



## Dye adsorption studies of Poly (N-tert-amylacrylamide-co-Acrylamide /Sodium acrylate) Hydrogels

\*C.Deepa \*\*B.A.Brundha \*\*P.Pazhanisamy

\* Research and Development Centre, Bharathiar University.Coimbatore, India.

\*\* Department of Chemistry, Sir Theagaraya College, Chennai-600 021, India.

\*\* Department of Chemistry, Sir Theagaraya College, Chennai-600 021, India.

### ABSTRACT

A series of ionic Poly (N-tert-amylacrylamide-co-acrylamide / Ac Na) Hydrogels were synthesized by free-radical copolymerization in Water/Methanol medium using Ammonium persulfate (APS) as the initiator and N,N-methylenebisacrylamide (MBA) as a crosslinker at 60°C. These hydrogels showed up to 48% removal efficiency towards Methylene Blue dye adsorption study.

### Introduction

Hydrogels are formed of three-dimensional crosslinked polymer networks of flexible chains, which are able to absorb and retain water and solute molecules. The higher water content and porous network structures allow solute diffusing through the hydrogel structure [1]. As hydrogels possess ionic functional groups such as carboxylic acid, amine, hydroxyl and sulfonic acid groups, they can absorb and trap metal ions [2,3] or cationic dyes such as MB [4] from wastewater. Therefore, the hydrogels may be used as an alternative adsorbent for the removal of cationic dyes from aqueous solution.

Methylene blue is a cationic dye that can be widely used in medical science, coloring paper, dyeing cottons, wools etc. Although, methylene blue is not strongly hazardous, it can cause some harmful effects such as increased heart rate, vomiting, shock, Heinz body for motion, cyanosis, jaundice, quadriplegia and tissue necrosis in humans. Also this dye in water can affect plant life and is aesthetically unpleasant [4,5]. Therefore, the removal of MB from waste effluents becomes environmentally important. In particular, these polymeric hydrogels have been used to deal with the removal of dyes because they can absorb and trap ionic dyes due to possessing ionic functional groups [6, 7]. In the present study, we aimed to synthesize Poly (N-tert-amylacrylamide-co-Acrylamide /Sodium acrylate) Hydrogels via free radical polymerization at 60°C. The dye adsorption study was carried out using Methylene Blue.

### Experimental

#### Preparation of Hydrogels

Free-radical cross linking copolymerization was carried out in methanol /water mixture as the polymerization solvent, at 60 °C in the presence of APS as initiator and MBA as crosslinker. Aqueous solution containing NTA (0.5g), AM (0.5g), 0.045g MBA 0.005 g APS, AcNa ( 0.00, 0.10, 0.20 and 0.30) were prepared in methanol water mixture. After bubbling nitrogen for 15 min, the contents were placed in thermostatic water bath at 60 °C and the polymerization was conducted for 1 day. After the reaction, the hydrogels were cut into pieces 3-4 mm long. The extracted hydrogels were dried in vacuum oven at 50 °C to constant weight for further use (Scheme-1).

### Swelling behavior

The swelling characteristics were measured by immersing weighed samples of dry hydrogels in double distilled water. The degree of swelling (Ds%) most commonly described as swelling ratio is expressed as increase in weight / gm of dried hydrogel after keeping in contact with water for selected period of time.

$$(D_s \%) = [(W_s - W_d / W_d)] \times 100 \quad \text{----- (1)}$$

Where,  $W_s$  is the weight of the swollen gel at a given time and  $W_d$  is the weight of the dry gel.

### Dye adsorption study

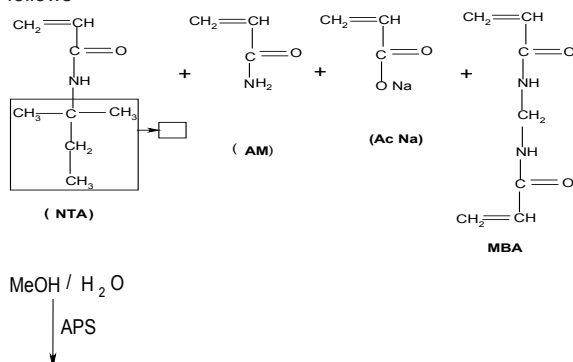
A weighed quantity of dry nanocomposite hydrogel (0.1 g) with different composition was immersed in enough methylene blue (30 ppm) and kept at 34°C. The amount of MB adsorbed was measured spectrophotometrically ( $\lambda$ : 661.6 nm) in periodically taken solution samples and again placed in the same vessel so that the liquid volume was kept constant. The removal efficiency (RE %) of the dye by the hydrogels with different composition was calculated by

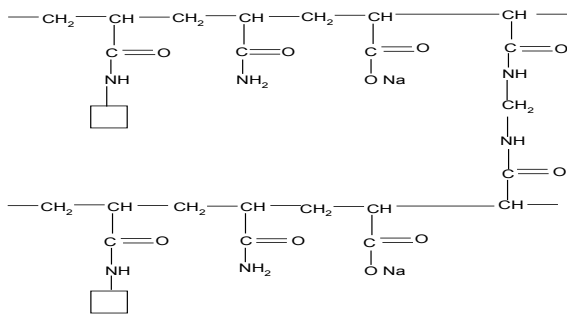
$$RE\% = [(C_0 - C / C_0)] \times 100 \quad \text{----- (2)}$$

where  $C_0$  and  $C$  are the initial and equilibrium concentration of the MB dye solution, respectively.

