

Removable of Heavymetals and dye Studies of Poly (N-tert-amylacrylamide-co-acrylamide/Maleic acid) OMMT

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Abstract

The present study describes the preparation of Poly (N-tert-amylacrylamide-co-acrylamide/Maleic acid) OMMT denoted as Poly(NTA-co-AM/MA)OMMT. The first step is the synthesis of Poly(NTA-co-AM/MA)OMMT. The second step is the incorporation of OMMT Nanoclay. The properties of the gel can be modified by the OMMT clay. The amount of MA and Nanoclay places essential role in the adsorption. The adsorption rate of dye stuff is slow at the initial and increases further.

Keywords: NTA, Maleic acid(MA), Acrylamide, Organically modified montmorillonite nanoclay(OMMT nanoclay).

Introduction

Hydrogel Nanocomposites are in the category of multiphase system. It is produced by the mixture of Polymer with inorganic solid clay at nanometric scale[1-4]. The structures are more complicated than microcomposites but these are more influenced by structure, composition, interfacial interaction and component of individual property. The properties of gel can be significantly enhanced by the incorporation of inorganic clay into system. It possesses eco-friendly nature and offer high usage in automobile, electronic, electrical, food packaging material. They are commonly designed to present wide range of properties like stiffness and strength, low coefficient of expansion, resistant against fatigue, resistance to corrosion etc. This can be widely used in medicine due to bio-compatible nature. A further important characteristic of these materials is their ability to respond to external physical/chemical/mechanical stimuli with a structural change. This ability is used in the preparation of “intelligent” material possessing certain self-control mechanisms. Elasticity of the gel is important to give flexibility to the crosslinked chains, to facilitate the movement of incorporated bioactive agent. Thus, a compromise between mechanical strength and flexibility is necessary for the appropriate use of the material.

Poly(NTA-co-AM/MA) OMMT Nanocomposite hydrogels were synthesized by free radical copolymerization in methanol/water medium using APS as an initiator and MBA as a crosslinker. The amount of NTA and AM monomer were fixed and the amount of MA monomer and OMMT clay were varied[6-8]. Study of heavy metal adsorptions and removal efficiency of organic dyes is covered in this article. As per EU regulations 92/59/EEC, The usage of forty hazardous dye is restricted. The removal of these dye is very much essential.

The adsorption study was carried out using crystal violet which is mutagenic effect reported by USFDA. The higher dosage of crystal violet is linked to bladder cancer in human. The present study aimed at the synthesis of Poly (N-tert-amylacrylamide-co-acrylamide/MA) OMMT which serves as an alternative adsorbent for the removal of dyes and heavy metals.

Experimental

Synthesis of Poly (N-tert-amylacrylamide-co-acrylamide/Maleic acid) OMMT Nanocomposites

Free-radical crosslinking copolymerization 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), MBA (0.050g), APS (0.050g), MA (0.1, 0.3 and 0.5g), OMMT (0.050g, 0.100g and 0.200g) were prepared in methanol/water mixture. After bubbling nitrogen for 30 min, the contents were placed in thermoplastic water bath at 60°C and the polymerization was conducted for 1day. After the reaction, the resulting Nanocomposites were cut into pieces of 3-4mm long. The extracted Nanocomposites were dried in vacuum oven at 50°C to constant weight for further use[9]. Nanocomposite Hydrogels compositions are given in the below table-1.

Table 1. Nanocomposite hydrogels prepared from varying amount of Maleic acid(MA)

S.No	Wt. of NTA (g)	Wt. of AM (g)	Wt. of MA (g)	Wt. of APS (g)	Wt. of MBA (g)	Methanol / Water (3:1)	Wt. of Nanoparticle (g)
1	0.500	0.500	0.1	0.050	0.050	10	0.050
2	0.500	0.500	0.3	0.050	0.050	10	0.100
3	0.500	0.500	0.5	0.050	0.050	10	0.200

Results and Discussion

The schematic representation of poly(NTA-co-AM/MA) OMMT nanocomposite hydrogel is shown in Figure 1.

