

Reuse of a Waste Adsorbent Poly(AAc/AM/SH)-Cu Superabsorbent Hydrogel, for the Potential Phosphate Ion Removal from Waste Water: Matrix Effects, Adsorption Kinetics, and Thermodynamic Studies

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ABSTRACT: The most commonly applied methods for the treatment of used adsorbents is to recover them in acid/alkaline medium or direct enflame them. This work dealt with a new potential and economic method to utilize a waste adsorbent. Poly(AAc/AM/SH) superabsorbent hydrogels have proved to be a good adsorbent for Cu^{2+} ions and after adsorption the hydrogels were recovered in acid medium. In this report, the Cu^{2+} ion adsorbed hydrogel has not undergone any regeneration process and applied directly to phosphate ion adsorption. The Cu^{2+} ions-loaded poly(AAc/AM/SH) hydrogels, were stable within a wide pH range and suitable for phosphate ion adsorption. The factors affecting the phosphate adsorption, such as pH, ionic strength, contact time, temperature, initial concentration of the phosphate ion, and coexisting ions were systematically investigated. The phosphate adsorption was highly pH dependent; and the maximum adsorption of 87.62 mg/g was achieved at pH 6.1. The adsorption data fitted the Langmuir adsorption isotherm better than the Freundlich isotherm. The concomitant anions show profounder adverse influence on phosphate ion adsorption of poly(AAc/AM/SH)-Cu hydrogel and the effect follows the order citrate > sulfate > bicarbonate > chloride > nitrate. The thermodynamic parameters including ΔH° , ΔG° , and ΔS° for the adsorption processes of phosphate ions on the gel were also evaluated, and the negative ΔG° and ΔH° confirmed that the adsorption process was spontaneous and exothermic. The adsorption kinetic results suggest that the adsorption process was well described by the pseudo second-order kinetic model. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 3126–3139, 2013

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INTRODUCTION

Over the recent years, with the rapid development of modern industries there has been an increasing concern for environmental risk. These industries have increased the threat of water pollution to the environment. The chief water pollutant consist hydrocarbons, non biodegradable matter, dyes, metal ions, anions etc. that has been rapidly increased in water. Therefore, various efficient treatment methods have been developed. The commonly used waste water treatment technologies include chemical precipitation (with alum, lime, iron salts etc.), cross flow filtration, chelating ion exchange, crystallization, reverse osmosis, electrochemical treatment, neutralization, and adsorption.^{1–5} However among these methods the adsorption process is found to be a highly efficient, regenerable, economical, and promising method. Adsorption process is also beneficial in terms of good collection as well as reusability of adsorbate and adsorbents.^{6,7}

In this regard, more studies have been focused on novel adsorbents; and so a variety of adsorbents have been intro-

duced and used for treatment of wastewater. Superabsorbent hydrogels (SAHs) are a special class of adsorbents which are lightly crosslinked three dimensional macromolecular polymeric networks with the ability to absorb huge amounts of water and the absorbed water is hard to remove even under pressure. Development of hydrogel adsorbents is based on the interaction of adsorbate with the active chelating functional groups such as carboxylic acid, sulfonic acid, amine group, amine hydroxyl etc. and the selectivity, effectiveness, and reusability of these hydrogels can be determined by these functional groups. These active groups adsorb and trap the adsorbate molecules, and make them more effective adsorbent.⁸ With the development and optimization of these adsorbents, production of waste products also occurs in industrial sectors. These products mainly include the already used adsorbents, which were applied for the adsorption process. These waste adsorbents can be (i) recycled for again adsorption process by regenerating them in acidic/basic elution medium for next cycle,⁹ (ii) disposed or cremated.

For any adsorption process as the adsorption proceeded and reaches to equilibrium, the original polymeric backbone structure of adsorbent hydrogel changed (because of an embedding layer of adsorbate molecules, which are stable in their optimized conditions), and they can function as a new type of adsorbent. The alteration in original macromolecular structure after adsorption may provide a new potential way to utilize these already used adsorbents, which were after adsorption either discarded or may be recovered by acidic/alkaline medium.

In the past few decades, phosphate has been recognized as a substantial nonpoint-source pollutant through out the world because of over application of both animal-based and synthetic fertilizers,¹⁰ pigment formulation, water treatment, the electronic industry, detergents, and mineral processing.^{11,12} Phosphorus (P) usually occurs in low concentrations in wastewater almost in the form of phosphates, including inorganic phosphate (orthophosphate), organic phosphate, and polyphosphate (particulate P). The existence of trace concentration of phosphate in the waste-water from industries and municipalities is responsible for eutrophication problems that lead to growth of aquatic plants, and depletion of dissolved oxygen in coastal areas, lakes, and other water bodies. Industrial treated wastewater phosphate level is in excess of 10 mg/L. Municipal treated wastewater contains 4 to 15 mg/L phosphorus.¹³ Therefore industrial and municipal wastewater having phosphate must be treated before discharging. The U.S. Environmental Protection Agency has established a discharge limit for phosphate is 0.5–1.0 mg/L. According to Indian Standards Bureau, for phosphate discharge limit is 5 mg/L P.¹⁴ Therefore, to archive the levels of phosphate ion below the limits set by Indian Standards Bureau, in recent years a variety of efficient adsorbents have been developed and investigated for phosphate ion adsorption. Adsorption of phosphate was reported by many type of adsorbents that include iron oxides,^{15,16} polymeric ligand exchanger,^{17,18} aluminum salts,¹⁹ chitosan-*g*-poly(acrylic acid)/vermiculite ionic hybrid.²⁰

Acrylic acid is cheap, smart in nature, highly hydrophilic and act as a good chelating agent. Polyacrylamide have high hydrophilicity, good biocompatibility, excellent resilience, permeable to oxygen and its pendant amide group acts as efficient chelating group for the ionic and polar species.

The development of hydrogel having abundantly available natural raw materials which are low in cost, nontoxic, have high removal capacity, renewable, and biodegradable in nature such as humic acid or humates has been focused on. Humic acid, a principal component of humic substances and is found in many places in nature. It consists of multifunctional aliphatic components and aromatic constituents that contain large number of functional hydrophilic groups (including carboxylates and phenolic hydroxyls, NH₂ groups and oxygen and nitrogen as bridge units).²¹ Presence of these carboxylate and phenolate groups helps sodium humate to form complexes/chelates with metal ions.

It is accepted that the removal capacity of an adsorbent is highly affected by the adsorption conditions (such as pH, temperature, and ionic strength). Chitrakar et al.²² reported that the influence of pH on the adsorption of phosphate ions onto

goethite and akaganeite was significant, that was because of the fact that the pH value was related to the factors such as net positive charge of adsorbent as well as the concentration of hydroxide ion and the phosphate ion. It was also observed that the mass transport through the solid–liquid film in the process of ion adsorption affected the rate of adsorption. Chubar et al.²³ prepared a novel inorganic ion exchanger for phosphate removal. It was found that the maximum adsorption capacity was increased with the increase in ionic strength because of the participation of Cl[−] as intermediate stage in the adsorption process. Unuabonah et al.²⁴ applied the kaolinite clay to bentonite for removal of lead. It was concluded that the rate constant of adsorption process increased on increasing the temperature from 25°C to 40°C.

