorption

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[6]. In the past few years, efforts have been made to remove toxic substances from wastewaters by using low cost adsorbents like hardwood mulch [7], rice husk [8], feather [9], crushed brick [10], cedar saw dust [10], clay [11], fibrous clay minerals [12], etc.

The content of organic materials increases substantially with the development of modern industry and living standard. Due to the particle surface of most wastewater is negatively charged, the treatment of wastewater cannot be satisfied with the non-ionic or anionic polymer adsorbent. Nowadays, the new absorbents having superior properties such as high adsorption capacity and fast adsorption rate have generated great interests for dyes [13]. The cationic adsorbent can treat the dyes effectively because of the charge neutralization and adsorption bridging action between adsorbent and wastewater. Cationic polyacrylamide (PAM) can be used in acidic environment and high organic matter content occasions, such as dyeing, paper madding, food and wastewater treatment [14–16]. The preparation of cationic PAM can be divided into two routes: first, cationic modified PAM; second, acrylamide (AM) copolymer with cationic monomer. Poly(dimethyl diallyl ammonium chloride) is water-soluble polymer, and its homopolymers or copolymers are charge density, easy to control molecular weight, non-toxic and low cost. So dimethyl diallyl ammonium chloride (DADMAC) is usually used as cationic monomer to prepare cationic hydrogel by copolymerization with AM.

The development of organic–inorganic hybrid hydrogel is fast as a new type composite material. Organic–inorganic hybrid composite material is a homogeneous multi-phase material consisting of organic and inorganic phase. In the material the size of inorganic can reach nanometer level, greatly enhance the interaction of interface, which makes this material rigidity, dimensional stability, thermal stability, resilience and so on [17–20]. Silica sol ($m\mathrm{SiO_2}n\text{-}\mathrm{H_2O}$) is made of nano-$SiO_2$ particles with non-toxic. The colloidal particle is fine (10–20 nm) with large specific surface area, colorless and transparent. In this paper, a novel hydrogel of nano-silica modified poly(AM co DADMAC) (PAMD) was synthesized with silica sol by solution polymerization method. The influences of silica sol content, pH values and temperatures on the adsorption amount were researched using batch and column adsorption methods. Poly(AM co DADMAC)/silica sol (PAMDS) displayed excellent adsorption property for methyl orange.

## 2. Materials and methods

### 2.1. Materials

Diallyl dimethyl ammonium chloride (DADMAC) and Silica sol were obtained from Zhejiang YuDa Chemical Industry Co., Ltd. and Zhejiang XinHaiTian Auxiliaries Co., Ltd. respectively. Acrylamide (AM) was chemical pure from Sinopharm Chemical Reagent Co., Ltd. Ammonium persulfate (APS) and *N*,*N*′-methylene bisacrylamide (MBA) were analytical grade and chemically pure which were purchased from Shanghai Reagent Corp. China. Methyl Orange (MO) was provided by Shanghai Reagent Factory.

### 2.2. Preparation of PAMD and PAMDS hydrogel

3 g AM and 3 g DADMAC were added in a 150 mL flask with a series amount of silica sol. Then the mixture of MBA (14.00 mg), APS (0.06 g) was added. The remaining was added by distilled $H_2O$ to keep the total consistent. The polymerization reaction was carried out at 65 °C for 2 h. After polymerization, the sample was dried to constant weight at 75 °C for 24 h and the product (PAMDS) was milled to use for future experiments. For comparison, the polymer hydrogel without silica sol (PAMD) was prepared based on the same synthetic procedure as PAMDS.

### 2.3. Adsorption procedure

The calibration curve of methyl orange was prepared at first in order to calculate the concentration in each experiment. Different concentrations were prepared and absorbance values were measured at the maximum adsorptive wave number. The effect of pH was studied by adjusting methyl orange solutions (30 mg/L) to different $pH_0$ values (2.0, 3.0, 5.0, 7.0, 9.0, 10.0 and 11.0) with 0.1 mol/L NaOH or HCl solutions using a pH meter. Then the mixture was agitated at 25 °C for 30 min.

Kinetic experiments were carried out with a similar arrangement by adding 0.08 g adsorbent into dye solution (30 mg/L). The change of the absorbance of dye was conducted for predetermined time intervals. For isotherm studied, a series of dye solutions in the range of 20–200 mg/L were prepared and then the adsorbent was added to each solution. The mixture was agitated at constant temperatures of 25, 35, 45 and 55 °C for 30 min.

The adsorption capacity of PAMDS for methyl orange was calculated by the following equation:

$$q = \frac{(C_i - C_f) \times V}{m \times 1000} \quad (1)$$

where $q$ (mg/g) represents the amount of methyl orange adsorbed onto adsorbent; $C_i$ and $C_f$ (mg/L) represent the methyl orange concentration before and after adsorption, respectively; $V$ (mL) is the methyl orange solution volume used and $m$ (g) is the weight of adsorbent.

### 2.4. Characterizations

The equilibrium methyl orange concentration was measured by UV–Vis spectrophotometer (TU-180, Beijing Purkinje General Instrument Co., Ltd.) at wavelengths of 462 nm and 505 nm.

pH Values were measured using E-201-9 pH meter.

FTIR spectra were taken as KBr pellets using a Thermo Nicolet Impact 410 FTIR spectrophotometer. TEM photographs of PAMDS were measured using JEM-2100.

SEM photographs of PAMD and PAMDS before and after adsorption were taken using Hitachi S-5200 scanning electron microscope.

The TG analysis of the adsorbent was performed on a Germany Netzach STA449C with a heating rate of 10 °C/min under flowing nitrogen.

## 3. Results and discussion

### 3.1. FTIR spectra of adsorbents

The polymer hydrogels were characterized by FTIR spectrum. From the comparison of PAMD and PAMDS spectrum in Fig. 1, it can be seen that the characteristic absorption bands at 466 and 1116 $cm^{-1}$ (PAMDS in Fig. 1) are attributed to stretching vibration and bending vibration of Si—O—Si and no new peak generates, which indicates that the silica sol and organic monomers are connected together by nonbonding [18]. In the drying process of PAMDS hydrogel, the water of silica sol evaporates, and the colloidal particles firmly attach to the PAMDS hydrogel surface through Si—O bond.

### 3.2. Thermogravimetric analysis

TG curves of PAMD and PAMDS were showed in Fig. 2, which displayed two steps of weight losses. The two samples showed a similar loss at 25–200 °C, corresponding to a loss of water existed in theses samples. The second weight loss occurred at 451 °C (85.23%) for PAMD and 461 °C (58.19%) for PAMDS. This may be attributed that