

Synthesis and Characterization of Novel Poly (Acrylic Acid/Sodium Alginate/Sodium Humate) Superabsorbent Hydrogels. Part II: The Effect of SH Variation on Cu^{2+} , Pb^{2+} , Fe^{2+} Metal Ions, MB, CV Dye Adsorption Study

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Abstract A novel superabsorbent hydrogel (SAHs) composed of (acrylic acid, sodium alginate and sodium humate) (AAc/NaAlg/SN) SAHs were tested as adsorbent for metal ions Cu^{2+} , Pb^{2+} , and Fe^{2+} ions as well as MB and CV dyes. The influence of SH concentration varies from 6.97, 8.04, 9.09, 10.11% and 11 wt% were designated as S_1 , S_2 , S_3 , S_4 , S_5 , respectively. The synthesized superabsorbent hydrogel were used for the adsorption of Cu^{2+} , Pb^{2+} , Fe^{2+} and MB and CV dyes from their aqueous solutions. The binding capacity for Cu^{2+} , Pb^{2+} , Fe^{2+} ions were 311 mg/gm/L at 850 mg/L, 209 mg/gm/L at 850 mg/L and 197 mg/gm/L at 850 mg/L for initial ion concentration respectively and MB and CV dyes molecules were 323 mg/gm/L at 360 mg/L, 289 mg/gm/L at 360 mg/L for initial molecule concentration per gram of AAc/NaAlg/SN containing 9.09 wt% SH content. The adsorption data obeyed Langmuir sorption isotherms.

Keywords Superabsorbent hydrogel (SAHs) · Sodium humate (SH) · Acrylic acid (AAc) · Sodium alginate (NaAlg) · Heavy metal ions · Dyes adsorption

Introduction

Now a days the increasing industrial activities have worsened the environmental health. So the demand for the use

of combination of natural polymers has improved to alleviate the poor environmental healths. The primary pollution of the textile effluents emerge from the dyeing process. Dyeing and finishing wastes are highly colored in textile industries and possesses high organic contents. Almost all the dye varieties are toxic, carcinogenic as well as mutagenic; thus they can cause health problems to living organisms. Removal of these dyes before the discharge of wastewater into the natural water bodies is highly important. It possesses ionic functional groups, these groups may adsorb and trap cationic dyes such as MB [1] or metal ions [2, 3] from waste water. With the advent of new and effective separation technologies different techniques are being used to remove heavy metals from wastewaters such as ion exchange [4], chemical precipitation [5], preconcentration [6], reverse osmosis [7], membrane filtration [8], and adsorption biological treatment [9–11]. Among these technologies, adsorption is the most common technique for the removal of heavy metal. The development of suitable adsorption techniques for the removal of dyes from aqueous medium becomes fascinating move towards. This process is convenient and effective and shared with appropriate bioadsorbent and regeneration steps. Thus a significant engrossment has been given to SAHS with efficient groups for the adsorption and separation of dyes from waste water.

In the research work a series of terpolymeric hydrogels based on (AAc/NaAlg/SN) (SAHs) were synthesized by crosslinking copolymerization method, and their application for adsorption of dyes and heavy metal ions were studied. Subsequently the desorption and regeneration of used hydrogels were also studied. Zhen Yi et al. [12] synthesized sodium humate/poly (*N*-isopropylacrylamide) hydrogels were examined found that swelling and decoloring in hydrogel properties therefore, it concluded that SH enhances the adsorption of methylene blue dye.

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Solpan et al. [13] prepared poly (acrylamide-*co*-acrylic acid) [poly (AAm-*co*-AAc)] hydrogels by illuminate with gamma radiation and applicative for the adsorption of cationic dyes such as Safranine-O (SO) and magenta (M). Hizal et al. [14] observed that in the presence of humic acid, clay mineral behaved more like a chelating agent for metal ions adsorption than a simple ion exchanger, in the presence of humic acid the stability of surfaces complexes was higher in comparison to binary metal ion of complexes. Hua and Wang et al. [15] synthesized SAHs sodium alginate-*g*-poly(acrylic acid)/sodium humate by graft copolymerization using sodium alginate, acrylic acid and sodium humate monomers in aqueous solution, with ammonium persulfate as an initiator and *N,N'*-methylenebisacrylamide as a crosslinker. They studied crosslinker, NaAlg and SH concentration on water absorbency of the SAHs. The swelling behavior in solutions has various pHs and the swelling kinetics in different saline solution were also explored. The results showed that the introduction of sodium humate into the SAHs system sodium alginate-*g*-poly (acrylic acid) could enhance the water absorbency and the SAHs having 10 wt% sodium humate achieved water absorbency. In our previous report we have synthesized a series of terpolymeric hydrogels based on (AAc/NaAlg/SH) by crosslinking copolymerization method, using sodium acrylate, sodium alginate and sodium humate and obtained 906 g/g water absorbency. In this research, a novel terpolymeric superabsorbent hydrogel composed of acrylic acid (AAc), sodium alginate (NaAlg), sodium humate (SH), were synthesized as a recipe of natural and artificial polymers. The synthesized SAHs were used for the adsorption of methylene blue (MB), crystal violet (CV) dye molecules and Cu²⁺/Pb²⁺/Fe²⁺ ions. The effects of different experimental parameters such as contact time, SH concentration, and initial metal ions/dyes concentration on the adsorption process were examined. The metal ion/dye loaded samples were regenerated and used again and again for further adsorption on basis of five consecutive adsorption desorption cycle.

Experimental

Materials

Acrylic acid [(AAc) analytical grade], potassium persulphate [(KPS) analytical grade] *N,N*-methyl bisacrylamide [(NMBA) analytical grade], sodium hydroxide (NaOH) analytical grade hydrated Copper sulphate [(CuSO₄·5H₂O)], hydrated Lead (II) nitrate [(PbNO₃)₂·6H₂O], (analytical grade) and hydrated ferrous (II) sulphate [(FeSO₄·5H₂O)] (analytical grade) and sodium humate (SH) (supplied from Aldrich) were purchased from CDH New Delhi, India, and sodium alginate (NaAlg) (supplied from Thomas baker) analytical grade was used as received. Methylene blue (MB) and crystal violet (CV) (spectroscopic grade) were purchased from Qualikems, New Delhi. Double distilled water was used throughout the experiments.

Synthesis of Poly (AAc-*co*-NaAlg-*co*-SH) Superabsorbent Hydrogels

A series of poly (AAc-*co*-NaAlg-*co*-SH) superabsorbent hydrogels were prepared using acrylic acid, sodium alginate, sodium humate were used as monomers. Five hydrogel compositions having weight of sodium humate (based on total solid content) 6.97, 8.04, 9.09, 10.11% and 11 wt% were prepared and designated as S₁, S₂, S₃, S₄, S₅, respectively shown in Table 1. *N,N*-methyl bisacrylamide (NMBA) was used as crosslinker, while potassium persulphate used as initiator. For hydrogels having sodium humate concentration lower than 6.97 wt% the polymerization did not take place.