In our previous report we synthesized a biodegradable multifunctional superabsorbent hydrogel based on acrylic acid and acrylamide monomers modified with sodium humate, and used this as an adsorbent for removal of Cu²⁺ ions.²⁵ The hydrogel showed excellent Cu²⁺ ion adsorption capacity, and after adsorption it was recovered in dilute acidic medium. As poly(AAc/AM/SH) hydrogels show higher affinity towards Cu²⁺ ions but hardly adsorb anions such as phosphates because of its characteristics of negative charge present on the polymeric surface. After the adsorption of Cu²⁺ ions it became positively charged moiety and being capable of phosphate ion removal. Therefore this Cu²⁺ ion-loaded gel without any prior treatment serves as a new kind of adsorbent i.e., metal-loaded adsorbents. Previous studies showed that the metal-loaded adsorbent has proven as a good phosphate adsorbent. Wilaiwan Chouyyok et al.²⁶ reported the ability of cationic metal-EDA complexes anchored inside mesoporous silica [Copper(II)-ethylenediamine-self-assembled monolayers on mesoporous supports {Cu(II)-EDA-SAMMS} and Iron(II)- ethylenediamine-self-assembled monolayers on mesoporous supports {Fe(II)-EDA-SAMMS}] adsorbents to capture phosphate ions, and they confirmed that these metal-loaded adsorbents can effectively bind the phosphate ions. C.P. Novo et al.²⁷ studied the influence of phosphate ion on the Cu²⁺ ions adsorption and suggest that Cu²⁺ ions show high affinity towards the phosphate ion.

This study deals with an economical and potential method to treat a waste adsorbent. So, the novelty of the present work is to identify applicability of waste adsorbent poly(AAc/AM/SH)-Cu hydrogels for the adsorption of phosphate ions so that to provide a new potential way to use an already used adsorbent without any regeneration or purification process. Although there are several studies on the adsorption of metal ions by hydrogels, and then recover them in acidic or basic solution but none of them have reported the reuse of their already used adsorbent for another adsorption process without any prior treatment. The experiments were performed as a function of different pH, contact time, various initial concentrations of phosphate ion, temperature, and also in presence of different coexisting anions to determine the optimum conditions for the adsorption of phosphate ion from aqueous solution. Langmuir and Freundlich adsorption isotherm models were applied to the experimental isotherms and isotherms constants to validate the usefulness of this waste hydrogel in the field of wastewater

treatment. Thermodynamic parameters for the adsorption process of phosphate ions were also investigated. The desorption capacity and reusability of the solid adsorbent were assessed based on five consecutive adsorption–desorption cycles.

EXPERIMENTAL

Materials

Acrylic acid ((AAc), analytical grade), acrylamide ((AM), analytical grade), ammonium per sulfate ((APS), analytical grade), sodium hydroxide ((NaOH), analytical grade), *N, N*-methylene bisacrylamide ((NMBA), analytical grade), copper sulfate ((CuSO₄), analytical grade), potassium dihydrogen phosphate (KH₂PO₄), hydrochloric acid (HCl), sodium chloride (NaCl), sodium nitrate (NaNO₃), sodium bicarbonate, sodium sulfate (Na₂SO₄), sodium citrate were purchased from CDH New Delhi, India. Methanol (analytical grade) was purchased from Qualikems, New Delhi. Acrylamide was recrystallized from methanol before use. Sodium humate [(SH), analytical grade], (supplied from Aldrich) was used as received. Double distilled water was used throughout the experiments.

Synthesis of Poly(AAc/AM/SH) Superabsorbent Hydrogels

The detailed synthesis and adsorption behavior of poly(AAc/AM/SH) hydrogel was reported in our previous study,²⁵ in short the synthesis can be describe as-AAc (7 g) and AM (7 g) were dissolved in 30 mL distilled water. Then after neutralizing the reaction mixture with NaOH solution, the solution was poured in a 250-mL three-neck round bottom flask equipped with a stirring rod, a nitrogen inlet and a reflux condenser. Then (0.20 wt % of total monomer) NMBA was added to the monomer solution, subsequently dispersed SH (0.35 g) into mixed solution. The reaction mixture was stirred under nitrogen atmosphere for 30 min to remove the dissolved oxygen, after that the mixed solution was heated in a thermostat oil bath for 1 h at 60°C, and then the initiator, APS (0.40 wt % of total monomer), was introduced into the flask. The solution was again stirred under nitrogen atmosphere for 2 h at 60°C for homogeneity. Then the resulting reaction solution was poured into Petri-dishes, and kept in a hot air oven at 60°C for 2 h to complete polymerization and subsequent cross-linking process. After polymerization (completion of reaction) in 2 h, the firm SAHs, in the form of thick sheet was then carefully removed from the Petri-dish surface. The resultant SAHs sheet was cut into small pieces (0.1–0.5 cm in thickness). Thereafter, the separation of unreacted monomers was done by washing with methanol, followed by swelling in distilled water for 4 h and then dried in an oven at 60°C up to the constant weight. The dried hydrogels were stored in desiccators.

Preparation of Cu²⁺ Ions-Loaded Superabsorbent Hydrogels Poly(AAc/AM/SH)

To prepare the Cu²⁺ ions-loaded superabsorbent hydrogels poly(AAc/AM/SH) 50 mg of dry hydrogel was introduced in 100 mL of Cu²⁺ ions salt solution (initial ion concentration 1 g/L) at pH 5.0 and was left in solution for 24 h. The samples were withdrawn at different time intervals (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, and 24 h), then 2 mL of solution was sampled and analyzed for Cu²⁺ ions content left in solution. The initial and final Cu²⁺ ions content in the solution was analyzed by using ethyl-

enediamine as a developing agent with UV-VIS spectroscopy at a wavelength of 545 nm. The adsorption capacity of the hydrogel for Cu²⁺ ions was evaluated through the following equation-

$$q_e = \frac{C_o - C_e}{m} \times V \quad (1)$$

where q_e is the amount of Cu²⁺ ions adsorbed at equilibrium, C_o is the initial concentration of Cu²⁺ ions, C_e is the equilibrium concentration of Cu²⁺ ions; V is the volume of the Cu²⁺ ions solution; and m is the mass of hydrogel sample.

All assays were done in triplicate and average data was used for the analysis.

Desorption Study of Cu²⁺ Ions From Poly(AAc/AM/SH)-Cu Hydrogel

To evaluate the stability of Cu²⁺ ions into poly(AAc/AM/SH)-Cu hydrogel at adsorption process, 50 mg of poly(AAc/AM/SH)-Cu hydrogel was added to 12 conical flasks with 100 mL of deionized water. The pH of solution of each conical flask was adjusted to 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0, and 12.0, respectively. After being shaken at 30 ± 0.5°C, 180 rpm in a shaker, the solutions were filtered and analyzed for the desorbed Cu²⁺ ions. The final Cu²⁺ ions concentration in the aqueous phase was determined by above given method. The desorption percentage was calculated by the amount of Cu²⁺ ions adsorbed on the hydrogel surface and final Cu²⁺ ions concentration in the desorption medium.

Desorption percentage was calculated using the following expression-

$$\text{Desorption percentage} = \frac{\text{Amount of Cu}^{2+} \text{ ion desorbed to the elution medium}}{\text{Amount of Cu}^{2+} \text{ ion adsorbed on the superabsorbent hydrogel}} \times 100 \quad (2)$$

All assays were done in triplicate and average data were used for the analysis.

Adsorption Analysis of Phosphate Ions

For the determination of phosphate adsorption experiments, 50 mg the adsorbent poly(AAc/AM/SH)-Cu hydrogel was loaded into a conical flask with 100 mL of phosphate ions solution in various initial concentrations. The phosphate ions solution was obtained on dissolving potassium dihydrogen phosphate (KH₂PO₄) in 100 mL deionized water. The initial pH of the phosphate solution was adjusted to 6.1 by 0.1 mol/L HCl or 0.1 mol/L NaOH solutions. Then the sealed flasks were put in a shaker bath at different constant temperatures (±0.5°C) for 24 h, and shaken at the 180 rpm. Following the adsorption, the samples were withdrawn at different time intervals (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, and 24 h), then 2 mL of solution was sampled and analyzed for phosphate ions content left in solution. The capacity of phosphate adsorption was also calculated using eq. (1). All assays were done in triplicate and average data was used for the analysis.