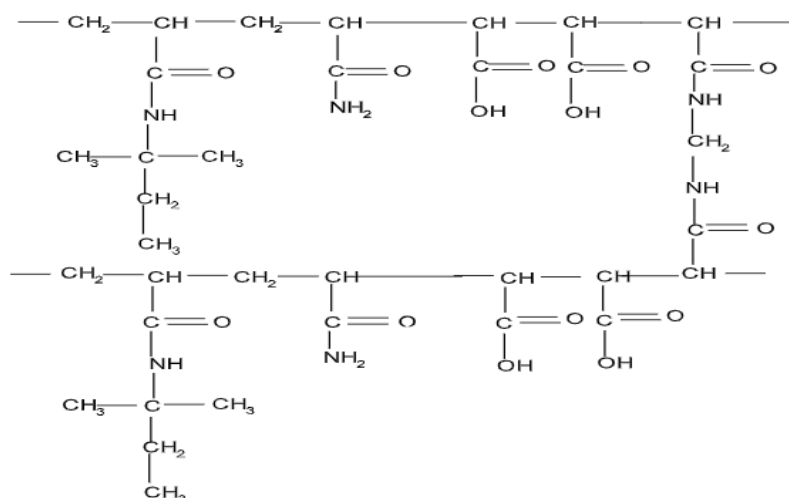


Figure1. Schematic representation of poly (NTA-co-AM/MA) OMMT Nanocomposite Hydrogel

Characterization: FT-IR Spectroscopy

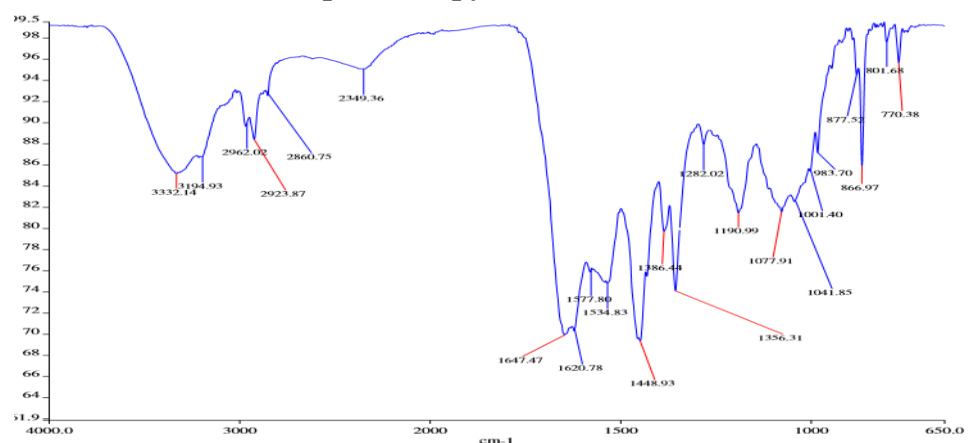


Figure 2. FT-IR spectra of poly (NTA-co-AM/MA)NCH

FT-IR spectra of poly(NTA-co-AM/MA) NCH is shown in Figure 2. A large peak corresponding to NH stretching of NTA observed around 3332.14 cm^{-1} . In addition to this, the peak also observed at 1647.47 cm^{-1} corresponding to $\text{C}=\text{ONH}_2$ of AM unit. The band at 2950 cm^{-1} is due to C-H stretching of polymer backbone, and peaks at 2349.36 cm^{-1} indicates coupled OH in-plane bending and C-O stretching. Peaks at 3332.14 cm^{-1} due to $-\text{OH}$ group between the two planes of the clay, Si-O-Si symmetric stretching mode was observed at 1190.99 cm^{-1} . Peak at 770.38 cm^{-1} indicates R-O-Si (R=A1, Mg or Li) respectively, which confirms the incorporation of the clay into the polymer matrix. The IR analysis indicates the presence of all monomeric unit sin the crosslinked hydrogels.

XRD Studies

The X-ray diffraction patterns of poly(NTA-co-AM/MA) NCH are shown in Figure 4.4. Some diffraction peaks at 2θ : 28-60 are clearly seen and can be indexed as the OMMT clay. The wide peak show that the size of the clay is very small, which confirms more amorphous and less crystallinity. It showed that the more the amorphous in the matrix more will be the swelling. It was clear that the regular crystal structure of clay was partly destroyed and the clay platelets were intercalated and dispersed in the Nanocomposite hydrogel matrix

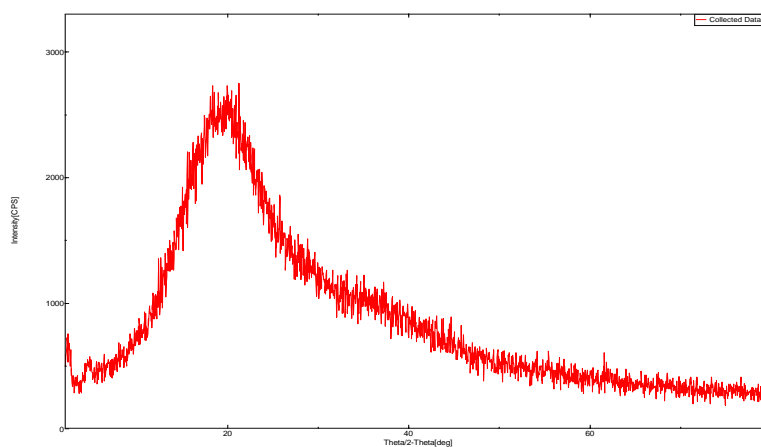


Figure 3: XRD of poly (NTA-co-AM/MA) NCH

SEM Analysis

The SEM image of poly (NTA-co-AM/MA) NCH is shown in figure 3. From the SEM micrograph the surface seems very rough, granule and homogeneous. On the other hand SEM photographs of poly (NTA-co-AM/MA) NCH that has the higher metal adsorption shows that it has more porous in surface. This provides higher dye removal capacity and was dispersed in the polymer network.

