SYNTHESIS, CHARACTERIZATION, SWELLING BEHAVIOR AND DIFFUSION STUDIES OF POLY(*N*-CYCLOHEXYLACRYLAMIDE-CO-ACRYLAMIDE-2-ACRYLAMIDO-2-METHYLPROPANE SODIUM SULPHONATE) SILVER NANOCOMPOSITE HYDROGELS

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ABSTRACT

In the present study Poly(N-cyclohexylacrylamide-co-acrylamide-2-acrylamido-2-methyl-1- propane sodium sulfonate) Ag nanocomposite hydrogels was synthesized by *in situ* free-radical copolymerization in water/methanol medium using ammonium persulfate as the initiator, tetramethylethylenediamine as accelerator and N,N'-methylenediaminde as cross-linker at 60ºC. Analysis and characterization of the silver nanocomposite hydrogel was performed through monitoring its swelling behavior, diffusion studies, FTIR spectroscopy, SEM/EDX and XRD studies. Effects of monomer ratio on the swelling properties of the samples were investigated. Samples were used to remove organic dye (methylene blue) and heavy metal ion (Cd^{2+}) from aqueous solution and it was found that increase in monomer concentration into the hydrogel network increased the adsorption capacity of the silver nanocomposite hydrogel.

KEYWORDS: Silver nanocomposite hydrogel, swelling property, organic dye, heavy metal ion.

1. INTRODUCTION

Hydrogels are a unique class of macromolecular networks that may contain a large fraction of aqueous solvent within their structure. The ability of hydrogels to absorb water arises from hydrophilic functional groups attached to the polymer backbone while their resistance to dissolution arises from cross-links between network chains. The amount of water absorbed in

hydrogels is related to the presence of specific groups such as –COOH, –OH, –CONH$_2$, –CONH– and –SO$_3$H. Capillary effect and osmotic pressure are other variables that also influence the equilibrium water uptake of hydrogels.[1] Water inside the hydrogel allows free diffusion of some solute molecules, while the polymer serves as a matrix to hold water together. Hydrogel networks can be formed by conventional crosslinking methods or free-radical polymerization processes. The excellent hydrophilic properties of hydrogels along with their high swelling ratio and biocompatibility, promote their usage widely in agriculture[2], biomedical area as antibacterial materials[3], tissue engineering[4], biosensors[5], sorbents for the removal of heavy metals[6] and drug delivery.[7] Hydrogels have been paid great attention in the research on adsorption for removal of dyes and metal ions from waste water due to their relatively low cost and the possibility to confer them specific and selective properties. Because of its anionic properties, these hydrogels can adsorb and trap cationic dyes from aqueous solutions by electrostatic attraction force. When hydrogels come in contact with aqueous solutions, they can effectively sorb and retain the dissolved substances, depending on the nature of the monomeric units comprising the hydrogel. For this reason, hydrogels have been proposed in several studies as water purification agents.[8] The residual dyes from textile wastewater and heavy metals from industries are considered as a very crucial source of pollutants into the natural water resources or wastewater treatment systems.[9] This high discharge into the water creates a very important environmental problem on the ecological system as they are toxic and carcinogenic.[10] In the recent years several works have been appeared in the scientific literature reporting adsorption of several dyes and heavy metals by both natural and synthetic sorbents.[11] The objective of the present work is to synthesize silver nanocomposite hydrogels (SNCHS), characterize them and to determine its efficiency in removing methylene blue and cadmium ions.

2. MATERIAL AND METHODS

2.1. Materials

N-cyclohexylacrylamide (NCA) was prepared by the reaction of cyclohexanol with acrylonitrile**.** Acrylamide(AM), ammonium persulfate (APS), N',N'-methylenebisacrylamide (MBA)**,** 2-acrylamido-2-methylpropane sulfonic acid (AMPS), sodium hydroxide, N,N,N',N'-tetramethyl ethylene diamine (TEMED) and silver nano particles were purchased from Merck and Aldrich.