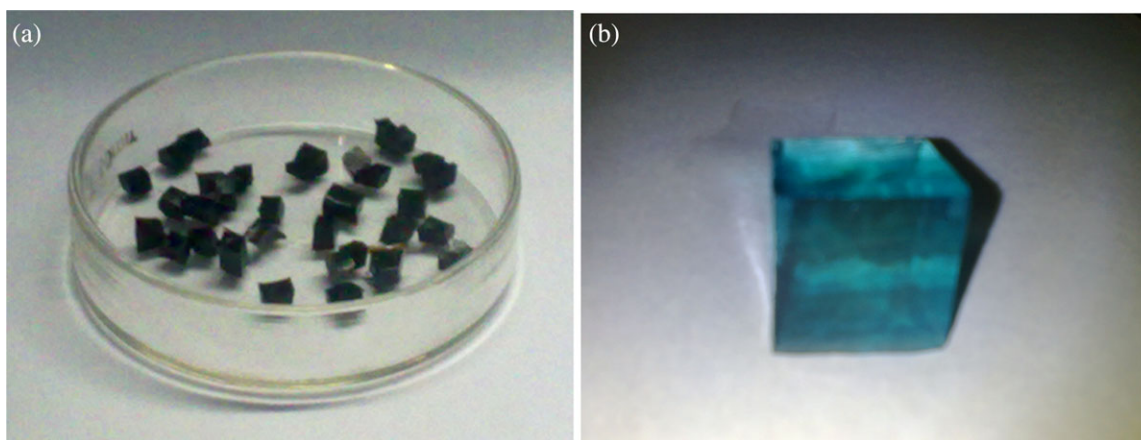


Figure 1. (a) Macroscopic image of poly(AAc/AM/SH) superabsorbent hydrogel and (b) macroscopic image of poly(AAc/AM/SH) superabsorbent hydrogel on swelling in copper sulfate solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

To determine the influence of temperature on adsorption capacity, isotherms were established at 30, 45, and 60°C.

For the kinetic study adsorption experiments were conducted as follow: 50 mg of adsorbent was suspended in 100 ml solution containing 180 mg/L of phosphate. The pH of solution was adjusted 6.1 with 0.1 mol/L HCl or 0.1 mol/L NaOH solutions. Then the sealed flasks were put in a shaker bath at $30 \pm 0.5^\circ\text{C}$, shaken at the 180 rpm for different time intervals. The flasks were then taken out at different times for the analysis of phosphate concentrations. The rate of phosphate ions adsorption was evaluated from the amount of phosphate ions adsorbed at different times.

To evaluate the influence of pH on phosphate ion adsorption, experiments were performed at different initial pH, ranging between 1.0 and 12.0. Initial phosphate ion concentration of 180 mg/L and 50 mg of adsorbent was used. The solutions were shaken for 24 h at $30 \pm 0.5^\circ\text{C}$.

The effect of ionic strength on the phosphate removal were investigated in the aqueous solution containing 180 mg/L phosphate ions and various concentrations of NaCl (0.1M, 0.01M, and 0.001M).

To investigate the influence of coexisting anions on adsorption of phosphate ions, various anions, citrate, sulfate, bicarbonate, chloride, and nitrate were added into phosphate ion solutions in the sodium form. The concentrations of the various anions in these experiments were all 0.01M. Initial phosphate ion concentration of 180 mg/L and 50 mg of adsorbent per liter of solution were used. The solution initial pH was adjusted to 6.1. The solutions were shaken for 24 h at $30 \pm 0.5^\circ\text{C}$.

Concentration of phosphate ion was analyzed based on ascorbic acid method and detected spectrophotometrically with UV-vis spectrophotometry at 700 nm wavelength.²⁸ The capacity of phosphate adsorption was also calculated using eq. (1). All assays were done in triplicate and average data was used for the analysis.

Fourier Transforms Infrared Spectroscopy (FTIR) Studies

The FTIR spectra of poly(AAc/AM/SH) and poly(AAc/AM/SH)-Cu superabsorbent hydrogel were recorded with Perkin Elmer

Spectrophotometer using solid pellet potassium bromide (KBr) after completely drying the sample at 60°C up to constant weight.

Desorption and Regeneration

In order to explore the potential of reusability of adsorbent and recovery of phosphate ions consecutive adsorption-desorption cycles were repeated five times using the adsorbent prepared following the described procedure in adsorption experiments. The poly(AAc/AM/SH)-Cu samples were first equilibrated with phosphate ions in a solution having initial concentration of 180 mg/L at pH 6.1, temperature at $30 \pm 0.5^\circ\text{C}$ and for 24 h.

Desorption of phosphate ions from the superabsorbent hydrogel poly(AAc/AM/SH)-Cu (having 87.62 mg/g) was carried out in batch mode using 50 mg adsorbent in 25 mL of 0.1M NaOH solution (elution medium) for 48 h. After being shaken at $30 \pm 0.5^\circ\text{C}$, 180 rpm in a shaker, the hydrogel was taken out and then washed several times with distilled water followed by methanol and then dried at 60°C for 24 h. The regenerated hydrogel was used for another adsorption. The final phosphate ions concentration in the aqueous solution was determined by above given ascorbic acid method by UV-VIS spectroscopy. Desorption ratio was evaluated from the amount of phosphate ions adsorbed on the polymer surface and final phosphate ions concentration in the elution medium.

Desorption ratio was calculated by applying the eq. (2).

To determine the reusability of the superabsorbent hydrogel poly(AAc/AM/SH)-Cu consecutive adsorption-desorption cycle was repeated for the five times of the same sample.

RESULTS AND DISCUSSION

Characterization of Poly(AAc/AM/SH)-Cu Hydrogel

The macroscopic image of dried poly(AAc/AM/SH) hydrogel, and swollen poly(AAc/AM/SH)-Cu hydrogel was given in Figure 1(a,b) respectively. It can be seen that the surface appearance of dried poly(AAc/AM/SH) hydrogel was rectangular (0.1–0.5 cm in thickness), hard and dark brown in color. The swollen poly(AAc/AM/SH)-Cu hydrogel was soft but strong enough to retain its shape and blue in color. This observation indicate that the

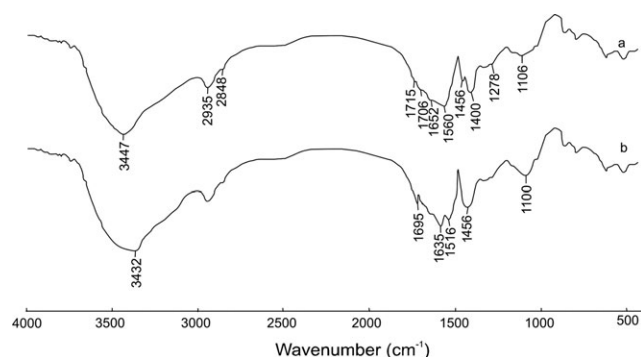


Figure 2. FTIR spectrum of (a) crosslinked poly(AAc/AM/SH) and (b) poly(AAc/AM/SH)-Cu superabsorbent hydrogel.

Cu^{2+} ions were adsorbed on the surface of poly(AAc/AM/SH) hydrogel.

From the molecular structure of poly(AAc/AM/SH) hydrogel, there were free $-\text{COOH}$, $-\text{OH}$, and NH_2 groups on the backbone of poly(AAc/AM/SH) hydrogel, Cu^{2+} ions were attached with these functional groups. The equilibrium adsorption capacity of poly(AAc/AM/SH) hydrogel for Cu^{2+} ion was 29.9 mg/g at 30°C with an initial pH 5.0.

The FTIR technique was applied for the characterization of poly(AAc/AM/SH) superabsorbent hydrogel before and after the adsorption of Cu^{2+} ions. Figure 2 shows the FTIR spectrum of (a) crosslinked poly(AAc/AM/SH) (b) poly(AAc/AM/SH)-Cu hydrogel. Existence of broad band at 3447 cm^{-1} is corresponding to $-\text{NH}$ stretching vibrations of the $-\text{NH}_2$ group of acrylamide and overlapping absorption bands of $\text{O}-\text{H}$ because of hydrogen bonding and acrylic acid, was broadened and shifted to 3432 cm^{-1} after adsorption because of combined interaction of Cu^{2+} ions with the $-\text{OH}$ and $-\text{NH}_2$ groups. The absorption band at 1715 cm^{-1} attributed to $\text{C}=\text{O}$ group of carboxyl group after adsorption appeared at 1695 cm^{-1} .²⁹ Absorption band at 1560 cm^{-1} ascribed to symmetric stretching of the carboxylate and at 1400 cm^{-1} due to asymmetric stretching of the carboxylate were appeared at 1516 cm^{-1} and 1456 cm^{-1} respectively.³⁰ From the FTIR analysis it can be concluded that the Cu^{2+} ions adsorption onto the poly(AAc/AM/SH) surface chiefly occur through chelation and ion exchange between positively charged Cu^{2+} ions and carboxylates as well as phenolic hydroxyls.