Polymerization Procedure of Poly (AAc/NaAlg/SH) Superabsorbent Hydrogels

The terpolymeric hydrogels were synthesised using solution co-polymerization with water as solvent. A three neck glass flask (500 mL) fitted with stirrer condenser and thermometer pocket was taken. The reaction was carried out in

Table 1 Feed ratios for synthesizing a series of poly (AAc/NaAlg/SH) superabsorbent hydrogel

Sample designation	Monomer ratio wt. (%) (AAc/NaAlg/SH)	Weight of AAc (gm)	Weight of NaAlg (gm)	Weight of SH (gm)	Weight of KPS (gm)	Weight of NMBA (gm)
S ₀	90/10	7.2	0.80	0.00	0.095	0.0077
S ₁	83.72/9.30/6.97	7.2	0.80	0.60	0.089	0.0071
S ₂	82.75/9.19/8.04	7.2	0.80	0.70	0.008	0.0070
S ₃	81.83/9.09/9.09	7.2	0.80	0.80	0.087	0.0069
S ₄	80.89/8.98/10.11	7.2	0.80	0.90	0.086	0.0068
S ₅	80/9/11	7.2	0.80	1.00	0.085	0.0067

Other conditions: distilled water 30 mL for polymerization, temperature 70 °C

oil bath at room temperature 70 °C for 6 h. Firstly sodium alginate in specified amount was added in the flask and then 10 mL water was added to it. Then the mixture was vigorously stirred for 30 min at 60 °C. Then KPS was dissolved in 5 mL distilled water and then added in the reaction flask. In this synthesis, 75% neutralized acrylic acid was used. The neutralization of 75% acrylic acid was carried out by using 34.5% solution of sodium hydroxide until pH of acrylic acid is reached upto 4.5 and then the specified amount was added in the three neck flask. The NMBA in the specified amount was dissolved in 5 mL distilled water and introduced into three neck flask. Now the reaction mixture in the flask was stirred and heated continuously and sodium humate was dissolved in 10 mL distilled water, and then added to the reaction mixture for 6 h. The reaction was continued until the hydrogel was formed. Afterwards hydrogel was removed from flask and washed with 100 mL distilled water for 1 h, under unstirred condition. This process was repeated 4 times till the water became clear from the residue of sodium humate which is brown in colour. Afterward the washed hydrogel was dried in oven at 70 °C up to a constant weight.

Dynamic Swelling Behaviour

The completely dried superabsorbent hydrogel having approximately 0.50–0.51 g small rectangular shape was placed in 1500 mL containing distilled water (sink condition) at room temperature. The swollen hydrogel was taken in bath container at 1 h intervals; it was kept in the same bath container again. The mass measurements of swollen hydrogel were continued until no increment in weight of hydrogel was observed. The equilibrium swelling ratio (S_{eq}) was express following conventional gravimetric technique using the following equation

$$S_{eq}(g/g) = \frac{\text{Equilibrium Swollen weight} - \text{Dry weight}}{\text{Dry weight}}. \quad (1)$$

Fourier Transforms Infrared Spectroscopy (FTIR) Studies

The FTIR spectra of (AAc/NaAlg/SH) superabsorbent were recorded with Perkin Elmer spectrophotometer using solid pellet potassium bromide (KBr) after completely drying the sample at 60 upto constant weight.

Scanning Electron Microscopy (SEM)

The surface morphology of various poly (AAc/NaAlg/SH) hydrogels was examined under scanning electron microscopy (SEM). Dried hydrogels were covered with a thin

layer of pure gold in S150 Sputter coater, and imaged in a SEM (LEO Electron Microscopy Ltd. England).

Measurement of Metal Ions and Dyes Molecules Adsorption

First of all the aqueous solution of metal ion/dye was made by dissolving them in distilled water. Absorbance of this solution at corresponding λ_{max} was measured with double beam UV–VIS spectrophotometer (Perkin Elmer) using double distilled water as reference. To set up new calibration curve, the basic method ‘Standard Curve’ was selected and the parameters ‘wavelength’, ‘number of reference standards’, ‘units’ and ‘curve fit’ were entered. Then the concentration details for all reference standards were provided. During adsorption analysis, the instrument automatically enters the measured absorbance value for the respective reference standards. As the absorbance values were high (i.e. greater than 0.8), the solution was diluted with distilled water to a suitable degree, so that the absorbency values fall in between 0.2 and 0.8 approximately. This process was repeated by varying the degree of dilution for 6–8 different concentrations in order to get sufficient point for graph plotting. From the reference standard concentration and the value measured, the instrument automatically calculated the calibration curve. The calibration curve is drawn between absorbance versus concentration and it is a straight line passing through the origin. When a calibration curve is found to be reproducible, then calibration curve was used for further series of analyses.

SAHs were taken in 100 mL of metal ions salt solutions and dyes solution for the adsorption study. The solutions were left for 48 h, then the amount of hydrogel was added and the quantity of ions/dyes left in solution was analyzed by UV VIS spectroscopy.

The adsorption capacity was calculated by the equation

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

where C_o is the initial ion concentration, C_e is the equilibrium concentration V is the volume, and m is the mass of superabsorbent hydrogel of metal ions/dye molecules.

Desorption of Metal Ion/Dye Loaded (AAc/NaAlg/SH) SAHs

Elution of metal ions from the superabsorbent hydrogels was carried out in 25 mL of 0.1 M HNO_3 solution (elution medium) for 24 h. The metal ions loaded SAHs were placed in the elution medium and stirrer continuously. The superabsorbent hydrogel sample was washed with distilled water and the dried at 60 °C for 24 h. The dye molecules were recovered in the distilled water as elution medium.

The concentration of the final metal ion and dyes in the aqueous phase was determined by UV–VIS spectroscopy.

Desorption ratio was analyzed by following equation

$$\text{Desorption ratio} = \frac{\text{Amount of metal ions/dye desorbed to the elution medium}}{\text{Amount of metal ions/dye adsorbed on the superabsorbent hydrogel}} \times 100 \quad (3)$$

In order to determine the reusability of the SAHs consecutive adsorption desorption cycle was repeated of the five times of same sample shown in Tables 6 and 7.