2.1.1. Preparation of silver nanocomposite hydrogels (SNCHS)

SNCHS were prepared by *in situ* free-radical cross linking copolymerization. Monomers NCA (0.500g), AM (0.500g) and AMPS Na (0.100, 0.300, 0.500 and 0.700g) were charged into the reaction vessel, followed by addition of APS (0.050g) as initiator, TEMED (1µL) as accelerator, MBA(0.050g) as cross-linker and Ag nanoparticles (0.050g) in methanol water mixture at room temperature. They were purged with nitrogen for 15 min, and then heated to 60^0C in thermostatic water bath and polymerization was conducted for 1 day. After the reaction, the extracted hydrogels were dried in vacuum oven at 50ºC to constant weight for further use. The compositions of monomer, initiator (APS), cross linker (MBA) and silver nanoparticles (AgNPS) are specified in table 1.

Table. 1: Poly (NCA-co-AM/AMPSNa)Ag nanocomposite hydrogels prepared from varying amount of AMPSNa.

S. No	Wt. of NCA (g)	Wt. of AM (g)	Wt. of AMPSNa (g)	Wt. of APS (g)	Wt. of MBA (g)	Wt. of AgNPS (g)	Methanol/water (3:1) (ml)
1	0.500	0.500	0.100	0.050	0.050	0.050	20
2	0.500	0.500	0.300	0.050	0.050	0.050	20
3	0.500	0.500	0.500	0.050	0.050	0.050	20
4	0.500	0.500	0.700	0.050	0.050	0.050	20

2.2. Swelling experiments

2.2.1. Swelling behavior (Gravimetric Method)

The swelling characteristics were measured by immersing weighed samples of dry hydrogels in double-distilled water. The excess surface water in the swollen gel was removed by blotting and then the swollen gel was weighed. The swollen gel was blotted several times till three consecutive weights are same within limits of experimental error of 1%. All measurements were performed thrice and the reported values are average of at least three individual measurements. 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.[12,13]

$$Ds (\%) = (W_t - W_d)/W_d \times 100 \qquad ....(1)$$

Where W_t is the weight of the swollen gel at a given time and W_d is the weight of the dry gel.

2.2.2. Diffusion studies

Analysis of mechanism of diffusion in swellable polymeric systems has received considerable attention in recent years because of the important applications of swellable

polymers in various fields. The following equation is used to determine the nature of diffusion of water into nanocomposite hydrogels. $\mathbf{F = M_t/M_\infty = kt^n\ M_\infty}$ **....(2)**

Where F is the fractional uptake at time t, M_t and M_∞ denotes the amount of solvent or dyes diffused into the gel at time t and infinite time (at equilibrium), respectively. k is a constant related to the network and the exponent n is a number to determine the type of diffusion. Depending on the relative rates of diffusion, three classes of diffusion mechanisms are distinguished. In Fickian or Case I transport, the polymer chains have high mobility and water penetrates easily in the rubbery network. Therefore, the solvent diffusion rate, Rdiff, is clearly slower than the polymer chain relaxation rate, R_{relax}, ($R_{diff} << R_{relax}$). Case I diffusion is characterized by a linear increase of polymer weight gain as a function of the square root of sorption time. In non-Fickian diffusion, the polymer chains are not adequately mobile to permit urgent penetration of water into the polymer core. Depending on the relative rates of chain relaxation and diffusion, non Fickian diffusion is commonly classified to two subsections: "Case II transport" and "anomalous transport". Case II transport is dominated when the diffusion is very rapid compared to relaxation ($R_{diff} >> R_{relax}$), with relaxation occurring at an observable rate. Here, the rate of mass uptake is directly proportional to time. The anomalous transport is observed when the diffusion and relaxation rates are comparable ($R_{diff} \approx R_{relax}$). If n ≤ 0.5 it indicates Fickian diffusion, n > 0.5-1 it indicates anomalous transport and n > 1 implies case II (relaxation-controlled) transport.[14,15]

2.3. Adsorption of Methylene blue: A weighed quantity of dry hydrogel (0.1g) was immersed in methylene blue dye solution (50ppm, 50ml) at room temperature. The amount of MB adsorbed was measured spectrophotometrically (spectrophotometer-106, systronics) at 661.6nm at predetermined time intervals in periodically taken solution samples which were again placed in the same vessel so that the liquid volume was kept constant. The adsorption capacity Q (mg dye per g polymer) of hydrogel was calculated by using the following expression. $\mathbf{Q\ (mg/g) = (C_i\text{-}C_e)\ V/m}$ **.... (3)**

Where Ci and C_e are the initial and equilibrium concentrations of the dye in the solution, respectively (mg/l), V is the volume of the solution added (L) and m is the amount of hydrogel used (g).[16,17] The removal efficiency (RE %) of hydrogels was calculated using the following expression. $\mathbf{RE\ \% = (\ C_0\text{-}C/C_0)\ x\ 100}$ **.... (4)**

Where C_0 and C are the initial and equilibrium concentrations of the MB dye solution respectively.