Effect of pH on the Desorption Behavior of Cu^{2+} Ions From Poly(AAc/AM/SH)-Cu Hydrogel

In order to minimize the chance of leakage of Cu^{2+} ion during the phosphate adsorption the stability of poly(AAc/AM/SH)-Cu hydrogel is one of important aspects for the use of poly(AAc/AM/SH)-Cu superabsorbent hydrogel as a phosphate ion adsorbent. So, For the practical application of poly(AAc/AM/SH)-Cu hydrogel as an adsorbent for phosphate ions, it is required to determine its stability at different pH conditions. The release behavior of Cu^{2+} ions from poly(AAc/AM/SH)-Cu hydrogel was investigated at various pHs solutions under the identical conditions as the adsorption process for phosphate ion-containing water. Figure 3 shows the percent released of Cu^{2+} ions from poly(AAc/AM/SH)-Cu hydrogel at various pH range. It

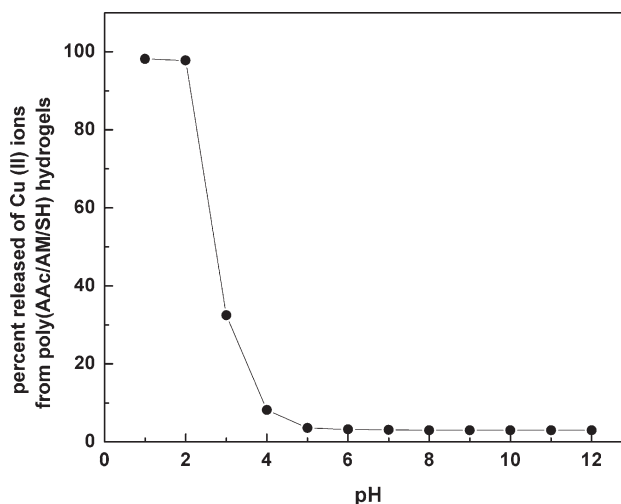


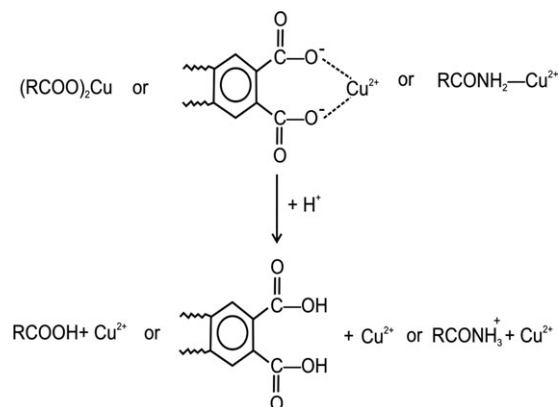
Figure 3. Effect of pH on percent released of Cu^{2+} ions from poly(AAc/AM/SH)-Cu superabsorbent hydrogel, temperature $30 \pm 0.5^\circ\text{C}$.

can be observed that concentration of remaining Cu^{2+} ions is intensively dependent on the pH of aqueous solution. At lower pH ($\text{pH} < 3.5$) the desorption of Cu^{2+} ions occur extensively ($>98\%$), due to competitive adsorption of protons for adsorption sites by substituting the Cu^{2+} ions from the Cu-loaded hydrogel surfaces (Scheme 1).

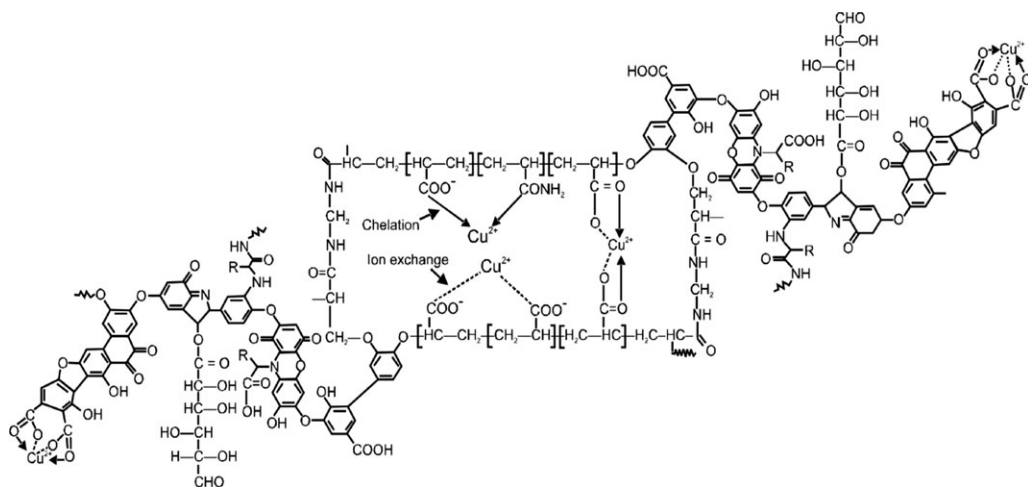
This is why the desorption of Cu^{2+} ions from poly(AAc/AM/SH)-Cu hydrogel was carried out in acidic solution.²⁵ On further increasing the pH ($\text{pH} > 4.2$) desorption of Cu^{2+} ions decreased sharply and the sample shows very little desorption. This can be explained because of the chemical bonding formed due to chelation of the $-\text{NH}_2$, $-\text{COOH}$, and $-\text{OH}$ groups with the Cu^{2+} ions (Scheme 2). The observation reveals that the poly(AAc/AM/SH)-Cu hydrogel was stable enough at high pH range ($\text{pH} > 4.2$) and can be effectively used as a adsorbent for phosphate ions.

Adsorption Mechanism

In the case of SAHs metal ions adsorption is assumed to be because of electrostatic forces and co-ordinate bonds. For the Cu^{2+} ions; adsorption on to the adsorbent poly(AAc/AM/SH)

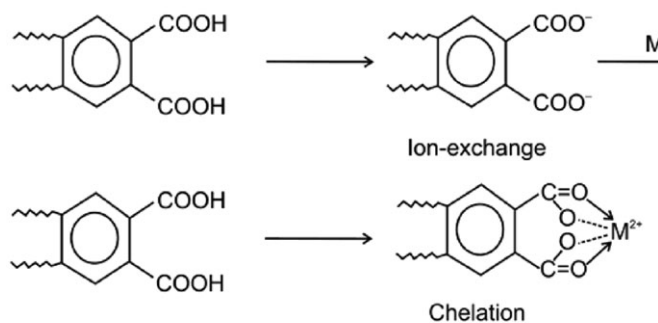


Scheme 1. Desorption of Cu^{2+} ion from poly(AAc/AM/SH)-Cu at $\text{pH} < 3.5$ via competitive adsorption of protons by substituting Cu^{2+} ion.



Scheme 2. Proposed mechanism for removal of copper ions onto the superabsorbent hydrogel poly (AAc/AM/SH).

hydrogel mainly occur through the ion exchange and chelation between positively charged Cu^{2+} ions and phenolic hydroxylics as well as carboxylates groups (Scheme 2).