Result and Discussions

FTIR Spectra

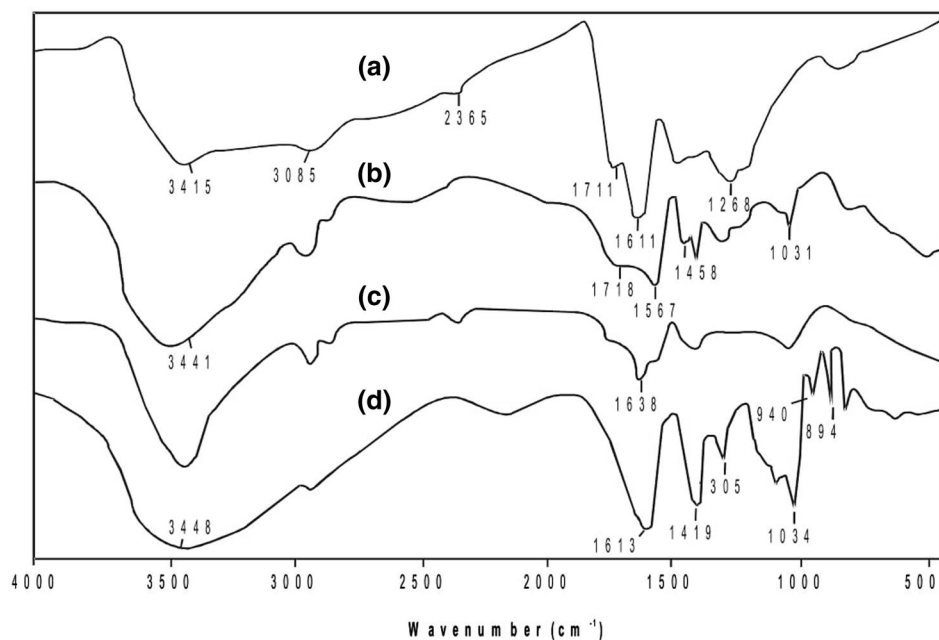
IR spectra of NaAlg/AAC, SH, NaAlg are shown in Fig. 1. In Fig. 1d the absorption bands at 1613 and 1419 cm^{-1} for the COO^- group shift to 1567 and 1458 cm^{-1} respectively and the absorption band 940 and 894 cm^{-1} disappeared in IR spectrum of NaAlg/PAA Fig. 1b suggested the reaction of AAC on NaAlg. Comparing with IR spectrum of Fig. 1a the absorption bands at 1711 cm^{-1} (C=O stretching of carboxylic group of SH), 1611 cm^{-1} ($-\text{COO}^-$ asymmetric stretching of SH) and 1268 cm^{-1} (phenolic C–O stretching of SH) almost disappeared in the spectrum of AAC/NaAlg/SH superabsorbent hydrogels. The results obtained from IR analysis showed that the reaction of both NaAlg and SH with acrylic acid monomer took place during the polymerization process. The free radicals on NaAlg initiated the

polymerization of AAC and SH and then formed superabsorbent network [15].

Scanning Electron Microscopy (SEM)

The adsorption of metal ions Pb^{2+} , Cu^{2+} and MB, CV dyes were confirmed by SEM analysis Fig. 2 shows the images of poly (AAC/NaAlg/SH) SAHs, the SEM image of Fig. 2a is the before image of metals/dyes adsorption, but the SEM image shown in Fig. 2b–e are the after metal ions/dyes adsorption images. Figure 2a shows the large depression surface area because (Fig. 2a) sample was contact in the solution of dye/metal ions. Besides this (Fig. 2b–e) contact in solution of Pb^{2+} , Cu^{2+} , metal ions CV and MB dye respectively. The change in surface morphology after adsorption of metal ions and dyes support the successful by the S_3 SAHs. SEM images of SAHs indicated their highly porous structure that allows better accessibility of dye molecules and metal ions to the adsorbent [16]. The adsorption of dyes and metal ions on SAHs were confirmed by SEM images metal ions loaded and dyes loaded SAHs as pores got closed after the adsorption of dyes and metal ions on SAHs. These evidences clearly reveal that metal ions/dyes adsorption have a prominent effect on the structure of poly (AAC/NaAlg/SH) SAHs S_3 surface by sealing the pores [17].

Fig. 1 FTIR spectra of (a) SH, (b) NaAlg/AAC, (c) AAC/SH/NaAlg, (d) NaAlg Superabsorbent hydrogels



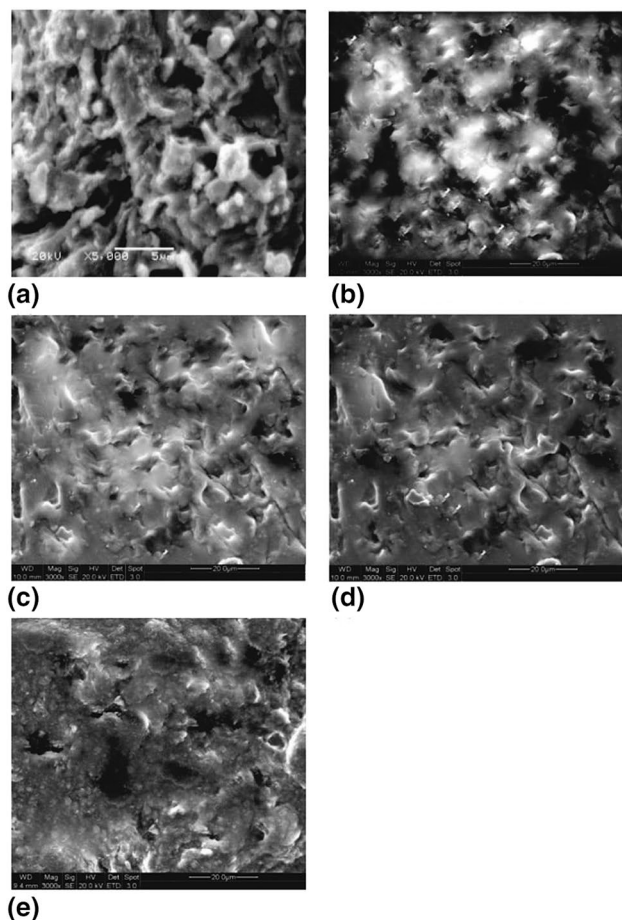


Fig. 2 a SEM of micrographs of (AAc/NaAlg/S₃) SAHs b poly(AAc/NaAlg/S₃) SAHs after swelling in Pb (II) ions solution c poly(AAc/NaAlg/S₃) SAHs after swelling in Cu(II) ions solution d (AAc/NaAlg/S₃) SAHs after swelling in CV dye solution e (AAc/NaAlg/S₃) SAHs after swelling in MB dye solution

Study on the Effect of Sodium Humate Content on Metal Ion/Dye Adsorption

In order to observe the influence of SH content on Cu²⁺ ions, Pb²⁺ ions, Fe²⁺ metal ions and MB, CV dye adsorption six SAHs samples S₀, S₁, S₂, S₃, S₄ and S₅ having different concentration of SH were selected. Figure 3 shows that the under the same conditions the removal capacities of poly (AAc/NaAlg/S₃) with different concentration of SH are different. SAHs with SH showed higher removal capacity than those without SH. It was observed that adsorption capacity for metal ions/dyes increases uptill the SH content reaches 9.09 wt%. This increase can be due to the fact that SH has many functional groups his may be attributed due to fact that as SH has many functional groups which have the ability to react with AAc and NaAlg during polymerization/crosslinking process that could progress the polymeric

group and then increase the adsorption capacity to a certain extent [18]. Comparable type of effect have been done by Liu et al. studied chitosan-g-poly (acrylic acid)/SH containing different amount of SH for superabsorbent hydrogel [19]. However, increasing the SH concentration beyond 9.09 wt% lead to decrease in adsorption capacity. This can be because there is large number of –OH groups on surface of SH. Thus SH particles may act as crosslinking points in polymeric web.

