



# Removal of crystal violet from aqueous solution by sorption into semi-interpenetrated networks hydrogels constituted of poly(acrylic acid-acrylamide-methacrylate) and amylose

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## ARTICLE INFO

### Article history:

Received 14 July 2009

Received in revised form 30 October 2009

Accepted 10 November 2009

Available online 6 December 2009

### Keywords:

Crystal violet

Hydrogel

Poly(acrylic acid-acrylamide-methacrylate)

Amylose

## ABSTRACT

The dynamic remove of Crystal Violet (CV) by Semi-IPN hydrogels constituted of poly(acrylic acid-acrylamide-methacrylate) and amylose was studied. Adsorption capacity, kinetic and isotherm studies of CV onto hydrogels have been evaluated. It was found that the sorption process agreed very well with the Langmuir model and the adsorption of CV depended on the length of the side chain, amylose content and pH of the solution. For three types of hydrogels, *n*1-1, *n*2-1 and *n*4-1, the equilibrated amounts of CV adsorbed on the hydrogels decreased in the following order: *n*4-1 (28.6 mg/g) > *n*2-1 (25.0 mg/g) > *n*1-1 (20.0 mg/g). Increasing the amylose content led to decrease the equilibrated amounts of CV adsorbed on the hydrogels. Moreover, adsorption kinetic studies showed that the adsorption followed a pseudo-second-order kinetic model, indicating that the chemical adsorption was the rate-limiting step.

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## 1. Introduction

Dye contamination has gained much attention due to increasing damage to natural ecosystems when they are discarded into wastewater (Bayramoglu and Arica, 2007; Beydilli et al., 1998; Bechtold et al., 2001). These dye molecules or their metabolites (i.e., aromatic amines) may be highly toxic, potentially carcinogenic, mutagenic and allergenic on exposed organisms. They contaminate not only the environment but also traverse through the entire food chain, leading to biomagnification (Karcher et al., 2002). Cationic dyes can easily interact with negatively charged cells membrane surfaces, and can enter into cells and concentrate in the cytoplasm.

Crystal Violet (CV), which is a typical cationic dye, has been widely applied in coloring paper, temporary hair colorant, dyeing cottons, and wools. Although not strongly hazardous, it can cause some harmful effects, such as heartbeat increase, vomiting, shock, cyanosis, jaundice, quadriplegia, and tissue necrosis in humans (Kunz et al., 2002). It is very essential to remove crystal violet from industrial effluents before it is discarded into wastewater. Conventional methods for the removal of crystal violet from waste water include physical-chemical and biological treatment technologies. Among them, adsorption has been found to be superior to other techniques for dye wastewater treatment in terms of cost, simplicity of design, ease of operation and insensitivity to toxic substances. Many adsorbents have been investigated, which include

activated carbons, alginate, modified chitosan, functionalized polymeric resins and polymeric hydrogels (Walker et al., 2003; Dögan and Alkan, 2003; Xu et al., 2003; Kannan and Sundaram, 2001). Out of this, polymeric hydrogels have been the focus of research for environment scientists due to their characteristic properties such as adsorption-regeneration, economic feasibility and environmental friendly behavior. These polymeric hydrogels often have porous structure networks and allow solute diffusion through the hydrogel structure (Li and Liu, 2008). Moreover, as these polymeric hydrogels possess ionic functional groups, they can absorb and trap ionic dyes like CV.

Recently we synthesized hydrogels consisted of poly(acrylic acid-acrylamide-methacrylate) and amylose and reported a detailed investigation of their water uptake behavior (Li et al., 2007). In this connection, this paper describes the sorption of CV by the equilibration method onto these hydrogels.

## 2. Methods

### 2.1. Materials

Acrylic acid (AA), methyl methacrylate (MMA), ethyl methacrylate (EMA) and butyl methacrylate (BMA) (Tianjin Chemical Group, China) were distilled before use. Amylose, Acrylamide (AM), 2,2'-Azobis(isobutyronitrile) (AIBN), Dimethyl sulfoxide (DMSO) (Shanghai Chemical Group, China) and CV (Sigma-Aldrich, USA) were of analytical reagent grade and used without any further purification. 4,4'-Bis(methacryloylamino)azobenzene (BMAAB)

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was prepared as described previously (Liu et al., 2004), yield ratio: 30%, m.p. 268–269 °C,  $^1\text{H}$  NMR (300 MHz,  $\text{DCl}_3$ ):  $\delta$  2.10 (s, 6H,  $-\text{CH}_3$ ),  $\delta$  5.52, 5.83 (d, 4H,  $-\text{CH}_3\text{C}=\text{CH}_2$ ),  $\delta$  7.64 (s, 2H,  $-\text{NH}-$ ),  $\delta$  7.72–7.75, 7.81–7.84 (m, 8H, Ar-H).

## 2.2. Preparation of semi-IPN hydrogels

The hydrogels were prepared through aqueous free radical polymerization of AA, AM, *n*-alkyl MA (MMA, EMA, BMA), and BMAAB in the presence of amylose, according to the method described earlier (Li et al., 2007). The feed composition for the preparation of hydrogels is listed in Table 1. Briefly, the designed amount of AA, AM, *n*-alkyl MA, and BMAAB were dissolved in DMSO. Then the designed amounts of an aqueous solution containing 1.1% amylose and AIBN were added to the mixture solutions. This solution was bubbled with nitrogen to discharge oxygen for about 30 min. The copolymerization was carried out at 80 °C for 48 h. The solid copolymer slab was cut into circular disks using punches. The samples were immersed in absolute ethanol for 3 days, then in 60% ethanol/deionized water for 6 days, and gradually transferred into deionized water to remove the unreacted monomers and solvent. Finally, the samples were dried in vacuum at 50 °C to a constant weight and stored for further use. The samples are designated as *nx-y*, where *x* is the carbon number of the *n*-alkyl group and *y* denotes the amount of amylose (mL). In the hydrogel synthesis experiment, we found the copolymerization reacted completely when the free radical copolymerization was carried out at 80 °C for 48 h. Thus the feed composition of semi-IPN hydrogels could represent the original composition of semi-IPN gel after copolymerization approximately.

