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Original article

Superabsorbent amphoteric nanohydrogels: Synthesis, characterization and dyes adsorption studies

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ABSTRACT

The goal of the present research is to remove high percentage of cationic and anionic dyes such as, Neutral Red, Safranin O and Indigo Carmine from aqueous solutions by poly(NIPAAm/*N*,*N*-diallylpyrrolidinium bromide/AA) superabsorbent amphoteric nanohydrogels synthesized using the inverse microemulsion polymerization method. Effect of various parameters such as, treatment time, initial dye concentration, pH and adsorbent dose were investigated. Furthermore, kinetics and isotherms adsorption models were applied to determine the maximum adsorption and mechanism for adsorption, which shows that adsorption obeyed the *pseudo*-second order kinetics. From the results, removal of dyes within the nanohydrogel was found to be in the order: AB-74 < BR-2 ≤ BR-5.

1. Introduction

In the last few years, the removal of dyes from industrial effluents has been given much more attention, not only because of their potential toxicity, but also due to their damagining nature to environment [1–4]. In addition, the presence of these dyes even at a very low concentrations can pollute a large water body, which not only affects aesthetic nature but also reduces sunlight penetration and photosynthesis processes. They may also cause some adverse effects such as, allergic, dermatitis, skin irritation, cancer and mutations in humans [5–7]. Therefore, dye removal has been a very important but challenging research area of wastewater treatment.

Nowadays, adsorption of dyes is carried out with superabsorbent materials due to their high water absorption property [8,9]. Superabsorbent materials have specific functional groups that will increase the water as well as dye adsorption on their surface. Many attempts have been made to develop new superabsorbent hydrogels using various methods such as microemulsion, irradiation and chemical cross-linking [10,11]. Hydrogels prepared by the microemulsion polymerization method have small particles with high surface area that increase the water and dye absorbency [12,13]. Microemulsion polymerization has been widely studied due to the fact that it synthesizes particles of controlled size and shape, which can be divided into oil-in-water (direct), water-in-oil (reverse), and water-in-oil-in-water (double) polymerizations. Such nanohydrogels prepared by microemulsion polymerization have excellent properties, which have better water and dye absorption than hydrogels synthesized by simpler methods [14]. Also, the vast difference in swelling behaviors and large amount of dye adsorption was observed in the present studies than our previous research due to the fact that the synthesized hydrogels were nano particles in nature.

Based on the background information mentioned above, to acquire a new hydrogel with excellent properties in nano sized particles, inverse microemulsion polymerization was carried out to synthesize poly(NIPAAm/DAPB/AA) (NIPAAm: *N*-isopropylacrylamide; DAPB: *N*,*N*-diallylpyrrolidinium bromide; AA: Acrylic acid nanohydrogels). Adsorption ability of the nanohydrogel for the removal of dyes namely, Neutral Red (Basic Red 5 (BR-5)), Safranin O (Basic Red 2 (BR-2)) and Indigo Carmine (Acid Blue 74 (AB-74)) from aqueous solutions was investigated. After then, kinetics and isotherms adsorption models, such as *pseudo*-first order, *pseudo*-second order, Langmuir, and Freundlich were evaluated to examine the maximum adsorption and mechanism of the sorption process.

2. Experimental

Inverse microemulsion polymerization was employed to synthesize superabsorbent nanohydrogels in which DAPB monomer was used to adjust the ratio of hydrophilic and hydrophobic

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Table 1
The feed composition and relatively percentage swelling of nanohydrogel.

Sr. No.	Sample code	NIPAAm	DAPB	AA	EG DMA	AIBN	Swelling % after 4 h	Swelling % after 8 h	Swelling % after 16 h
1	V-01	40	30	30	1	3	21,650	24,680	24,800
2	V-02	40	20	40	1	3	23,570	28,560	28,610
3	V-03	40	10	50	1	3	24,980	32,580	32,880
4	V-04	30	10	60	1	3	23,890	29,350	29,650
5	V-05	45	5	50	1	3	22,670	30,650	31,000
6	V-06	50	10	40	1	3	21,200	28,540	29,010
7	V-07	60	10	30	1	3	21,050	26,340	27,200

segments of the nanohydrogel, which also produced the amphoteric nature of nanohydrogel framework for better adsorption. Firstly, in a continuous phase, 0.5 g of aerosol (2-hydroxyethyl sulfosuccinate) sodium salt) (AOT) was added to 5 mL of toluene and the mixture was stirred under dry N_2 for 30 min. The temperature of the flask was maintained at 60 °C using a temperature controller.

The disperse phase was prepared by dissolving a required amount of NIPAAm with different amount of DAPB and AA. The solution was stirred under N_2 till a homogeneous solution was obtained. The disperse phase was then added dropwise into the continuous phase to form W/O microemulsion. A cross-linking agent, ethylene glycol dimethacrylate (EGDMA) was added followed by the addition of 2,2′-azobisisobutyronitrile (AIBN) as a surface active initiator. Total conversion was obtained after 7 h of reaction.

