



## Research paper

# Adsorption dynamics, diffusion and isotherm models of poly(NIPAm/LMSH) nanocomposite hydrogels for the removal of anionic dye Amaranth from an aqueous solution



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## ABSTRACT

To investigate diffusion model and adsorption mechanism of hydrogel for the removal of anionic dye Amaranth from aqueous solution, poly(N-isopropylacrylamide)(abbreviated as PNIPAm)/clay lithium magnesium silicate hydrate (abbreviated as LMSH) nanocomposite hydrogels with various clay percentage of LMSH/NIPAm (named as NPX hydrogel) were prepared. Adsorption kinetics of NPX samples were investigated under different experimental conditions (including solution pH, initial concentration of Amaranth dye solution and clay percentage of LMSH/NIPAm). Based on the adsorption experiments, adsorption dynamics, diffusion mechanisms and adsorption isotherms of NPX samples in Amaranth solution were analyzed through pseudo first-order model, pseudo second-order model, film diffusion model, intra-particle diffusion model and different isotherm models. The adsorption kinetics showed that in acidic (pH = 2) Amaranth solution NPX nanocomposite hydrogel was more effective for the removal of Amaranth dye. With increasing clay percentage of LMSH/NIPAm from 5 to 40 wt.%, adsorption capacity of Amaranth dye onto NPX samples decreased due to shrunken pore effect of NPX nanocomposite hydrogels and enhanced electrostatic repulsive interactions between NPX samples and Amaranth molecules. Adsorption dynamics indicated pseudo second-order model was more suitable for the investigated adsorption process. The adsorption rate-controlling step mainly came from film diffusion, but not the only factor. Adsorption isotherm indicated the adsorption process from monolayer adsorption to multilayer adsorption. According to Dubinin-Radushkevich isotherm model (abbreviated as D-R model), the calculated mean free energy implied chemisorption nature between NPX nanocomposite hydrogel and Amaranth. Based on adsorption mechanism of NPX nanocomposite hydrogel on Amaranth established, the conclusion confirms the prospect of NPX nanocomposite hydrogel as effective adsorbent to dispose real dyeing wastewater.

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## 1. Introduction

Over the past decade, industrial water pollution, especially dyeing wastewater has caused serious environmental damage for atmosphere and soil due to its harmful residues and color pollution such as dyes (Ayranci and Duman, 2009; Tunc et al., 2013), heavy metals (Duman and Ayranci, 2010a), surfactants (Duman and Ayranci, 2010b), organic matters (Duman and Ayranci, 2006; Ayranci and Duman, 2010), and so on, even harming to human health (Tang et al., 2014). Based on the most effective processing method of adsorption, it has become an urgent demand for efficient adsorbents.

Hydrogels, due to its extraordinary optical, mechanical and rapid swelling/de-swelling properties (Haraguchi and Takehisa, 2002), have

been applied in different fields, such as tissue engineering, artificial muscles, hygiene, wound dressing, drug delivery, and so on (Haraguchi and Takada, 2005; Zhang and Gu, 2007; Kasgöz and Durmus, 2008; Rytwo, 2012; Zohdi et al., 2012; Li et al., 2013; Zhang et al., 2014a, 2014b). At present, as a polymer porous material, adsorption characteristics of hydrogels have caused wide public concern (Zhang et al., 2010; Zohuriaan-Mehr et al., 2010; Zhu et al., 2011; Kurecic and Smole, 2012; Liu et al., 2012; Neelesh and Giridhar, 2012; Bergaya et al., 2013; Shi et al., 2015). For example, Patel and Patel (2013a) reported poly(N,N-diallylpyrrolidinium bromide-co-N,N-dimethylacrylamide-co-acrylic acid sodium salt) superabsorbent hydrogel could remove 97% of Reactive Red 5B (RR5B) and Reactive Orange M2R (ROM2R) dyes from water under optimum experimental conditions. Kabiri et al. (2011) systematically investigated super adsorption characteristic of superabsorbent hydrogel composites (SHC) and superabsorbent hydrogel nanocomposites (SHNC) through

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addition of clays and organo-clay (OC). Unuabonah and Taubert (2014) reported the future of clay–polymer nanocomposites (CPN) as adsorbents for water treatment. The related results and relevant literatures approved that hydrogel, as a kind of efficient adsorbent on cationic dyes, had great potential for environmental protection because of super adsorption, biocompatibility and environment-friendly characteristic (Gupta and Suhas, 2009; Zhou, 2011; Irani et al., 2013; Mahdavinia and Asgari, 2013; Nakamura and Ogawa, 2013; Wang et al., 2013; Diao et al., 2014; Mahdavinia et al., 2014; Panic and Velickovic, 2014; Wu et al., 2014; Peng et al., 2015).

However, in dyeing wastewater, besides cationic dyes, anionic dyes are also largely left over, similarly affecting the chroma and purity of water resources as that of cationic dyes. Such as, Amaranth, an anionic azo dye used widely, can cause water discolor, even damages human body in high concentration because of its carcinogenicity. Literature research found a small number of relevant reports (Zhu et al., 2010; Salleh et al., 2011; Dawood and Kanti Sen, 2012; Silva et al., 2012; Meroufel et al., 2013; Patel and Patel, 2013b), mostly revealing the relatively lower adsorption capacity of hydrogels on different anionic dyes than that on cationic dyes. For improving the adsorption properties on anionic dyes, it is necessary to investigate the adsorption dynamics and adsorption mechanism of hydrogel on anionic dyes.