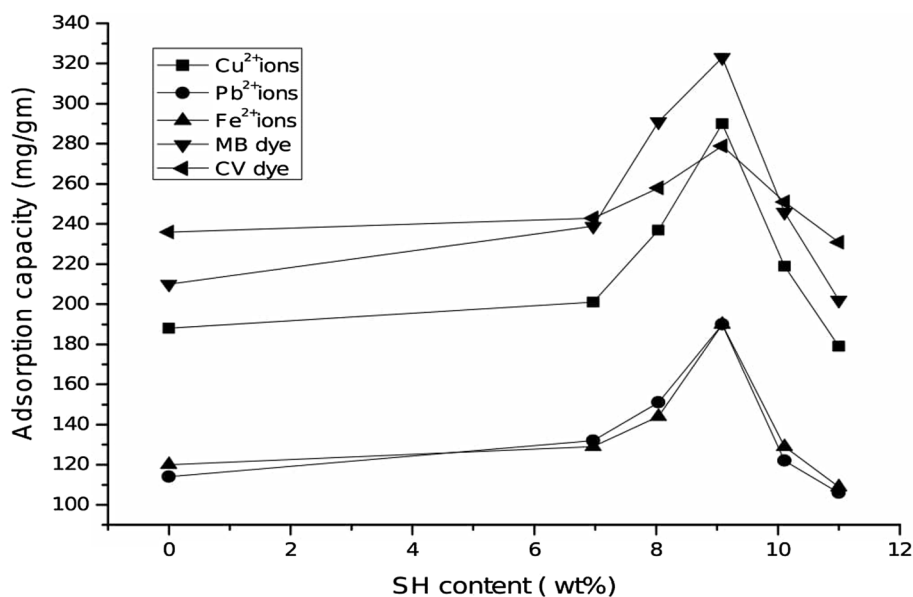
Effect of SH Content on Cu²⁺/Pb²⁺/Fe²⁺ Ions Adsorption

The reaction time is important feature of adsorption process of heavy metals in a solution phase [20]. The study of proper adsorption heavy metal ions is important for certain economic reasons in waste water management. Figure 4a–c shows the change in Cu²⁺/Pb²⁺/Fe²⁺ ions adsorption capacity. When the SH content in AAc/NaAlg/S₃ SAHs is varied. It can be analysed from Fig. 4a, Cu²⁺ ions at the adsorption equilibrium capacities are found to be 188, 201, 237, 290, 219, 179 mg/g/L for S₀, S₁, S₂, S₃, S₄, S₅ respectively, Fig. 4b Pb²⁺ ions at the adsorption equilibrium capacities are found to be 114, 132, 151, 190, 122, 106 mg/g/L for S₀, S₁, S₂, S₃, S₄, S₅ respectively and Fig. 4c Fe²⁺ ions at the adsorption equilibrium capacities are found to be 120, 129, 144, 190, 129, 109 mg/g/L for S₀, S₁, S₂, S₃, S₄, S₅ respectively. It can be experimental from the Fig. 4a–c that under the same conditions the removal capacities of poly (AAc/NaAlg/S₃) SAHs with different concentration of SH are different. Poly (AAc/NaAlg/S₃) SAHs showed higher removal capacity. The initial high adsorption could be attributed to the availability of the active adsorption sites suitably exposed on the surface of SAHs for adsorption of metal ions and as the time passes these active sites becomes saturated and equilibrium is achieved. It was observed that SAHs with SH showed higher removal capacity than those without SH which can be because of presence of many –OH groups on the surface of SH, thus SH particles may be act as crosslinking points in polymeric network. Similar types of result have been studied by Yi et al. studied that proper SH content of hydrogels was essential for the adsorption for SH/poly (*N*-isopropylacrylamide) hydrogels [12].

Effect of Initial Concentration of Cu²⁺/Pb²⁺/Fe²⁺ Ions on Adsorption Capacity

To study the effect of initial ion concentration on adsorption capacity five SAHs sample S₁, S₂, S₃, S₄, and S₅ were prepared, and then fixed amount of each sample (50 mg) was equilibrated with a series of Cu²⁺ Pb²⁺ and Fe²⁺ ions solutions of gradually increasing concentration, ranging

Fig. 3 Variation in the adsorption capacity of poly (AAc/NaAlg/SH) SAHs for Cu^{2+} / Pb^{2+} / Fe^{2+} ions, MB and CV dye as a function of SH concentration



from 250 to 1050 mg/L. Figure 5a–c shows the variation of adsorption capacity as a function of initial ion concentration. Solution with the 850 mg/L Cu^{2+} , Pb^{2+} and Fe^{2+} ions shows maximum removal of 311, 209, 197 mg/gm/L for S_3 superabsorbent hydrogels. After increasing the concentration to 1050 mg/L, adsorption capacity decrease to 323, 216 and 210 mg/gm/L. Initial ion concentration is one of the most important investigation as initial concentration of Cu^{2+} , Pb^{2+} and Fe^{2+} ions affects the adsorption amount of Cu^{2+} , Pb^{2+} and Fe^{2+} ions and adsorption kinetics, this is why effect of initial concentration on adsorption capacity was investigated. This can be explained as a fact of that initial metal ion concentration can provide the heavy force to conquer the resistance to the mass transport of metal ions between liquid and solid state [21]. From the Fig. 5a–c was observed, that adsorption capacity of metal ions increased with rising initial concentration of metal ions. The investigation of initial ion concentration is very important because it affects both, the adsorption amount of Cu^{2+} , Pb^{2+} and Fe^{2+} ions and the adsorption kinetics. All through the early phase of adsorption, a huge amount of empty face were available for adsorption. After a go down in time, the remain empty surface were occupied due to revolting forces among the solute molecules on the adsorbent exterior and the bulk stage [22].

Adsorption Isotherm for the Adsorption of Cu^{2+} / Pb^{2+} / Fe^{2+} Ions onto (AAc/NaAlg/SH) SAHs

Adsorption isotherms technique were determine the relationship between the concentration of ion solution and

the ions adsorbed on the solid phase when two phase are equilibrium. The experimental data for the adsorbed Cu^{2+} , Pb^{2+} and Fe^{2+} ions by AAc/NaAlg/SH (SAHs) have been calculated from Langmuir isotherm model of adsorption [23]. The Langmuir model checked the taken of metal ions is monolayer sorption with no any interaction among adsorbed ions [24]. The Langmuir isotherms equation is represented as

$$\frac{C_e}{q_e} = \frac{1}{K_e q_{\max}} + \frac{C_e}{q_{\max}}$$

where C_e is the equilibrium concentration mg/L, q_e , the amount uptake at equilibrium mg/gm/L, K_e and q_{\max} are Langmuir constants allied to energy of adsorption and adsorption capacity i.e. the quantity of adsorbate necessary covering a monolayer. The values of q_{\max} and K_e of Cu^{2+} , Pb^{2+} and Fe^{2+} ions are shown in Table 2 together with regression coefficient. The calculated monolayer adsorption capacity q_e for Cu^{2+} ions 201, 237, 290, 219, 179 mg/gm/L for Pb^{2+} ions, 132, 151, 190, 122, 106 mg/gm/L and for Fe^{2+} ions was 129, 144, 190, 129, 109 mg/gm/L for S_1 , S_2 , S_3 , S_4 , S_5 samples respectively. The applicability of Langmuir model and higher values of regression coefficient (R^2) value was found in the range of 0.990–0.993, 0.946–0.997, 0.993–0.997 which indicated favourable adsorption [25].