## 2.3. Adsorption studies

For the adsorption kinetics, the adsorptions of CV onto hydrogels consisted of poly(acrylic acid-acrylamide-methacrylate) and amylose. The hydrogel was immersed in 50 mL of 1–50 mg/L CV solution. The test temperature was 25 °C. During the adsorption, the CV solution was withdrawn from the adsorption system at indicated times for the analysis of CV concentrations by using a UV-visible spectrophotometer at  $\lambda_{\text{max}}$  (nm) = 598 nm. The amounts of CV adsorbed on the hydrogel at time *t*,  $q_t$  (mg/g dried hydrogel), were determined according to the following equation:

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

where, *V* is the solution volume (mL), *m* is the weight of dried hydrogel (g),  $C_0$  and  $C_t$  is the dye concentration at initial and indicated time (mg/mL), respectively.

For the adsorption isotherms and the effects of pH on CV adsorption behavior, the hydrogels investigated were placed in sealed bottles containing known initial concentrations of the dye at a certain pH, and allowed to equilibrate for 3 days at 25 °C. The equilibrated solutions were sampled and analyzed for the dye concentration as described above. The equilibrated amounts of CV adsorbed on the hydrogels were calculated from the initial

and final concentrations of the dye in the liquid phase according to the following equation:

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

where, *V* is the solution volume (mL), *m* is the weight of dried hydrogel (g),  $C_0$  and  $C_e$  is the dye concentration at initial and equilibrium time (mg/mL), respectively.

## 3. Results and discussion

### 3.1. Morphology of hydrogel

The morphology of dry hydrogel consisted of poly(acrylic acid-acrylamide-methacrylate) and amylose (i.e., *n4-1*) was observed in Fig. 1 using field emission scanning microscopy (FE-SEM). It was found that hydrophilic amylose disperses in continuous phases of poly(acrylic acid-acrylamide-methacrylate) hydrogel, indicating that the composite is homogeneous. It also revealed the formation of many open pores whose diameter is within 100  $\mu\text{m}$  in the hydrogel matrix, which may be favorable for CV absorption.

To further study the adsorption of CV, the hydrogel (i.e., *n4-1*) was placed in pH 7.4 aqueous solutions of cationic CV (10 mg/L) and allowed to equilibrate for 3 days at 25 °C. Fig. 2 shows the changes of color solutions of cationic CV and hydrogel *n4-1* during the adsorption process. After 3 days, the aqueous solution of CV containing hydrogel *n4-1* showed colorlessness (Fig. 2(b)) compared to the original bluish solutions (Fig. 2(a)). At the same time, the hydrogel *n4-1* became bluish from yellow color on the third day and the shape of hydrogel *n4-1* is bulgy due to the swelling (Fig. 2(c) and (d)). This phenomenon further confirmed that the hydrogel *n4-1* could swell and absorb CV completely from the cationic CV solution.

### 3.2. Effect of the length of the side chains of *n*-alkyl MA on dye adsorption

In general, the composition of hydrogel plays an important role in the sorption properties. Fig. 3(a) shows the effect of the length of the side chains of *n*-alkyl MA on CV adsorption kinetics for the hydrogel consisted of poly(acrylic acid-acrylamide-methacrylate) and amylose. It is clear that the length of the side chains of *n*-alkyl MA is an important factor affecting CV adsorption of the hydrogels. For three types of hydrogels, *n1-1*, *n2-1* and *n4-1*, the equilibrated amounts of CV adsorbed on the hydrogels decreased in the following order: *n4-1* (28.6 mg/g) > *n2-1* (25.0 mg/g) > *n1-1* (20.0 mg/g). In other words, the adsorption concentration of CV increases when the length of the side chains of *n*-alkyl MA increases. This result may be attributed to the hydrophobic interaction between the hydrophobic groups on the hydrogel and CV molecules. Although some researches have reported the dye adsorption can result from hydrophobic interaction between the hydrophobic groups on the hydrogel and CV molecules, there is seldom evidence to confirm it (Karadağ et al., 2002). In our adsorption experiments, *n*-alkyl MA with different length of the side chains was selected as mono-

**Table 1**  
Feed composition of semi-IPN hydrogels.

Sample	AA (mol%)	AM (mol%)	<i>n</i> -Alkyl MA (mol%)	BMAAB (mol%)	AIBN (mg)	DMSO (g)	Amylose (mL) <sup>a</sup>
<i>n1-1</i>	49.9	40	10(Methyl)	0.1	30	7	1
<i>n2-1</i>	49.9	40	10(Ethyl)	0.1	30	7	1
<i>n4-1</i>	49.9	40	10( <i>n</i> -Butyl)	0.1	30	7	1
<i>n4-2</i>	49.9	40	10( <i>n</i> -Butyl)	0.1	30	7	2
<i>n4-3</i>	49.9	40	10( <i>n</i> -Butyl)	0.1	30	7	3

<sup>a</sup> The concentration of amylose in deionized water was 1.1% (w/v).

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