Here M^{2+} represents bivalent metal ion (Cu^{2+})

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Cu^{2+} ion is a soft cation and has strong Lewis acid-base interaction with the strong Lewis acid characteristics. So, Cu^{2+} ion undergoes Lewis acid-base interaction with the nitrogen donor atoms strongly. The adsorption mechanism for the adsorption of Cu^{2+} ion on poly(AAc/AM/SH) SAHs can be supported by the given IR study in the section characterization of poly(AAc/AM/SH)-Cu hydrogel and also by the variation in pH of suspension at the equilibrium. As the adsorption process achieved equilibrium the pH value decreased. This can be explained as a fact that as the poly(AAc/AM/SH) SAHs have many $-\text{COOH}$ and $-\text{OH}$ groups; and they function as the adsorption sites to metal ion exchange and chelation. These functional groups in their aqueous solutions dissociate to produce protons and so decrease the pH of solution. This phenomenon is testified by the change in solution pH before and after the adsorption. The findings obtained from IR study (i.e. shift in absorption band of NH stretching vibrations of the $-\text{NH}_2$ group, $\text{C}=\text{O}$ group of carboxyl group and symmetric and asymmetric stretching of carboxylate) reveals that the groups, $-\text{NH}$, $-\text{COO}^-$ and $-\text{COOH}$

groups were involved in adsorption mechanism. The IR results (involvement of $-\text{NH}$, $-\text{COO}^-$, and $-\text{COOH}$ groups for adsorption) are also confirmed by change in pH value of solution.

After phosphate ion adsorption two coordination sites of Cu^{2+} ions are satisfied by different chelating functional groups of poly(AAc-AM-SH) hydrogel network and due to that the Cu^{2+} ions are held tightly onto hydrogel surface. The residual two coordination sites are satisfied with one HPO_4^- ion. Therefore coulombic interaction (ion pair formation to balance the electroneutrality) is accompanied with the Lewis acid base interaction by a bidentate fashion in which the electron deficiency of the coordination sphere of Cu^{2+} ions (Lewis acid) are maintained by the one HPO_4^- ion (two donor oxygen atom) (Scheme 3), which results in enhanced phosphate adsorption efficiency of poly(AAc/AM/SH)-Cu superabsorbent hydrogel.

Cu^{2+} ions a Lewis-acid type metal cation, coordinated strongly with the chelating functional group in a way that its positive charges are not neutralized. Electrostatic interaction or ion-pairing (IP) as well as Lewis acid–base (LAB) both interactions are concurrently operative, and lead to enhanced adsorption of phosphate ion. Therefore the overall free energy change of the adsorption of phosphate ion onto the poly(AAc/AM/SH)-Cu SAHs may be presented as follows:

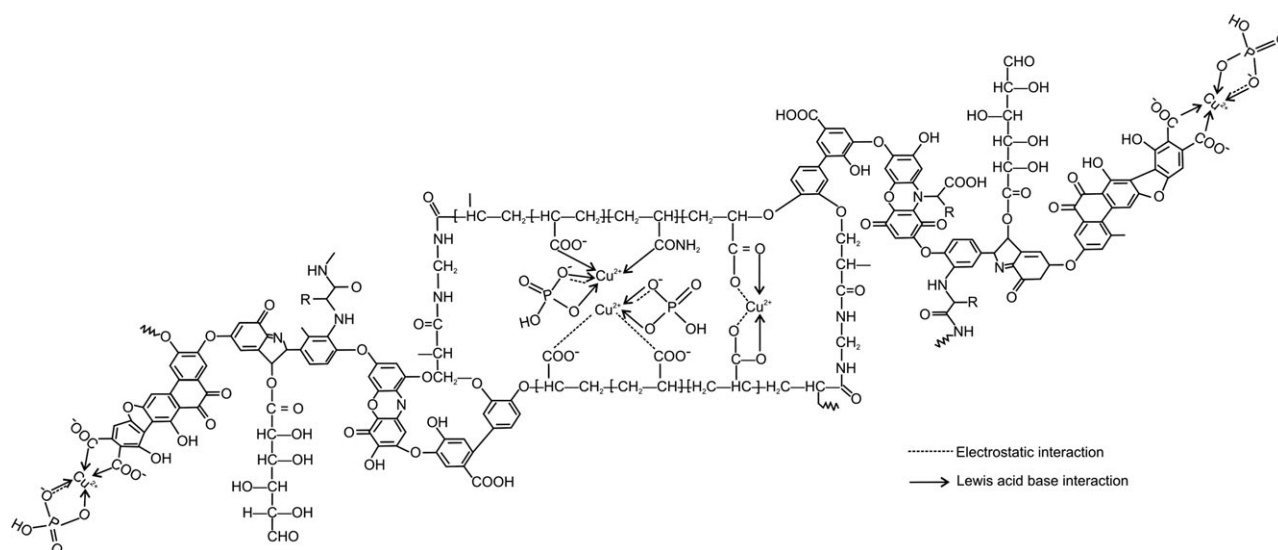
$$\Delta G_{\text{overall}}^0 = \Delta G_{\text{IP}}^0 + \Delta G_{\text{LAB}}^0 \quad (3)$$

where $\Delta G_{\text{overall}}^0$ represents the change in overall free energy at the standard state, subscripts IP and LAB refer to contributions from Ion pairing interaction and Lewis acid–base interaction, respectively.

$$-RT \ln K_{\text{overall}} = -RT \ln K_{\text{IP}} - RT \ln K_{\text{LAB}} \quad (4)$$

$$K_{\text{overall}} = K_{\text{IP}} K_{\text{LAB}} \quad (5)$$

where R is universal gas constant, K = respective equilibrium constants and T is absolute temperature. With all other conditions remaining identical, a negatively charged ion such as



Scheme 3. Proposed schematic mechanism for adsorption of phosphate ions onto the superabsorbent hydrogel poly (AAc/AM/SH)-Cu.

phosphate ion having a fairly strong Lewis-base property (i.e., high K_{LAB}) is expected to show good selectivity toward poly (AAc/AM/SH)-Cu superabsorbent hydrogel [containing Cu^{2+} ions (a Lewis-acid type metal cation)] adsorbent.

Effect of Contact Time on Adsorption of Phosphate Ions

To investigate the effect of contact time on the adsorption of phosphate ions on poly(AAc/AM/SH)-Cu hydrogel from aqueous solution, the hydrogel were equilibrated with adsorbate aqueous solution for predetermined time period. Figure 4 shows the influence of contact time on the phosphate uptake. As clear from Figure 4, the adsorption of phosphate ion increases rapidly with increase of contact time initially and then reaches at a constant value beyond which no phosphate ion was further adsorbed from the solutions. The adsorption curve was smooth and continuous leading to saturation. More than 92% of the

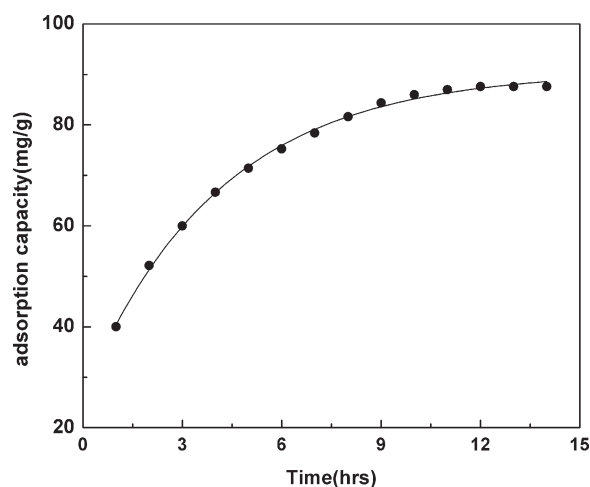


Figure 4. Effect of contact time on the adsorption of phosphate ions onto poly(AAc/AM/SH)-Cu superabsorbent hydrogel [initial ion concentration, 180 mg/L; pH of solution, 6.1; temperature $30 \pm 0.5^\circ C$; hydrogel content, 50 mg].

equilibrium removal capacity occurred within 8 h. This can be explained by the fact that, initially adsorption binding sites were void and phosphate ions may easily interact with these sites. The phosphate ion uptake almost remained constant after 12 h, and with prolonged time, the removal capacity hardly increased, so 12 h could be considered as the equilibrium contact time. At the equilibrium condition, the amount of phosphate ion desorbed from the taken hydrogel, was in dynamic equilibrium with the concentration of phosphate ion being adsorbed on the hydrogel surface. The results suggest that the phosphate ion adsorption was fast at the initial part of the contact time, and thereafter it goes slower at near the equilibrium point. This phenomenon was because of the fact that more number of vacant active surface sites was available for the adsorption during initial stage, but after a lapse of time, the residual vacant surface sites were became difficult to be occupied because of repulsive forces among the solute molecules present on the solid and bulk phases.