2.4. Adsorption of Cd^{2+} using atomic absorption spectroscopy (Perkin Elmer Optima 5300DV ICP-OES)

A weighed quantity of dry hydrogel (0.1g) was immersed in cadmium chloride solution (100ppm, 50 ml) at room temperature. The amount of cadmium adsorbed (228.802 nm) was measured using atomic absorption spectroscopy (Perkin Elmer Optima 5300DV ICP-OES) at predetermined time intervals in periodically taken solution samples which were again placed in the same vessel so that the liquid volume was kept constant. Using Eq.5, the adsorption capacity Q in mg g^{-1} was calculated.

Q = (C_o-C_f)V/W   **…. (4)**

Where C_f and C_o represents the respective final and initial concentrations (mg L^{-1}) of Cd^{2+}, **V** and **W** are the volume (L) of the solution and the weight (g) of the polymer.[18]

3. RESULTS AND DISCUSSION

3.1. Swelling behavior

Water uptake by SNCHS was monitored for an extended period of time till equilibrium was achieved. Ds% of P(NCA-co-AM/AMPSNa)Ag nanocomposite hydrogels with different feed contents of AMPSNa at room temperature was determined and shown in Figure 1.
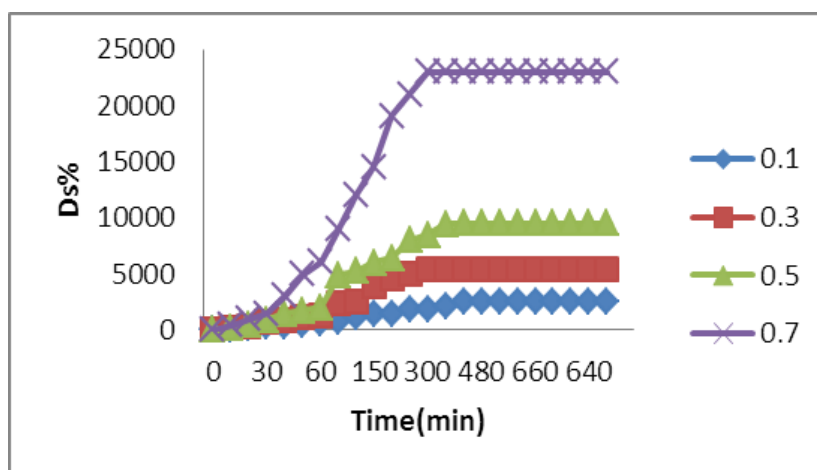

Figure. 1: Swelling behavior of P(NCA-co-AM/AMPSNa)Ag nanocomposite hydrogel in double distilled water.

The hydrogels swelled rapidly in water and attained equilibrium within 7 hrs. The figure shows the influence of varying amounts of AMPSNa on swelling characteristics of the SNCHS. It is observed that as the amount of AMPSNa increases, the swelling of hydrogels also increases. This is due to the increase in hydrophilic groups and increase in hydrodynamic free volume to accommodate more of the solvent molecules. The penetrated water is

absorbed by hydrophilic groups in AMPSNa and AM through formation of hydrogen bonds. The swelling is driven by repulsion of hydrophilic groups inside the network and osmotic pressure difference between the gels and the external solution. The swelling rate gradually increases until the equilibrium swelling is reached.[12,19] Compared to other hydrogels, the hydrogels with AMPSNa as a co-monomer swell more due to the presence of SO_3Na groups, which are highly water attractive in nature and thereby increase the water absorbing capacity.

3.1.1. Diffusion studies

Plot of ln F Vs ln t curves of P(NCA-co-AM/AMPSNa)Ag nanocomposite hydrogels in water are given in Figure 2 and the n values are shown in Table 2. It can be observed that the results support non-Fickian (anomalous transport). In non-Fickian diffusion, the polymer chains are not adequately mobile to permit urgent penetration of water into the polymer core. The anomalous transport is observed when the diffusion and relaxation rates are comparable ($R_{diff} \approx R_{relax}$). ($n \leq 0.5$ Fickian diffusion, $n > 0.5-1$ anomalous transport and $n > 1$ case II (relaxation-controlled) transport).