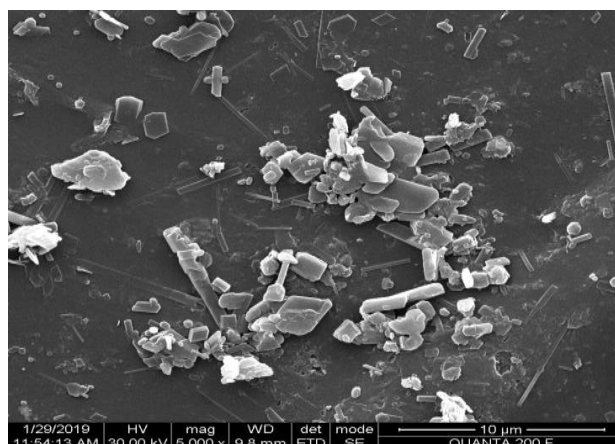


Figure 4. SEM image of poly (NTA-co-AM/MA) NCH

Adsorption of crystal violet

The adsorption curves of nanocomposite hydrogels are shown in Figure 5. The maximum adsorption capacity is about 62.84% at 0.1g of MA and 50mg of clay content and it is decreasing at 100mg of clay and without clay. After one day all nanocomposite showed dark color compared with the original composites. Also, the color of CV solution became colorless compared with the original solution. The cationic dyes like CV have electronegative atoms such as nitrogen and sulfur behave like hydrophilic groups and form hydrogen bonds with water. Thus, the swelling increased because the CV brings water into them.

Calculation of Removal efficiency

A weighed quantity of hydrogel (0.1g) is immerse in crystal violet dye solution of known concentration (1ppm) the amount of dye adsorbed was measured spectrophotometrically at different intervals. The Removal efficiency (RE%) of Nanocomposites was calculated by using the following expression

$$RE\% = (C_0 - C/C_0) \times 100$$

Where C_0 and C are the initial and equilibrium concentration of the crystal violet dye solution.

Table 2. Concentration of dye varying in time (OD) of NTA-AM-MA (0.1)

	OMMT	SAMPLE NO.	INTIAL	2HRS	4HRS	6HRS	8HRS	24HRS
NTA-AM-MA(0.1)	0	22	0.455	0.406	0.385	0.3495	0.3183	0.2866
	50	23	0.455	0.216	0.196	0.1916	0.1826	0.169
	100	24	0.455	0.394	0.384	0.367	0.3504	0.2998

Table 3. Removable efficiency in % on adsorption of NTA-AM-MA (0.1)

OMMT	SAMPLE NO.	2HRS	4HRS	6HRS	8HRS	24HRS	
NTA-AM-MA(0.1)	0	22	10	15.28	23.18	30	36.8
	50	23	52.52	56.83	58.97	59.85	62.84
	100	24	13.45	15.65	19.3	22.95	34.08

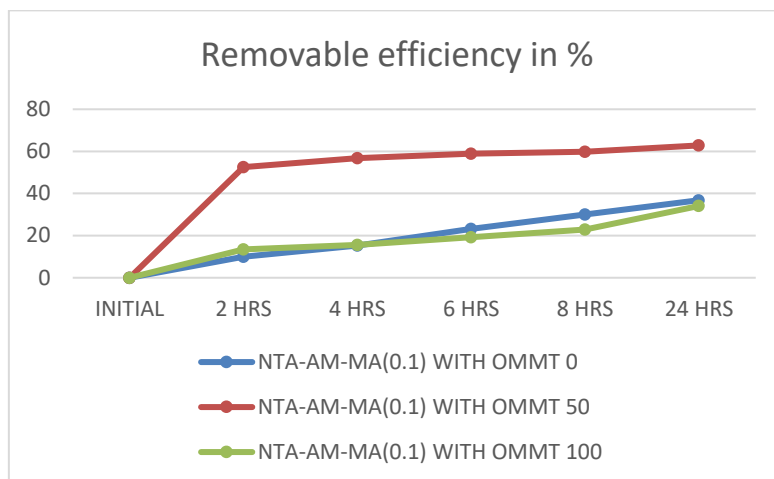


Figure 5. Removable efficiency in % of NTA-AM-MA (0.1g)