Effect of pH and Ionic Strength of Solution on Adsorption of Phosphate Ions

The pH of aqueous solution is one of the most important factors influencing the adsorption amount of cations and anions. It influences the solution chemistry of the different metal ions (such as complexation, and hydrolysis) as well as the protonation of the functional groups present on the adsorbents.²⁶ In addition to this, natural waste water normally contains anions and these coexisting anions may influence or compete with the phosphate ions for the adsorption sites. Consequently, in this study influence of pHs and ionic strength on removal amount of phosphate ion was examined at various initial pHs namely between 2.00-12.0 and at different NaCl concentration (0.001-0.1M). At lower pHs value (<2.15), the predominant species in solution is the neutral H_3PO_4 , between pHs range of 2.15 to 7.20, the main species in solution is $H_2PO_4^-$, and at pHs values between 7.2 to 12.33 the predominant species is HPO_4^{2-} .³¹ Figure 5 shows the variation in removal capacity of phosphate ion on the poly(AAc/AM/SH) hydrogel and poly(AAc/AM/SH)-

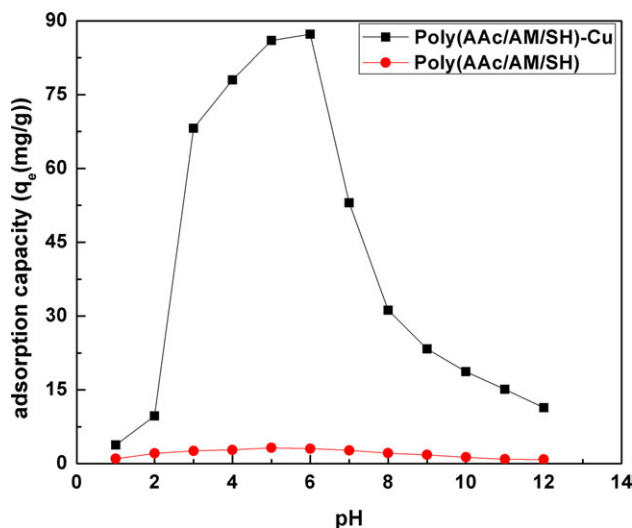


Figure 5. Effect of pH on the adsorption of phosphate ions onto poly(AAc/AM/SH) and poly(AAc/AM/SH)-Cu superabsorbent hydrogel [contact time, 24 h; initial ion concentration, 180 mg/L; temperature $30 \pm 0.5^\circ\text{C}$; hydrogel content, 50 mg]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

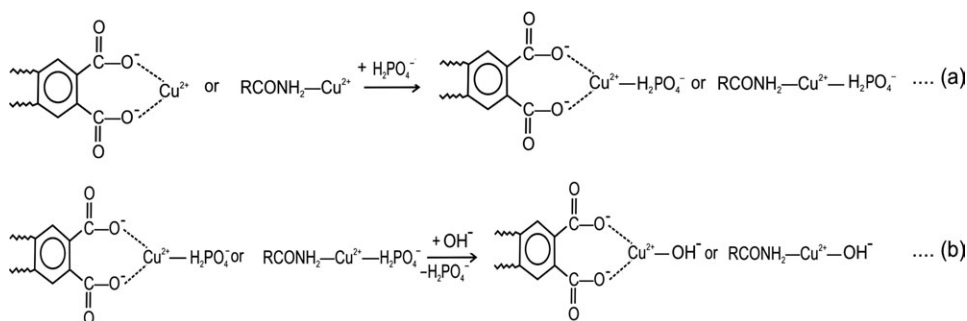
Cu hydrogel from aqueous solution with respect to initial pH. It was observed from Figure 5 that poly(AAc/AM/SH)-Cu hydrogel shows higher adsorption capacity than the poly(AAc/AM/SH) hydrogel, which shows negligible adsorption in all measured pH ranges. This indicates that the incorporation of the Cu^{2+} ions on the polymeric surface is favorable to enhance the adsorption capacity as well as played an important role in phosphate adsorption. The phosphate ion uptake increases sharply with an increase in initial pH (1-4) and then increased slowly until reaching a maximum 87.62 mg/g at pHs 6.1. After that on further increasing the pH it goes down. It was practically independent on pH values in the range of 5.0–6.1. When pH value was lower than 3.8 and higher than 6.1, a remarkable decrement in adsorption uptake was observed. These results can be interpreted as follows. At low pH, Cu^{2+} ions desorbed from the poly(AAc/AM/SH)-Cu hydrogel, and for the poly(AAc/AM/SH) hydrogel, on the one hand, there is strong competition between hydrogen ions and phosphate ions for the active adsorption sites, that made the availability of phosphate ions to adsorption sites difficult to occur; on the other hand, after the release of Cu^{2+} ion from the

poly(AAc/AM/SH)-Cu hydrogel the COO^- ions present on the gel surface are transformed to their protonated form, which hinder the interaction of poly(AAc/AM/SH) with phosphate ion, so the removal capacity for the phosphate ions decreases (scheme 1). Conversely, at the higher pH ($4 < \text{pH} < 6.1$), amount of Cu^{2+} ions attached on poly(AAc/AM/SH) hydrogel was not leaked out and as they are the active adsorption site for phosphate ions. Therefore, increase in interaction between phosphate ions and poly(AAc/AM/SH) hydrogel that result in an increase in phosphate ion adsorption (Scheme 4a). However, the removal capacity was dramatically decreased on further increasing the pH. This was because of the high content of the hydroxide anions at a higher pH range, having strong competition with phosphate ions for the binding sites of poly(AAc/AM/SH)-Cu hydrogel (Scheme 4b). Clearly, the pH of the aqueous solution plays an important role for the adsorption of phosphate ions similar to other reports using various adsorbents (which bind phosphate ions more effectively under acidic conditions in comparison to alkaline conditions).^{32,33}

Figure 6 displays the effect of ionic strength on the phosphate removal at various pH values. It can be seen from Figure 6 that at low sodium chloride concentration (0.001–0.01M), the maximum adsorption capacity (85.34 mg/g) was obtained from pH 3–6, while incase of higher concentration (0.1M), the maximum phosphate adsorption capacity (59.82 mg/g) was achieved from pH 2.5–6. The possible reason for decrease in adsorption capacity at high ionic strength is the screening of electrostatic interaction of opposite charges on the adsorbent surface.

Effect of Temperature on the Adsorption

Temperature is one of the most important parameters that have a pronounced influence on the adsorption capacity of adsorbents. It was observed that adsorbent capacity decreased from 87.62 to 70.23 mg/g, with increase in temperature from 30°C to 60°C . The decrease in the adsorption amount of phosphate ions with increase in temperature indicated that the phosphate ion adsorption was favorable at low temperature. Since adsorption process is an exothermic reaction, therefore it was expected that increase in temperature of adsorption system would cause a decrease in adsorption capacity. Adsorption is a dynamic process, which involves both adsorption and desorption phenomenon. The adsorbate molecules are attracted by the surface force and attach on the surface of the adsorbent. They are in constant motion also. The increase in temperature increases the energy



Scheme 4. (a) Model of adsorption of phosphate ions onto poly(AAc/AM/SH)-Cu superabsorbent hydrogels at pH ($4 < \text{pH} < 6.1$). Model of competitive adsorption of hydroxide ions onto poly(AAc/AM/SH)-Cu superabsorbent hydrogels at higher pH value ($\text{pH} > 7$).