The equilibrium adsorption of ions Cu^{2+} , Pb^{2+} and Fe^{2+} of our S_3 hydrogel was compared with the other researchers work in Table 3. It can be seen that the q_{\max} value of AAc/NaAlg/SH SAHs was best than those of other adsorbents in treatment of waste waters containing heavy metal ions.

Fig. 4 **a** Influence of SH concentration on the adsorption capacity for Cu(II) ions of AAc/NaAlg/SH SAHs with different amount of SH content. **b** Influence of SH concentration on the adsorption capacity for Pb(II) ions of AAc/NaAlg/SH SAHs with different amount of SH content. **c** Influence of SH concentration on the adsorption capacity for Fe(II) ions of AAc/NaAlg/SH SAHs with different amount of SH content

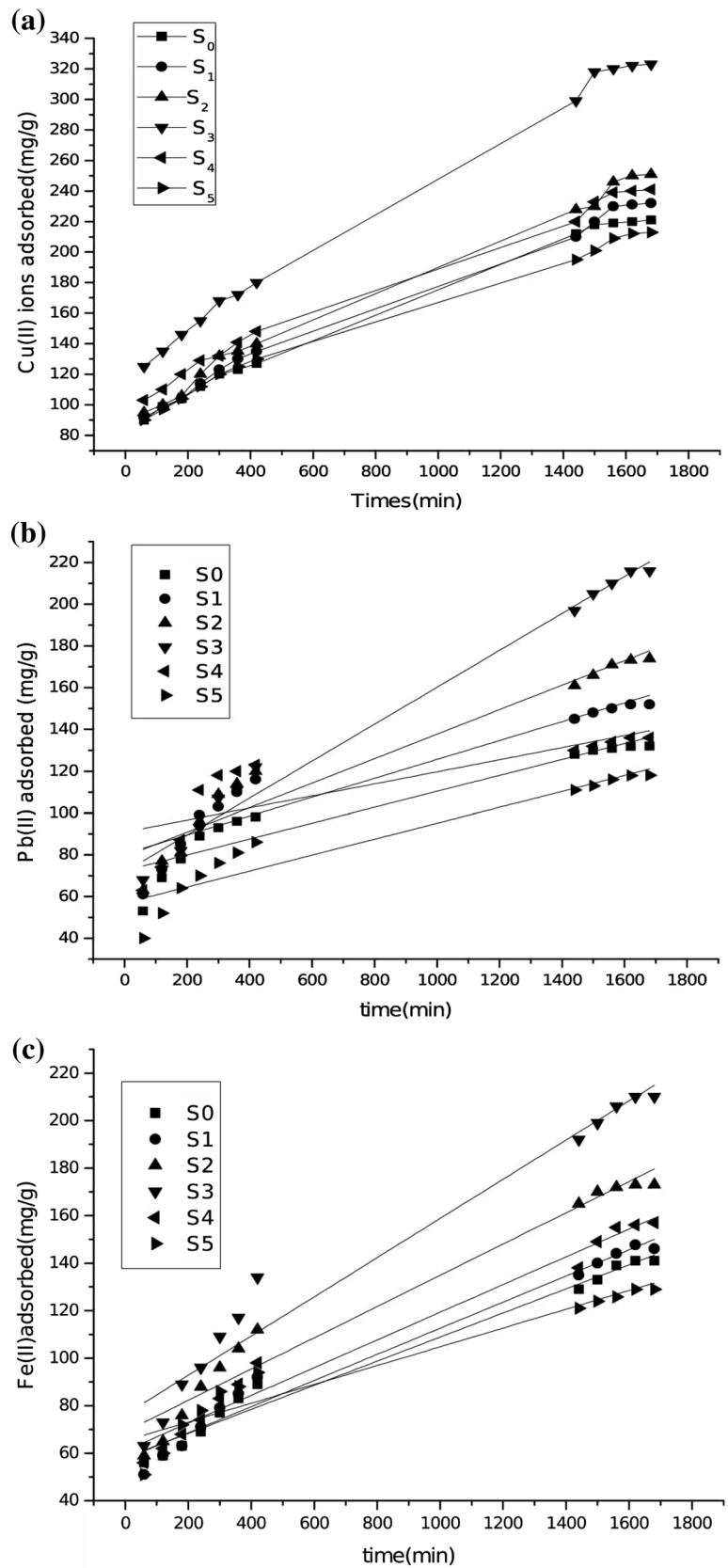


Fig. 5 **a** Variation in the adsorption capacity as function of initial Cu(II) ions concentration using AAC/NaAlg/S_H SAHs with the different amount of SH. **b** Variation in the adsorption capacity as function of initial Pb(II) ions concentration using (AAC/NaAlg/S_H) SAHs with the different amount of SH. **c** Variation in the adsorption capacity as function of initial Fe(II) ions concentration using (AAC/NaAlg/S_H) SAHs with the different amount of SH