In our previous work, a novel poly(N-isopropylacrylamide)/clay lithium magnesium silicate hydrate hydrogels (abbreviated as NP nanocomposite hydrogel) was developed (Zhang et al., 2014a, 2014b). The nanocomposite structure of NPX hydrogel was observed (Figs. S1, S2), and adsorption characteristic of NP nanocomposite hydrogel on cationic dye Crystal Violet (CV) was reported, indicating the removal amount over 99%, higher than that of the widely used adsorbent activated carbon on CV (the removal amount up to 90%) (Mezohgyi et al., 2012; Li et al., 2013).

In this work, with anionic dye Amaranth as adsorbate, NPX nanocomposite hydrogels with various clay percentage of LMSH/NIPAm as adsorbent were used to carry out adsorption experiments. Adsorption kinetics of NPX nanocomposite hydrogels under different experimental conditions, such as adsorption time, initial concentration of dye Amaranth solution, clay percentage of LMSH/NIPAM and dye solution with different pH, were investigated by UV–visible (UV/vis) spectrophotometric method. Furthermore, adsorption dynamics and diffusion mechanisms of NPX nanocomposite hydrogels for the removal of Amaranth dye were analyzed through pseudo first-order, pseudo second-order, intra-particle diffusion and film diffusion models, respectively. Adsorption isotherms of the above adsorption process were evaluated through Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D–R) models. Finally, the adsorption mechanism of Amaranth onto NPX nanocomposite hydrogel was revealed.

## 2. Materials and methods

### 2.1. Preparation of NPX hydrogel containing clays LMSH

According to the previous work (Zhang et al., 2014a, 2014b), NPX nanocomposite hydrogel, based on monomer N-isopropylacrylamide (NIPAm, Tokyo Chemical Industry Co., Japan) and physical cross-linker clay lithium magnesium silicate hydrate (LMSH, Luancheng Zixin industrial and trading Co. Ltd, Shijiazhuang City, Hebei Province, P.R. China), was prepared in aqueous solution by in-situ free radical polymerization.

In the preparation process of NPX nanocomposite hydrogel, the dosage of NIPAm monomer was fixed to 1.0 g. The dosage of clay LMSH was controlled from 0.5 to 4.0 g. X indicated the mutative clay percentage of LMSH/NIPAm varied from 5 to 40 wt.%.

In the freeze-drying process, the swollen NPX samples were firstly frozen in a refrigerator for 24 h, and then the frozen samples were freeze-dried on a vacuum freezing dryer (FD-1A-50, Beijing BILON

Experimental Equipment Co. Ltd., P.R. China) for 10 h at  $-60\text{ }^{\circ}\text{C}$  until the formation of dried solid.

### 2.2. Environmental scanning electron microscopy (ESEM) observation

Before observation, the freeze-dried NPX samples were treated by slicing and spraying gold film. The interior pore structures of NPX nanocomposite hydrogels before and after the adsorption of anionic dye Amaranth were observed with Quanta 200 environmental scanning electron microscope (ESEM, Czech FEI company).

### 2.3. Adsorption kinetics of NPX nanocomposite hydrogels on anionic dye Amaranth

Adsorption experiments in different conditions were carried out by determining the absorbance of adsorption solution at  $t$  time. According to Amaranth calibration equation (Eq. (S1)) and absorbance obtained, the concentration of adsorption solution at  $t$  time ( $C_t$ ) was calculated. The corresponding adsorption amounts of NPX nanocomposite hydrogels ( $Q_t$ ) were obtained by Eq. (1).

$$Q_t = \frac{(C_0 - C_t)V}{W} \quad (1)$$

where,  $V$  (mL) is the volume of adsorption solution,  $W$  (g) is the mass of dried NPX hydrogel,  $C_0$  and  $C_t$  ( $\text{mg} \cdot \text{mL}^{-1}$ ) are the concentration of Amaranth solution at initial and  $t$  time, respectively.

In adsorption experiments, some fixed experimental conditions except the changing factors were preset. Such as, the volume of each adsorption solution was set to 10 mL, the experimental temperature was kept at  $25\text{ }^{\circ}\text{C}$ , and the solution concentration of Amaranth was selected as 40 mg/L. In addition, before adsorption experiments the masses of dried NPX samples were weighed, as shown in Table 1, and the used NPX samples were swollen into deionized water for 24 h until swollen equilibrium.

#### 2.3.1. Adsorption kinetics of NP10 nanocomposite hydrogel in Amaranth solution with different pH

NP10 nanocomposite hydrogel was employed as adsorbent. Before experiments the pH values of Amaranth solutions were firstly regulated from acidity to basicity through hydrochloric acid or sodium hydroxide. Adsorption kinetics of NP10 nanocomposite hydrogel in Amaranth solution with pH = 2, 4, 6, 8 and 10 were investigated by UV/vis spectrophotometric method, respectively.

#### 2.3.2. Adsorption kinetics of NP10 nanocomposite hydrogel in Amaranth solution with different initial concentration

The swollen NP10 nanocomposite hydrogel was put into neutral Amaranth solution (pH = 7) for adsorption. At a given time, the absorbance ( $A$ ) of residual solution was recorded by UV/vis spectrophotometer. The initial concentration of Amaranth solution was controlled from 10 to 50 mg/L.

**Table 1**  
The mass of dried NPX nanocomposite hydrogel samples used as adsorbent in adsorption experiments

| NPX sample | Dried weight (g) |
|------------|------------------|
| NP05       | 0.0262           |
| NP10       | 0.0371           |
| NP15       | 0.0421           |
| NP20       | 0.0438           |
| NP30       | 0.0453           |
| NP40       | 0.0465           |

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