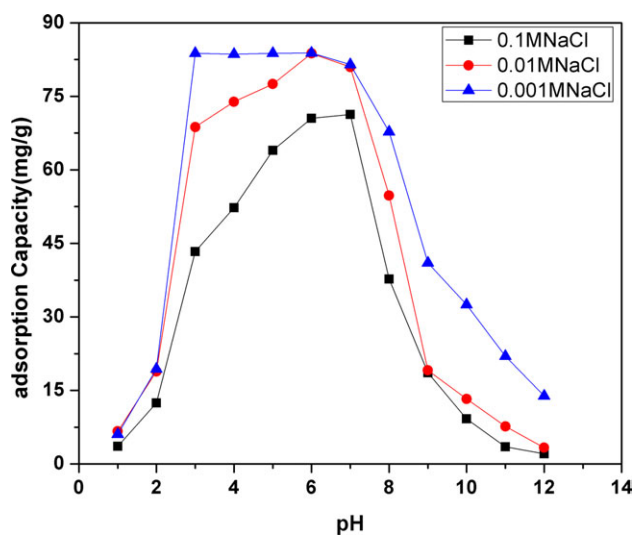


Figure 6. Effect of ionic strength on the adsorption of phosphate ions onto the poly(AAc/AM/SH)-Cu superabsorbent hydrogel [contact time, 24 h; initial ion concentration, 180 mg/L; temperature $30 \pm 0.5^\circ\text{C}$; hydrogel content, 50 mg]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

level of adsorbed molecules. The high energy, speeds up the Brownian motion, thus requiring a stronger force to keep the adsorbed molecules adhered onto the adsorbent surface (the higher the adsorption temperature, the higher the speed of the adsorbate molecules' Brownian motion, causing reduction in the possibility of adsorption of the adsorbate molecules). On the other hand, at the high temperature the adsorbed molecules have enough energy to overcome the attraction force and migrate back from the solid phase to bulk phase. Another reason is the presence of lesser number of active binding sites at higher temperature that may be attributed because of the deactivation of the surface of adsorbent or due to destruction of

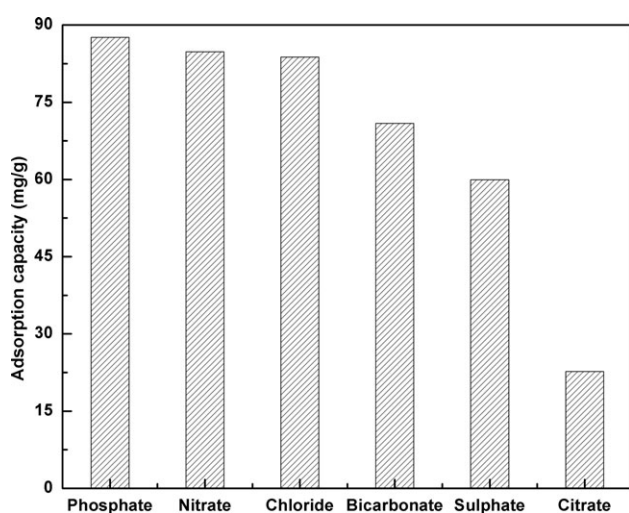


Figure 7. Effect of coexisting anions on the adsorption of phosphate ions onto the poly(AAc/AM/SH)-Cu superabsorbent hydrogel [contact time, 24 h; initial ion concentration, 180 mg/L; temperature $30 \pm 0.5^\circ\text{C}$; hydrogel content, 50 mg].

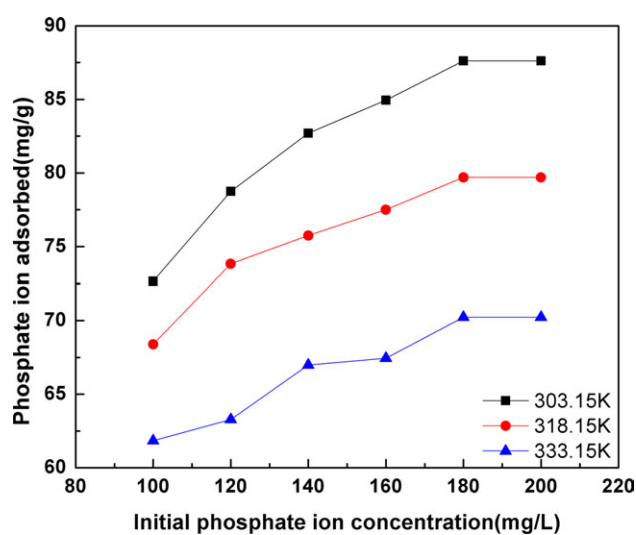


Figure 8. Variation in the adsorption capacity as a function of initial phosphate ion concentration using superabsorbent hydrogel poly(AAc/AM/SH)-Cu [contact time, 24 h; pH of solution, 6.1; temperature $30 \pm 0.5^\circ\text{C}$; hydrogel content, 50 mg]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

some active binding sites existing on the adsorbent surface because of bond rupture. So, 30°C was chosen as the solution temperature.

Effect of Coexisting Anion on Adsorption

Natural water and waste water generally contain coexisting ions that potentially interfere in the adsorption of phosphate ions. Therefore, in this section the competitive adsorption of coexisting anions, that includes nitrate, chloride, sulfate, bicarbonate, and citrate (0.01M) onto poly(AAc/AM/SH)-Cu hydrogel was investigated and shown in Figure 7. This may be attributed because of competition of these anions with the phosphate ions at the active sites. The adsorption capacity for phosphate ions was slightly influenced as the concentration of nitrate and chloride ions increased. The introduction of sulfate and bicarbonate inhibited modestly, and citrate ions strongly impacted the adsorption capacities of the adsorbent for phosphate ions. As Cu^{2+} ion is a soft cation (soft acid) so it binds more basic anions more strongly than the less basic anions. Of these anions (nitrate, chloride, sulfate, bicarbonate), sulfate possesses higher ionic charges (i.e., divalent) and so will offer greater competition through more electrostatic interaction. The citrate ion form chelate complex with the adsorbent, therefore it exhibit greatest competition to phosphate ion adsorption. This trend agrees well with the previous study on metalated ethylenediamine-self-assembled monolayers on mesoporous supports (metalated-EDA-SAMMS).³⁴

Effect of Initial Concentration of Phosphate Ions on Adsorption Capacity of the Poly(AAc/AM/SH)-Cu Hydrogel

Initial ion concentration is an important parameter because initial concentration of phosphate ions affects the adsorption quantity of phosphate ions and adsorption kinetics, so the effect of initial concentration on adsorption capacity was investigated. Figure 8 shows the adsorption capacity of the poly(AAc/AM/

SH)-Cu hydrogel for the phosphate ions as a function of varying initial ion solution concentrations ranging from 100 to 200 mg/L. It can be observed from Figure 8 that uptake amount of phosphate ions increased (from 72.66 to 87.62 mg/g) with increase in initial concentration of phosphate ions solution if the amount of adsorbent was constant. After reaching a maximum (87.62 mg/g) at 180 mg/L it remained nearly constant. This can be explained as a consequence of increase in the driving force of the concentration gradient with the higher initial phosphate ions concentration. It can also be seen that in the initial stage the adsorption is rapid and increases gradually with progress of adsorption or with the increasing concentration of phosphate ion, amount of removed phosphate ions increased but its adsorption percentage decreased. For the low initial concentration the ratio of initial number of phosphate ions to the available binding sites is low; therefore the fractional removal of phosphate ions becomes independent of initial concentration. On the other hand; the number of available binding sites become lesser at the high initial concentration and subsequently the adsorption of phosphate ions depends on the initial concentration.

Adsorption Isotherms

Adsorption characteristics and equilibrium data that is commonly known as adsorption isotherm, is fundamental in describing how adsorbate molecules interact with adsorbent and so, adsorption isotherms are critical in optimizing the application of adsorbent. The adsorption experimental data is generally interpreted with the Langmuir, Freundlich, and Dubinin–Radushkevich (D–R), isotherm models.