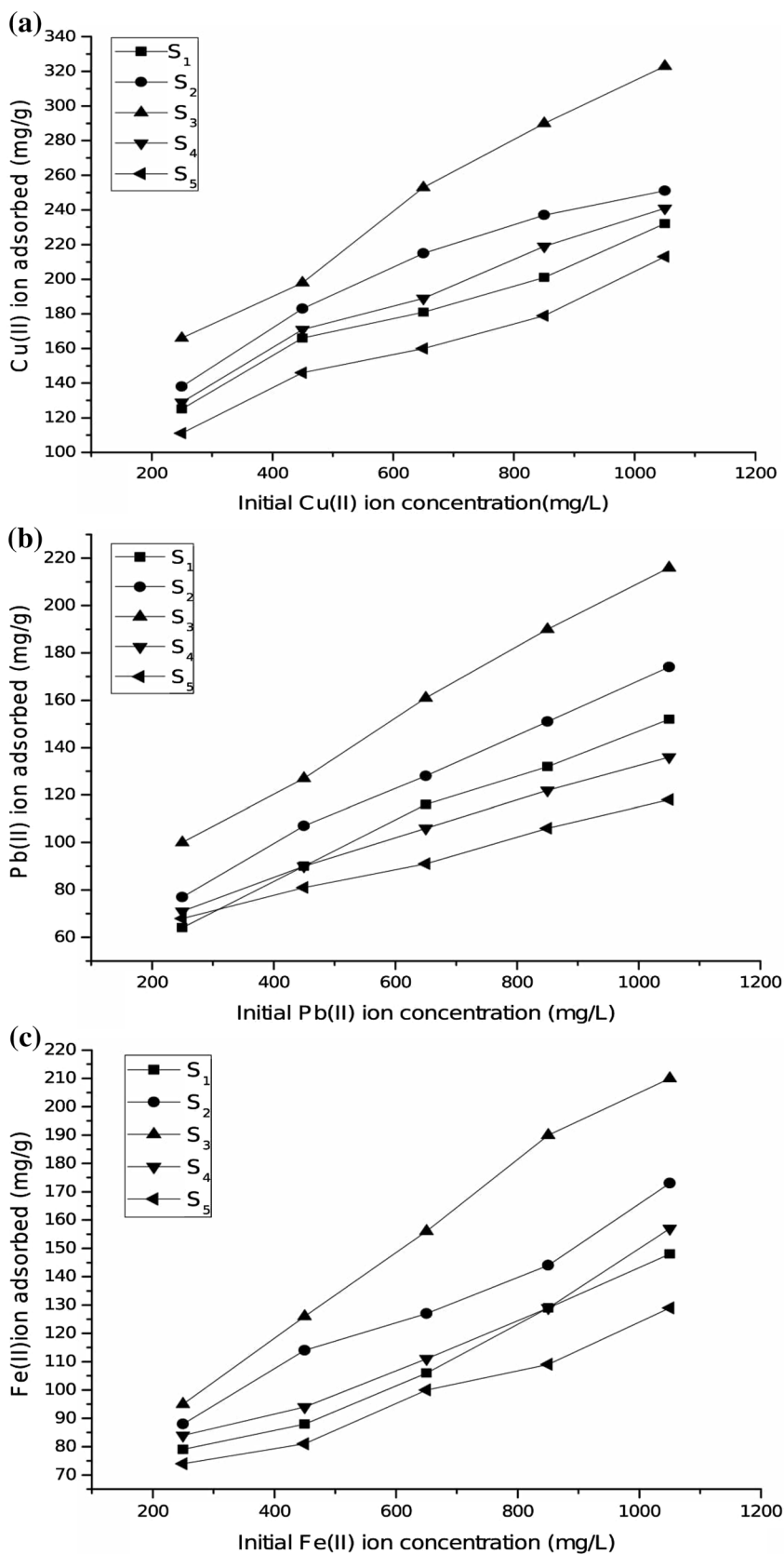


Table 2 Langmuir coefficients q_{\max} and K_e for the adsorption of Cu^{2+} , Pb^{2+} and Fe^{2+} ions on AAc/NaAlg/SH SAHs in aqueous solutions together with the regression coefficient (R^2)

Sample designation	Cu^{2+}			Pb^{2+}			Fe^{2+}					
	q_e (mg/g)	q_{\max} (mg/g)	$K_e \times 10^2$ (L/mg)	R^2	q_e (mg/g)	q_{\max} (mg/g)	$K_e \times 10^2$ (L/mg)	R^2	q_e (mg/g)	q_{\max} (mg/g)	$K_e \times 10^3$ (L/mg)	R^2
S ₁	201	232	60.2	0.990	132	152	49.5	0.94	129	148	51	0.990
S ₂	237	251	49.5	0.996	151	174	50.0	0.96	144	173	64	0.993
S ₃	290	323	46.3	0.999	190	216	46.2	0.99	190	210	48	0.996
S ₄	219	241	59.2	0.997	122	1361	52.0.1	0.992	129	157	50	0.985
S ₅	179	213	72.3	0.995	106	18	53.2	0.990	109	129	53	0.992

Effect of SH Content on the Adsorption of MB and CV Dye Molecules

The reaction time is important feature of adsorption process of heavy metals in a solution phase [20]. The study of proper adsorption time of heavy metal ions is important for certain economic reasons in waste water management. Figure 6a, b shows the after in MB and CV adsorption capacity. When the SH content in AAc/NaAlg/SH SAHs is varied. It can be analyzed from Fig. 6a, that for the MB molecules that at the adsorption equilibrium the adsorption capacities are found to be 210, 239, 291, 323, 246, 202 mg/gm/L for S₀, S₁, S₂, S₃, S₄, S₅ respectively. Figure 6b that for the CV molecules that at the adsorption equilibrium the adsorption capacities are found to be 236, 243, 258, 279, 251, 231 mg/gm/L for S₀, S₁, S₂, S₃, S₄, S₅ respectively. It is clear the effect of SH content on MB, CV dyes molecules adsorption capacity for AAc/NaAlg/SH (SAHs) S₀, S₁, S₂, S₃, S₄, S₅ respectively. It can be observed from the Fig. 6a, b that under the same conditions the removal capacities of (AAc/NaAlg/SH) SAHs with different concentration of SH are different. Poly (AAc/NaAlg/SH) SAHs showed higher removal capacity. It was observed that SAHs with SH showed higher removal capacity than those without SH which can be because of presence of many –OH groups on the surface of SH, thus SH may be act as crosslinking points in polymeric network. Comparable types of result have been investigated by Yi et al. studied that proper SH content of hydrogels was essential for the adsorption for SH/poly (*N*-isopropylacrylamide) hydrogels [12].

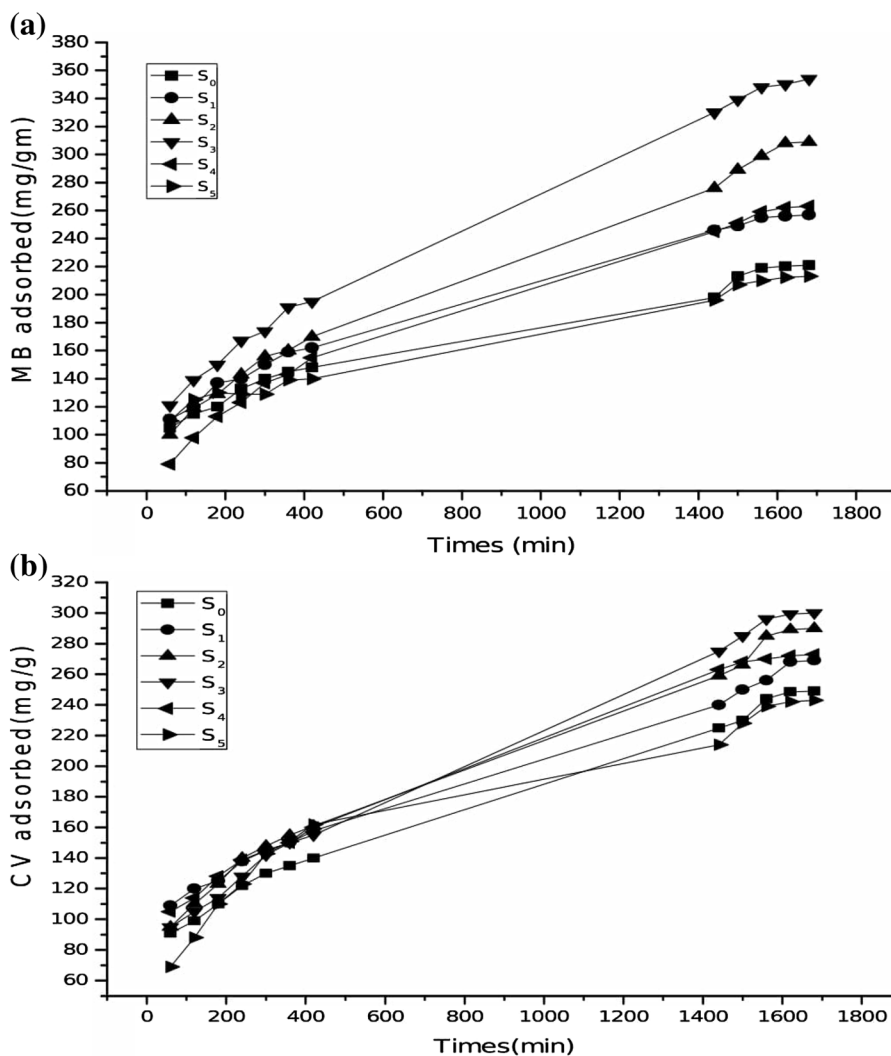
Effect of Initial Concentration of MB and CV Dyes Molecules on Adsorption Capacity