### Results and Discussion

The schematic representation of hydrogel preparation is as follows





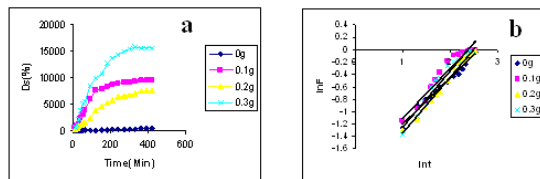
**Scheme 1. Poly(N-tert-amylacrylamide-co-Acrylamide / Sodium acrylate) Hydrogels**

**Swelling Behavior**

The swelling behavior of the hydrogels was carried out in water at room temperature and is depicted in the Figure 1(a). The swelling is driven by repulsion of hydrophilic groups such as NH<sub>2</sub>, C=O NH<sub>2</sub>, -COO Na, inside the network and osmotic pressure difference between the gels and the external solution. As the concentration of Ac Na increases the swelling behavior also increases and it is due additional osmotic pressure develops that expands the gel network further [8]. The Kinetic study of all hydrogels are determined using the equation 3 and are shown in Figure1(b). The plots of LnF against LnT gives a straight line whose slope is “n”, which is equal to 0.75, 0.81, 0.91 and 0.92. These values of “n” is in the range between 0.50< n<1.00 which indicates that the diffusion is non-Fickian.

$$F_{swp} = Kt^n \text{ ----- (3)}$$

Where K is the swelling constant, t is the time and n is swelling exponent

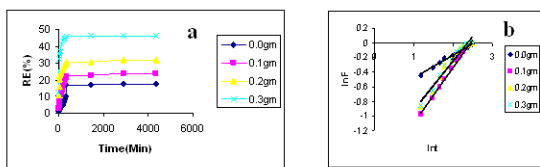


**Figure 1. Swelling behavior of Hydrogels**

**Dye adsorption study of Hydrogels**

**Dye adsorption study**

The MB dye adsorption studies of all hydrogels are shown in Figure 2. The dye removal efficiency towards methylene blue dye increases with increasing amount of Ac Na content in hydrogel( Figure 2a). The efficiency is reached up to 48%. Kinetic study shows that the diffusion of dye molecules follows both the Fickian and Non-Fickian. The ‘n’ value for 0.00 AcNa is 0.32 which follows Fickian and for 0.1,0.2,0.3 AcNa the ‘n’ values are 0.77,0.69,0.67 respectively, which follow Non-Fickian transport mechanism(Figure 2b).



**Figure 2. Dye adsorption study of Hydrogels**

**Acknowledgment**

The author Dr.P.Pazhanisamy thank the UGC, New Delhi, for financial support (MRP-2008, F.No.34-337/2008)

**REFERENCES**

[1] C.L. Bell, N.A. Peppas, Biomedical membranes from hydrogels and interpolymer complexes, *Adv. Polym. Sci.* 1995, 122, 125–175. | [2] V. Bekiaris, M. Sotiropoulou, G. Bokias, P. Lianos, Use of poly(N, N-dimethylacrylamide- co-sodium acrylate) hydrogel to extract cationic dyes and metals from water, *Colloids Surf. A* 2008, 312, 214–218. | [3] E.K. Yetimoğlu, M.V. Kahraman, O.E. Ercan, Z.S. Akdemir, N.K. Apohan, | N-vinylpyrrolidone/ acrylic acid/2-acrylamido-2-methylpropane sulfonic acid based hydrogels: synthesis, characterization and their application in the removal of heavy metals, *React. Funct. Polym.* 2007, 67, 451–460. | [4] A.T. Paulino, M.R. Guilherme, A.V. Reis, G.M. Campese, E.C. Muniz, J. Nozaki, Removal of methylene blue dye from an aqueous media using superabsorbent hydrogel supported on modified polysaccharide, *J. Colloid Interface Sci.* 2006, 301, 55–62. | [5] M.T. Uddin, M.A. Islam, S. Mahmud, M. Rukanuzzaman, Adsorptive removal of methylene blue by tea waste, *J. Hazard. Mater.* 2009, 164, 53–60. | [6] N. Kannan, M.M. Sundaram, Kinetics and mechanism of removal of methylene blue by adsorption on various carbons—a comparative study, *Dyes and Pigments.* 2001, 51, 25–40. | [7] L.C.A. Oliveira, R.V.R.A. Rios, J.D. Fabris, K. Sapag, V.K. Gargc, R.M. Lago, Clay–iron oxide magnetic composites for the adsorption of contaminants in water, *Appl. Clay Sci.* 2003, 22, 169–177. | [8] S. Anbarasan, B.A. Brundha, P.Pazhanisamy, N-cyclohexylacrylamide based hydrogels-II: Synthesis and characterization of poly(N-cyclohexylacrylamide-co-acrylamide/sodium acrylate) hydrogels, *Journal of Chemical and Pharmaceutical Research*, 2013, 5(7),302-306 |