Formed hydrogels were then transferred to a 1 L beaker containing double distilled water and left for 2–3 days by changing water at every 4 h of interval in order to remove the unreacted monomers and other reactants. The swollen gel was dried using acetone in order to confirm the porosity in hydrogel is generated during solvent drying. The process was repeated till the dry hydrogel was obtained. Finally, the hydrogel was kept in vacuum oven to constant weight. The feed composition and relative swelling percentage of the nanohydrogels (V-01 to V-07) are given in Table 1.

3. Results and discussion

3.1. Swelling studies

Swelling behaviors of poly(NIPAAm/DAPB/AA) nanohydrogels were determined by the gravimetry method at 25 °C by adopting a tea-bag [15]. Swelling percentage was calculated by the following equations:

$$Q_t = \left[\frac{(W_s - W_d)}{W_d}\right] \times 100 \quad (1)$$

$$Q_e = \left[\frac{(W_s - W_d)}{W_d}\right] \times 100 \quad (2)$$

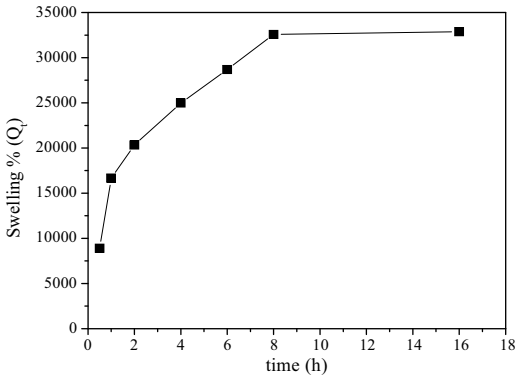


Fig. 1. The effect of the contact time on swelling percentage of the nanohydrogel.

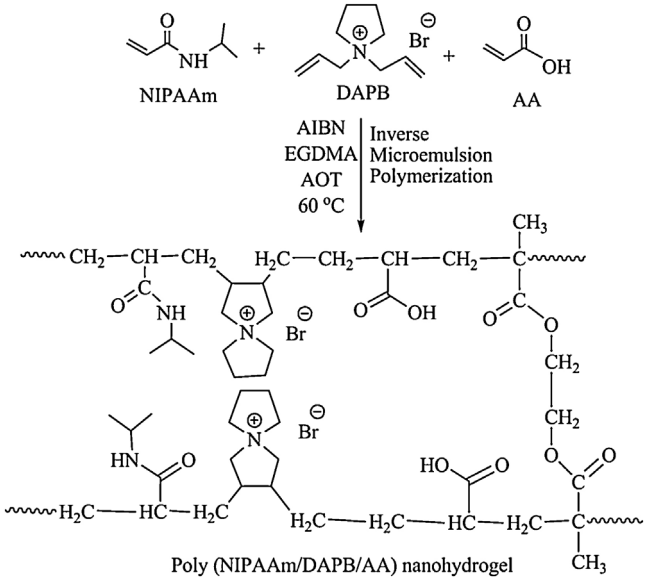
where Q_t is the swelling percentage for a given time, Q_e is the equilibrium swelling percentage and W_d and W_s are the weight of the nanohydrogels in dry and swollen states, respectively.

Fig. 1 shows the effect of the contact time on the swelling percentage of the nanohydrogel (V-03). Fast swelling of the nanohydrogels was achieved up to 8 h. After that, increasing the contact time up to 16 h resulted in insignificant swelling. Also, the results were identical for all the synthesized nanohydrogels (Table 1). Therefore, the equilibrium time was chosen as 8 h for further dye adsorption studies.

Poly(NIPAAm/DAPB/AA) superabsorbent nanohydrogels (V-01 to V-07) were synthesized using different composition of monomers, surfactant, initiator, and cross-linker. The schematic representation of the synthesis of nanohydrogels is shown in Scheme 1. Sample coded nanohydrogel V-03 shows a high equilibrium swelling percentage after 8 h and has good stability, absorption and mechanical properties than other, so V-03 was utilized for further characterization and dye adsorption studies.

3.2. Dye adsorption studies

It is well known that there are mainly two factors that affect the adsorption of dyes. The first one is electrostatic interactions and the other is hydrophobic interactions. Electrostatic interactions occur between ionizable groups of a hydrogel and the specific charges of a dye molecule, while hydrophobic interactions may involve the aromatic rings and the methyl group in the dye molecules and the methine groups in the nanohydrogel. It is interesting that the synthesized nanohydrogels are amphoteric in nature and therefore, they are capable of adsorbing both cationic and anionic dyes on their surface in high proportion.



Scheme 1. Reaction scheme of poly(NIPAAm/DAPB/AA) nanohydrogel.