Table. 2: Maximum swelling and diffusion parameters of P(NCA-co-AM/AMPSNa)Ag nanocomposite hydrogels in distilled water.

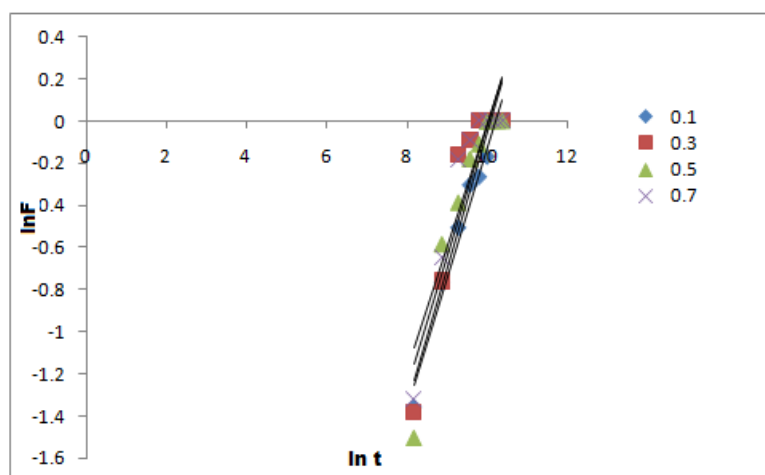| S. No.	Weight of AMPSNa (g)	Maximum Ds (%)	n
1	0.1	2511	0.582
2	0.3	5481	0.61
3	0.5	9500.5	0.622
4	0.7	22965.1	0.651

Figure. 2: Plots of lnF Vs lnt of P(NCA-co-AM/AMPSNa)Ag nanocomposite hydrogels in distilled water.

3.2. Characterization

3.2.1. Spectral studies –FTIR

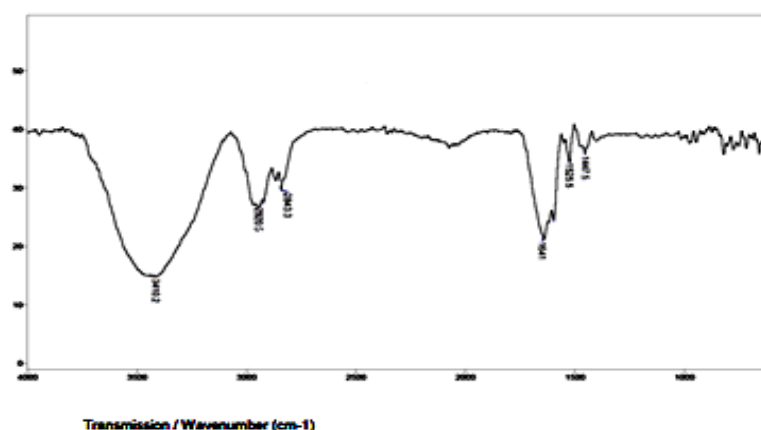FT-IR spectra of P(NTA-co-AM-AMPSNa) Ag nanocomposite hydrogel is shown in Fig 3.

Figure. 3: IR spectrum of P(NCA-co-AM/AMPSNa)Ag nanocomposite hydrogel.

A broad peak corresponding to NH stretching of NCA and acryl amide was observed around 3415.7 cm^{-1}. The peak observed at 1641 cm^{-1} corresponds to C=O stretching of NCA and acrylamide. The characteristic peak at 1597.5 cm^{-1} is attributed to N-H bending of AM unit. The peak at 2947.5 cm^{-1} is due to C-H stretching of polymer backbone. The peak at 1447cm^{-1} corresponds to the S=O stretching of SO$_3$Na. Peak around 600cm^{-1} confirmed the incorporation of the Ag nanoparticles into the polymer matrix. The above IR analysis indicates the presence of all monomeric units in the crosslinked hydrogels.