To study the effect of initial ion concentration on adsorption capacity five SAHs sample S₁, S₂, S₃, S₄, and S₅ were prepared, and then fixed amount of each sample (50 mg) was equilibrated with a series of MB and CV dyes solutions of gradually increasing concentration ranging from 160 to 400 mg/L. Solution with the 360 mg/L MB and CV dye shows maximum removal of 323, 289 mg/gm/L, for S₃ superabsorbent hydrogels. After increasing the concentration to 400 mg/L, adsorption capacity decreases to (341, 300 mg/gm/L) shown in Fig. 7a, b. Initial ion concentration is one of the most important investigations as initial concentration of MB and CV dyes and adsorption kinetics; this is why effect of initial concentration on adsorption capacity was investigated. This result may be due to the use of free adsorption sites on the adsorbent surface. During the early stage of sorption, a large number of free surface sites

Table 3 Comparison table for removal capacities (q_e) of Cu^{2+} , Pb^{2+} and Fe^{2+} by various adsorbent

Adsorbents	Metallions investigate	Q_{\max} (mg/g)	References
Chitosan itaconic acid and methacrylic acid	Cu^{2+} ion	122	[26]
Chitosan/perlite	Cu^{2+} ion	196.07	[27]
Poly(AAc/NaAlg/S _H)	Cu^{2+} ion	311	This work
Poly2-hydroxyethyl methacrylate (PHEMA) and copolymer 2-hydroxyethyl methacrylate with monomer methyl methacrylate P(MMA–HEMA)	Pb^{2+} ions	31.447	[28]
Poly (ethylene glycol dimethacrylate- <i>n</i> -vinyl imidazole) [poly(EGDMA–VIM)] hydrogel	Pb^{2+} ions	114.8	[29]
(AAc/NaAlg/S _H) SAHs	Pb^{2+} ions	209	This work
Chitosan nanohydrogels	Fe^{2+} ions	78	[30]
P(NVP–AAc–AMPS)	Fe^{2+} ions	40.9	[31]

Fig. 6 a Influence of SH concentration on the adsorption capacity for MB molecules of (AAc/NaAlg/S_H) SAHs with different amount of SH content. **b** Influence of SH concentration on the adsorption capacity for CV molecules of AAc/NaAlg/S_H hydrogels with different amount of SH content

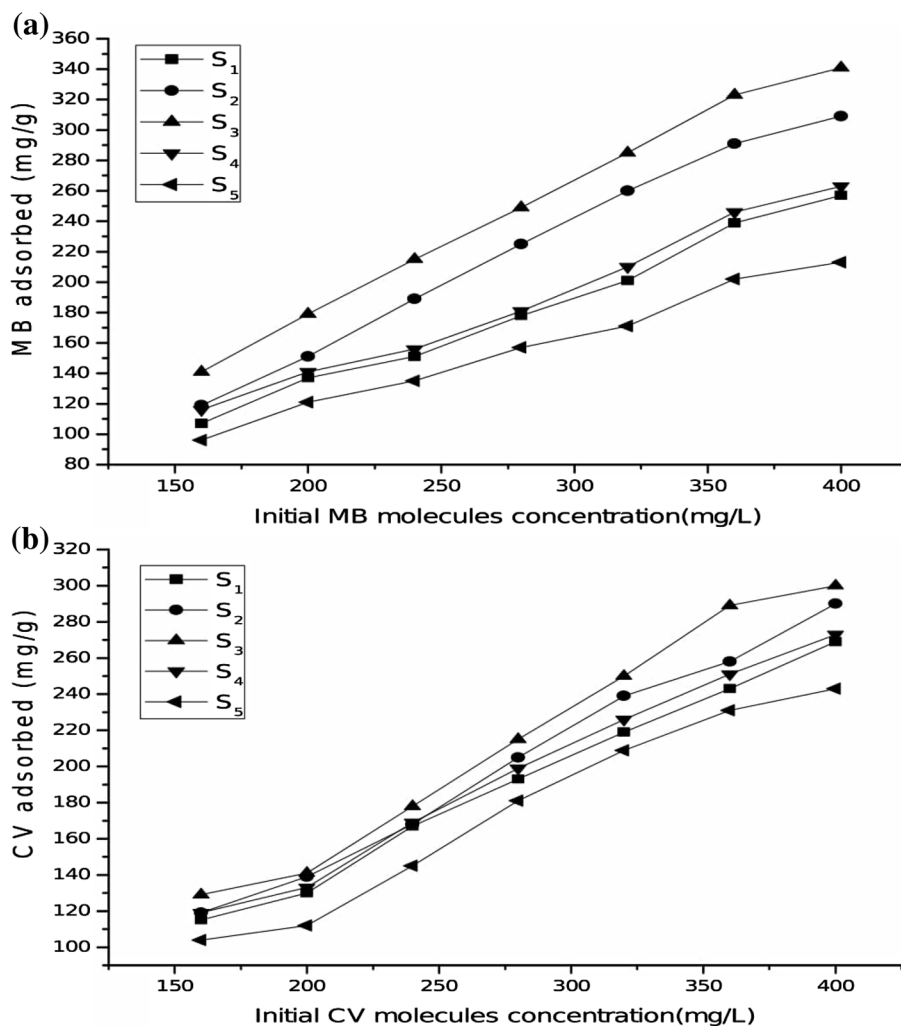


were available for adsorption phenomena. After a go down in time, the remain free surface sites were occupied due to revolving hold between the solute molecules on the adsorbent surface and the bulk stage [22].