Removal efficiency (RE%)

The adsorption curves of nanocomposite hydrogels are shown in Figure 5. The maximum removable efficiency is about 62.84% at 0.1g of MA and 50mg of clay content and it is decreasing at 100mg of clay and without clay. After one day all nanocomposite showed dark color compared with the original composites. Also, the color of CV solution became colorless compared with the original solution. The cationic dyes like CV have electronegative atoms such as nitrogen and sulfur behave like hydrophilic groups and form hydrogen bonds with water. Thus, the swelling increased because the CV brings water into them. The removal effect of CV increased when the clay was added from 50mg and less after that it had not adsorbed more CV as expected. The cationic dye may have interacted with the OMMT clay by different modes: 1. The cations on OMMT clay may exchange with CV cations from solution. 2. The adsorption is on through porous of OMMT without any ion-exchange. 3. The dye adsorbed on the surface of porous materials.



Figure 6: Adsorption of crystal violet dye on Poly (NTB-co-AM/MA) OMMT

Heavy metals adsorption in poly (NTB-co-AM/MA)

Poly (NTA-co-AM/MA) Nanocomposite Hydrogels Gel is (0.3g) & (0.5g) placed in mixture of heavy metals (1ppm) and reading were taken at different intervals of time in ICPMS. Heavy metals concentration on ICPMS at different intervals.

Table 4. Heavy metal Adsorption in poly (NTA-co-AM/MA)(0.3) Nanocomposites

Time	Cr	Mn	Co	Ni	Se	Cd	Pb
2hrs	1170	1167	1159	1180	1181	1141.6	1119
4hrs	530.4	524.4	528.6	546.2	515	533.08	536.35
6hrs	1125	1122.2	1114.5	1134.4	1135.9	1097.2	1075.6
8hrs	509.8	504.089	508.1	524.951	495.8	512.37	515.53
24hrs	1013	1011.92	1020.7	1043.8	1031.2	1022.8	1019.3

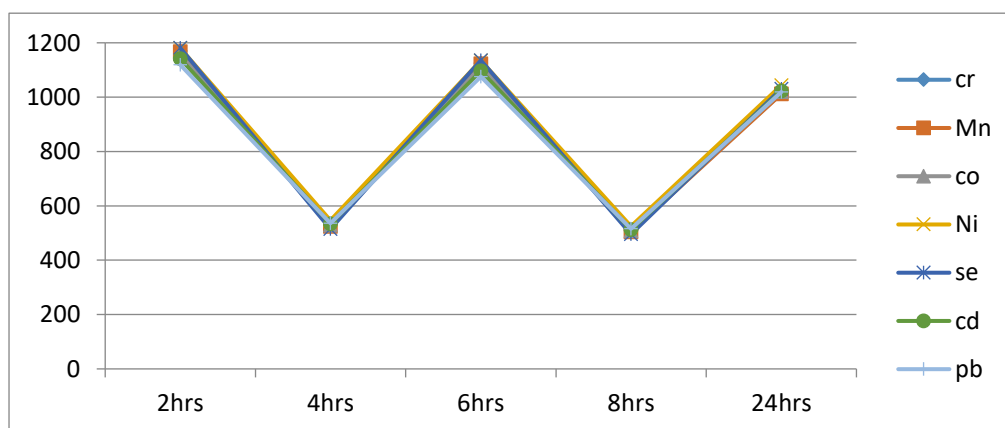


Figure 7. Heavy metal Adsorption in poly (NTA-co-AM/MA) Nanocomposites

Heavy metal adsorption of Cr, Mn, Co, Ni, Se, Cd, Pb take place at initial and desorption take place further from 2 to 4 hrs and again adsorption and desorption take place as same above in poly (NTA-co-AM/MA) Nanocomposites in both varying MA composite gel[10].

Conclusion

XRD and SEM analysis confirmed the amorphous nature and distribution of clay particle on gel. FT-IR frequencies confirmed the presence of C=ONH₂ of AM unit (3332.1cm⁻¹ and 1647cm⁻¹), C-H stretching of polymer backbone indicate (2950cm⁻¹), peak at 3332.14cm⁻¹ of –OH group, Si-O-Si symmetric stretching at 11190.99 cm⁻¹ and 770.38cm⁻¹ indicate R-O-Si (R=Al, Mg and Li) the incorporation of clay. The maximum removable efficiency of dye in Nanocomposite is about 62.84% in 0.1g of MA at 50mg of OMMT. Heavy metal adsorption showed less due to de-adsorption. From this, it can be better substitute for other adsorbent particularly for the removal of dye chemicals. From the experimental data it is possible to

design and optimise the economical treatment process the removal of dyes in industrial effluent.

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