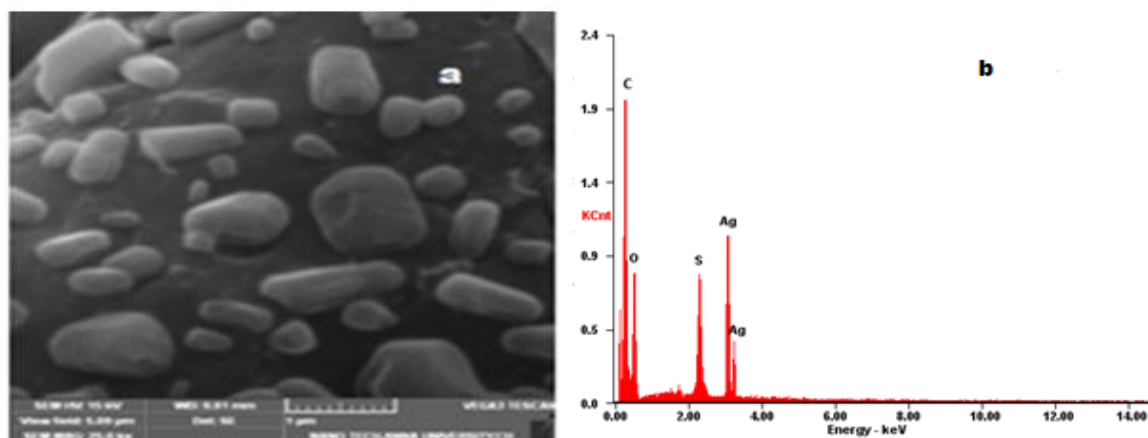### 3.2.2. Scanning electron microscopy (SEM) and energy-dispersive microanalysis (EDX)

Figure. 4: SEM images of a) Poly (NCA-co-AM/AMPSNa)Ag nanocomposite hydrogel.

b) EDX spectrum of P(NCA-co-AM/AMPSNa)Ag nanocomposite hydrogel

The scanning electron micrograph of co-polymeric-silver nanocomposite hydrogel is shown in figure 4a. It shows the formation of well-defined nanostructures in the hydrogel networks. This clearly indicates silver nanoparticles are dispersed in the hydrogel matrix. The element analysis of the silver nanoparticles was performed using EDX (Figure 4b) on the SEM of P(NCA-co-AM-AMPSNa) silver nanocomposite hydrogel. The peaks around 3.40 keV correspond to the binding energies of AgL which confirmed the existence of silver nanoparticles in the hydrogel matrix.

3.2.3. X-ray Diffraction studies

The crystallinity of P(NCA-co-AM/AMPSNa)Ag nanocomposite hydrogel was confirmed by the analysis of X-ray diffraction (XRD) pattern(Figure 5).
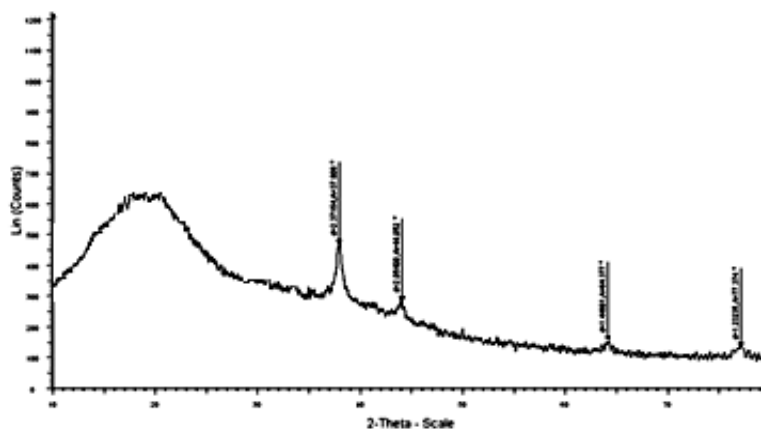

Figure. 5: XRD spectrum of P(NCA-co-AM/AMPSNa)Ag nanocomposite hydrogel.