Adsorption Isotherm for the Adsorption of MB and CV Dyes Molecules onto (AAc/NaAlg/SH) SAHs

Adsorption isotherms technique were determine the relationship between the concentration of ion solution and the

Fig. 7 a Variation in the adsorption capacity as function of initial MB dye concentration using (AAc/NaAlg/S_H) SAHs with the different amount of S_H. **b** Variation in the adsorption capacity as function of initial CV ions concentration using (AAc/NaAlg/S_H) with the different amount of S_H



ions adsorbed on the solid phase when two phase are equilibrium. The experimental data for the adsorbed MB and CV dye molecules by AAc/NaAlg/S_H (SAHs) have been calculated from Langmuir isotherm model of adsorption [23]. The Langmuir model checked the taken of dye is monolayer sorption with no any interaction among adsorbed ions [24]. The Langmuir isotherms equation is represented as

$$\frac{C_e}{q_e} = \frac{1}{K_e q_{max}} + \frac{C_e}{q_{max}}$$

where C_e is the equilibrium concentration mg/L, q_e , the amount uptake at equilibrium mg/gm/L, K_e and q_{max} are Langmuir constants allied to energy of adsorption and adsorption capacity i.e. the quantity of adsorbate necessary covering a monolayer. The applicability of the Langmuir isotherm of the dye on the surface of AAc/NaAlg/S_H (SAHs) defined the monolayer contact. The value of q_{max} and K_e were shown in (Table 4) together with regression coefficient. The calculated monolayer adsorption capacity

q_{max} for MB molecules 257, 309, 323, 263, 213 mg/gm/L for CV molecules 269, 290, 289, 273, 243 mg/gm/L for S₁, S₂, S₃, S₄, S₅ samples respectively. Similar behaviour was also found for the adsorption of MB quaternary ammonium compounds modified montmorillonite and kappa-Carrageenan beads for CV dyes [32, 33]. The applicability of Langmuir model and higher values of regression coefficient (R^2) value were found in the range of (0.986–0.989, 0.969–0.975) showed favourable and monolayer adsorption [25]. The equilibrium adsorption of dye MB and CV of our S₃ hydrogel was compared with the other researchers work shown in (Table 5). It can be seen that the q_{max} value of AAc/NaAlg/S_H (SAHs) was best than those of other adsorbents in treatment of waste waters containing MB and CV dyes.

Desorption or Regeneration of Adsorbent

The desorption studies are very important as it deals with the recovery and revival of adsorbent. In this way the

Table 4 Langmuir coefficients q_{max} and K_c for the adsorption of methylene blue and crystal violet dye on AAc/NaAlg/SH SAHs in aqueous solutions together with the regression coefficient (R^2)

Sample Des-ignation	Methylene blue				Crystal violet			
	q_e (mg/g)	q_{max} (mg/gm)	$K_c \times 10^2$ (L/mg)	R^2	q_e (mg/g)	q_{max} (mg/g)	$K_c \times 10^2$ (L/mg)	R^2
S ₁	239	257	30.7	0.986	243	269	35	0.969
S ₂	291	309	20.1	0.985	258	290	29	0.978
S ₃	323	341	49	0.996	289	300	19.7	0.995
S ₄	246	263	29.3	0.951	251	273	30	0.965
S ₅	202	213	35.29	0.983	231	243	49	0.953

Table 5 Comparison table for removal capacities (q_e) of methylene blue (MB), crystal violet (CV) by various adsorbent

Adsorbents	Dyes investigate	q_{max} (mg/g)	References
Rice husk	MB	40.60	[34]
Modified gum Arabic, polyacrylate, and polyacrylamide	MB	48	[35]
Chitosan hydrogels beads	MB	129.44	[36]
Magnetic bionanocomposite based carrageenan	MB	130.42	[37]
Poly(AAc/NaAlg/SH)	MB	323	This work
Poly(sodium acrylate)-carrageenan/Na-montmorillonite nanocomposite superabsorbents	CV	29.6	[38]
AAm/Laponite clay	CV	95.56	[39]
CarAlg/MMt nanocomposite hydrogels	CV	83.33	[40]
Magnetic kappa-carrageenan/PVA nanocomposite	CV	78.2	[41]
Carra-g-poly MMA (with% 30 Fe ₃ O ₄)	CV	172.4	[42]
(AAc/NaAlg/SH) SAHs	CV	289	This work

Table 6 Adsorption amount of Cu²⁺ ion after repeated adsorption–desorption cycle

Cycle No.	S ₁		S ₂		S ₃		S ₄		S ₅	
	A	D	A	D	A	D	A	D	A	D
1	201	98.9	237	98.6	311	99.9	219.7	96.9	179.8	95.8
2	200	98.9	236.6	98.8	310.8	99.8	218.7	96.7	178.7	96.7
3	200	98.10	236.4	98.7	310.4	99.6	218.6	96.5	178.7	96.6
4	200	98.10	235.8	98.8	310.2	99.5	218.5	96.3	178.4	96.5
5	200	98.11	235.2	98.7	310.1	99.1	218.3	96.2	178.4	96.3

Table 7 Adsorption amount of MB dye after repeated adsorption–desorption cycle

Cycle No.	S ₁		S ₂		S ₃		S ₄		S ₅	
	A	D	A	D	A	D	A	D	A	D
1	239	98.8	291	99.7	323	99.8	246	96.8	189	95.8
2	238.5	98.7	290	99.6	322.48	99.7	246	95.7	188.5	95.7
3	238.7	98.5	290	99.5	322.10	99.6	245	95.7	188.3	95.6
4	238.6	98.5	290	99.5	322	99.6	245	95.7	188	95.6
5	238.1	98.5	290	99.5	322	99.1	245	95	188	95.5

A adsorption (mg/g), D desorption (%)

desorption studies helped to recover the Cu²⁺ ions and MB dye molecules from the adsorbent by superabsorbent hydrogels, due to which it can be used again and again for

the further adsorption. As seen in Tables 6 and 7 the SAHs poly (AAc/NaAlg/SH) showed Cu²⁺ ions and MB dye removal capacities after repeated regeneration respectively.

The poly (AAc/NaAlg/SH) superabsorbent hydrogel samples which were used for the adsorption of Cu^{2+} ions and MB dye molecules were placed in elution medium (25 mL of 0.1 M HNO_3) solution for Cu^{2+} and distilled water for MB dye for 24 h and the amount of Cu^{2+} ions and MB dye molecules desorbed to the elution medium was measured using Eq. (3). As seen in Tables 6 and 7. The synthesised adsorbent exhibited excellent removal capacity for Cu^{2+} ions and MB dye and could be considered as a latest candidates for solving ecological effort.

Conclusion

In this present work the polymerized AAc/NaAlg/SH (SAHs) was used in the adsorption study for metal ions (Cu^{2+} , Pb^{2+} and Fe^{2+}) and dyes (MB and CV) having variation of Sodium Humate (6.97–11 wt%) content. The present work showed that both metal ions (Cu^{2+} , Pb^{2+} and Fe^{2+} ions) and CV and MB dyes were removed more effectively and in high quantities from aqueous solutions. Superabsorbent hydrogels (SAHs) S_3 have highest removal capacity for metal ions (Cu^{2+} , Pb^{2+} and Fe^{2+}) and dyes (MB and CV). The binding capacity of metal ion and dyes molecules of superabsorbent hydrogels were also studied. The binding capacity for Cu^{2+} , Pb^{2+} , Fe^{2+} ions were 311 mg/gm/L at 850 mg/L, 209 mg/mg/L at 850 mg/L and 197 mg/gm/L at 850 mg/L for initial ion concentration respectively, MB and CV dyes molecules were 323 mg/gm/L at 360 mg/L, 289 mg/gm/L at 360 mg/L for initial molecule concentration respectively. The adsorption isotherms for dyes and metal ions agree well with the Langmuir model. In this present work results proposed that AAc/NaAlg/SH superabsorbent hydrogels assure to exist the prospective adsorbents for the removal of heavy metal ions Cu^{2+} , Pb^{2+} , Fe^{2+} and MB and CV from waste water and aqueous effluents.

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