In the diffractogram, four diffraction peaks were obtained at an angle, 2θ = 38, 44, 64 and 77 which could be attributed to the Braggs reflections of (111), (200), (220) and (311) planes of face centered cubic (FCC) structure of Ag NPs. A broad diffraction peak 2θ seen at 20° was due to the amorphous nature of SNCH. Similar type of observations was found previously in reported work.[20,21]

3.3. Adsorption of Methylene blue

The equilibrium swelling ratio of P(NCA-co-AM/AMPSNa)Ag nanocomposite hydrogel in methylene blue depends on the hydrophilicity of polymer chain, porosity and structure of hydrogel network. The SNCHS when in contact with aqueous solution, water diffuses into it and causes swelling. The removal effect of MB by nanocomposite hydrogel increased as the

concentration of AMPSNa is increased. The ionic functional groups can adsorb and trap cationic dyes such as methylene blue from wastewater. The porous surface of the hydrogel may be convenient for the penetration of dye molecules into the polymeric network, leading to the increase in the removal efficiency and adsorption capacity of methylene blue to a certain extent. The adsorption uptake was found to increase with time, which slows down later and approaches saturation. It is basically due to saturation of the active site which do not allow further adsorption to take place.[22]
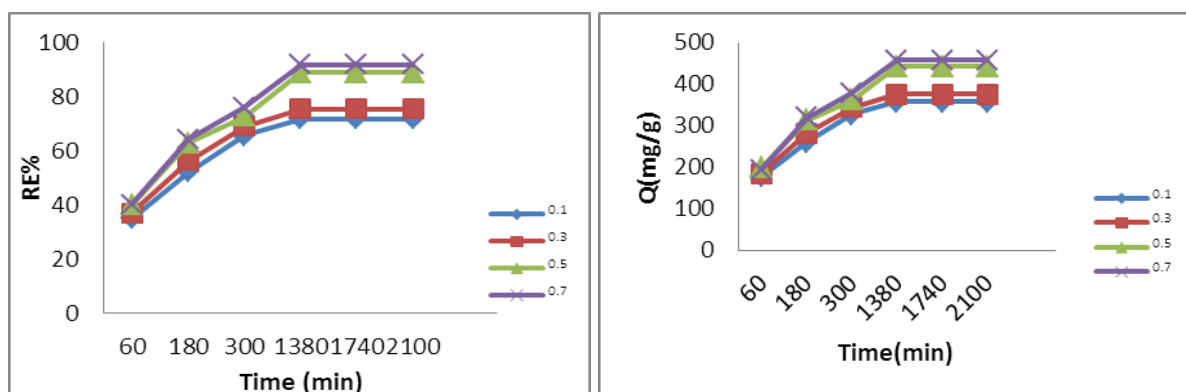

Figure. 6: Removal efficiency and adsorption capacity of Poly(NCA-co-AM/AMPSNa)Ag nanocomposite hydrogel.

Table. 3: Removal efficiency and adsorption capacity of Poly(NCA-co-AM/AMPSNa)Ag nanocomposite hydrogel.

S.NO	Weight of AMPS Na (g)	Max RE (%)	Q (mg/g)
1	0.1	71.7	357.6
2	0.3	75.4	375.6
3	0.5	88.7	442.1
4	0.7	91.7	457.0

The above data shows the removal efficiency and adsorption capacity of Poly(NCA-co-AM-AMPSNa)Ag nanocomposite hydrogels. As these hydrogels have more swellability, the adsorption capacity and removal efficiency of methylene blue is more, as swelling develops charges which can adsorb the cationic dye. The SNCH with 0.7g of AMPSNa concentration shows maximum removal efficiency of 91.7% which is due to the increase in ionic functional groups.

3.4 Adsorption of cadmium ions based on swelling behavior

The adsorption capacities of SNCHS towards Cd^{2+} showed that, the concentration of cadmium ions decreased rapidly with increase in both adsorption time and AMPSNa concentration. This faster adsorption kinetics may be correlated with the structure of the hydrogels containing lots of super hydrophilic sulfonic, carboxylic, hydroxylic and amide groups, which are considered as the adsorption sites for heavy metals.[23] The SNCHS when in contact with aqueous solution would be swollen quickly and the hydrophilic groups within the polymeric networks will capture the cadmium ions.[24] The cadmium uptake increases with time to reach its maximum capacity in 7 hrs and then becomes constant at higher contact times. It is basically due to saturation of the active site which does not allow further adsorption to take place. The figures (6a &b) show the effect of adsorption time and ionic monomer concentration, on the concentration of cadmium ions and adsorption capacities of Cd^{2+} by SNCHS.

The initial concentration of blank Cd^{2+} ions was found to be 52.59 mg/L (wavelength 228.802nm). The decrease in concentration of Cd^{2+} ions after dry SNCHS (0.1g) was immersed in cadmium chloride solution (100ppm) at room temperature was noted at predetermined time intervals. In P(NCA-co-AM/AMPSNa)Ag nanocomposite hydrogels (0.1g), the concentration of Cd^{2+} ions decreased to 31.3, 22.0, 13.3 and 10.7 mg/L with increase in AMPSNa concentration as 0.1, 0.3, 0.5 and 0.7g (figure 130a). The adsorption capacities also found to increase rapidly with increase in adsorption time as shown in the figure 7.
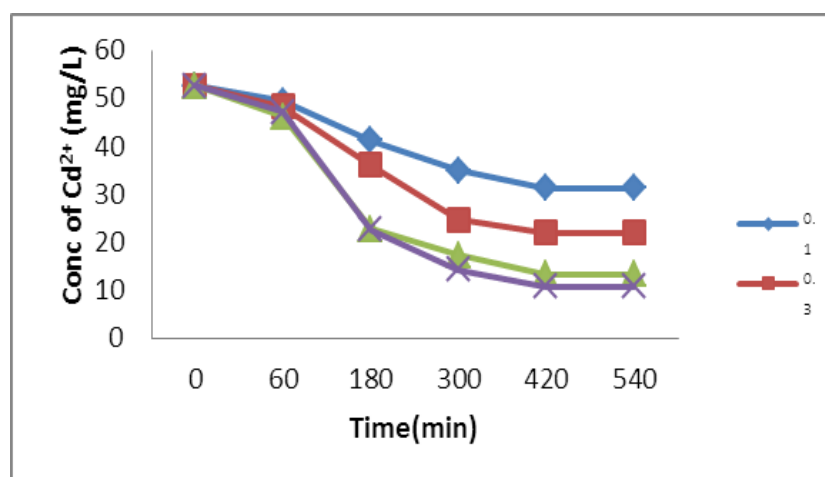

Figure. 7a: Effect of adsorption time and ionic monomer concentration on concentration of cadmium ions.
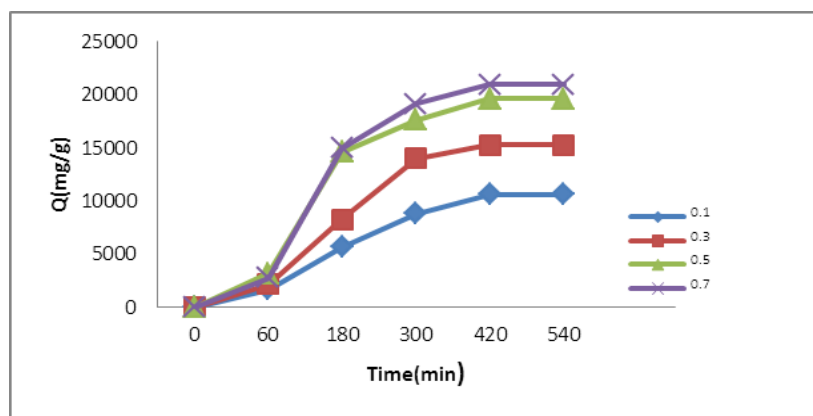
Figure. 7b: Effect of adsorption time and ionic monomer concentration on adsorption capacity of cadmium ions.

The above data shows that the decrease in concentration of cadmium ions and increase in adsorption capacity with adsorption time of P(NCA-co-AM/AMPSNa)Ag nanocomposite hydrogel, as the swelling ratio of these hydrogels is high in water, cadmium ion uptake is also high as swelling develop charges which can adsorb the Cd^{2+} ions easily.

4. CONCLUSION

Poly(NCA-co-AM-AMPSNa)Ag nanocomposite hydrogels were successfully prepared via a free radical polymerization along with varying doses of co-monomer and was characterized using swelling behavior, FTIR, XRD, SEM and EDX. It is shown that these hydrogels can be employed as efficient sorbents for retaining organic dyes and heavy metals from aqueous solutions. The results indicate that more the swelling more will be the adsorption capacity and removal efficiency of methylene blue and cadmium ion as swelling develops charges which can adsorb the cationic dye. Thus the SNCHS can provide new opportunities to develop more cost-effective and environmentally acceptable water treatment technology.

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