The most widely used adsorption isotherm for the modeling of adsorption data is the Langmuir adsorption isotherm. The adsorption data of phosphate ions with the poly(AAc/AM/SH)-Cu gel have been interpreted using this model. It is a mathematical model and represents a quantitative relationship between the concentration of phosphate ions in the solution and the amount of phosphate ions adsorbed onto adsorbent surfaces when the two phases are at equilibrium. It is based on following assumption (i) maximum removal corresponds to a saturated monolayer of adsorbate on the adsorbent surface, (ii) the adsorption energy is constant, and (iii) no transmigration of adsorbate in the adsorbent surface plane. Langmuir adsorption isotherm equation may be described as^{35,36}

$$\frac{C_e}{q_e} = \frac{1}{K_e q_{\max}} + \frac{C_e}{q_{\max}} \quad (6)$$

where K_e [sorption equilibrium constant (L/mg)] and q_{\max} [maximum amount of adsorption of phosphate ions (mg/g)], C_e is the equilibrium concentration of the phosphate ions in the solution (mg/L), q_e the amount of phosphate ions adsorbed at equilibrium mg/gm. The Langmuir constants and regression coefficients were calculated from the linear plots of C_e/q_e vs. C_e .

The Freundlich model is an empirical equation and provides an expression encompassing heterogeneous surface system and exponential distribution of active binding sites and their energies.

This model characterizes reversible adsorption and is not limited to the production of the monolayer. The Freundlich model may be expressed as follows³⁷;

$$\log(q_e) = 1/n \log(C_e) + \log K_f \quad (7)$$

where K_f (L/g) is the Freundlich constant related to the adsorption capacity and $1/n$ (dimensionless) related to intensity or energy of adsorption. K_f and $1/n$ can be obtained from the intercept and slope of the plot of $\log q_e$ versus $\log C_e$, respectively.

The D–R isotherm can also be subjected to depict the nature of adsorption as a physical or chemical process on both homogeneous and heterogeneous surfaces.³⁸ A linear form of D–R equation is presented by the following relationship:

$$\ln/q_e = \ln/q_m - \beta/\varepsilon^2 \quad (8)$$

where β is a constant correlated to mean free energy of adsorption ((mol/J)²), q_m is the theoretical equilibrium capacity and ε is the Polanyi potential, which is related to the equilibrium phosphate ion concentration (J/mol), illustrated as follows:

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (9)$$

where R ((8.314 J/(mol K)) is the gas constant and T (K) is the absolute temperature. The D–R constant may give valuable information about the mean free energy, E (J/mol), can be evaluated from constant β ,³⁹: using the following equation

$$E = (2\beta)^{0.5} \quad (10)$$

The constant parameters and regression coefficients were obtained from Langmuir, Freundlich and D–R adsorption equations mentioned above are summarized in Table I. The fit of the data for phosphate ion adsorption suggests that the values of regression coefficients of Langmuir model were higher than those of Freundlich and D–R models that indicate the Langmuir isotherm model correctly fitted the equilibrium data. The q_{\max} values of the poly (AAc/AM/SH)-Cu hydrogel obtained by Langmuir adsorption model were quite consistent with the experimental one (Table I). The applicability of Langmuir isotherm model suggests favorable monolayer adsorption and involvement of the chemical adsorption mechanism in phosphate adsorption process. In addition the q_{\max} value decreases with the increase in temperature and the analogous behaviors are also ascribed by the removal capacities (K_f and q_{\max}) as well. The higher values of K_f indicate higher affinity of the poly (AAc/AM/SH)-Cu hydrogel for the phosphate ions, and the values for the empirical parameter $1/n$ lying in the range $0 < 1/n < 1$ show also a favorable adsorption. K_e and K_f both values decreases at higher temperature, so indicating that adsorption capacity diminished at higher temperature. The information thus specifies an exothermic nature of existing process. The applicability of Langmuir isotherm model suggests favorable Furthermore, according to the evaluation from the D–R adsorption model, the mean free adsorption energy (E) may be

Table I. Estimated Adsorption Isotherm Parameters for the Adsorption of Phosphate Ions on Poly(AAc/AM/SH)-Cu SAHs in Aqueous Solutions

Temperature (K)	Langmuir model				Freundlich model			D-R equation			
	q_e (mg/g)	q_{max} (mg/g)	$K_e \times 10^3$ (L/mg)	R^2	K_f (mg/g)	n	R^2	q_m (mg/g)	$\beta \times 10^6$ (mol ² /kJ)	R^2	E (kJ/mol)
303.15	87.62	94.33	1.245	0.99	44.66	6.80	0.98	86.79	20.92	0.95	15.40
318.15	79.70	85.47	1.180	0.99	46.77	8.88	0.94	79.94	23.67	0.96	14.53
323.15	70.23	74.62	1.116	0.98	41.11	9.06	0.96	69.74	26.38	0.83	13.76

primarily deduced as listed in Table I. The E value was higher than 8.0 kJ/mol, although the values of R^2 was less than 0.9, meaning that adsorption rates of phosphate ion onto poly(AAc/AM/SH)-Cu hydrogel is probably controlled by the chemical process.

Thermodynamic Parameters of Adsorption

Temperature dependence for the phosphate adsorption onto the poly(AAc/AM/SH)-Cu hydrogel has been evaluated. Temperature dependence for an adsorption process is accompanied with change in thermodynamic parameters including Gibbs free energy change (ΔG), standard enthalpy change (ΔH), and standard entropy change (ΔS) as they are the real indicators for the practical application of an adsorption process. From the values of these thermodynamic parameters, spontaneity of an adsorption process can be determined. The Gibbs free energy change for any reaction was obtained by applying following relationship⁴⁰

$$\Delta G = \Delta G^0 + RT \ln K_e \quad (11)$$

At the equilibrium adsorption state, ΔG becomes zero, and so

$$\Delta G^0 = -RT \ln K_e \quad (12)$$

where K_e is the Langmuir equilibrium constant, R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), and T is temperature in Kelvin.

The Gibbs free energy change is related to standard entropy change and standard enthalpy change at constant temperature by the given relation;

$$\Delta G^0 = \Delta H^0 - T\Delta S \quad (13)$$

On combining eqs. (12) and (13) we get following equation

$$\ln K_e = -\Delta G^0/(RT) = (\Delta S^0/R) - (\Delta H^0/(RT)) \quad (14)$$

Assuming that standard enthalpy change ΔH^0 is approximately independent of temperature, then ΔH^0 can be determined from the slope of the plot of $\ln K_e$ versus $1/T$ using the equation

$$\Delta H^0 = [R (d \ln K_e / (d1/T))] \quad (15)$$

Changes in ΔS^0 and ΔG^0 would be considered to evaluate whether the process is spontaneous. The Gibbs free energy change indicates the spontaneous nature of the adsorption pro-

cess and higher negative value shows a more energetically favorable adsorption.⁴¹ The results of experiments are summarized in Table II. The equilibrium constants determined from Langmuir equation at 303.15, 318.15, and 333.15 Kelvin were used to determine thermodynamic parameters of the adsorption. Negative change in ΔG^0 suggests the spontaneity and feasibility of adsorption process, further, with the increasing temperature the decrease in the values of ΔG^0 indicates that the adsorption reaction was more spontaneous at higher temperatures. The negative values for standard enthalpy change indicates that the adsorption of phosphate ions are exothermic, which is also confirmed by the decrement in the adsorption of phosphate ions with rise in the temperature. The positive value for entropy change reveals the increased randomness at the solid-solution interface at the time of the adsorption with few structural changes in adsorbate molecules and adsorbent surfaces. Positive value of ΔS^0 also corresponds to an increase in the degree of freedom for the adsorbed species.⁴²

Adsorption Kinetics

Adsorption kinetics shows an important role for adsorption capacity and field deployment costs of adsorbent. It may also be beneficial to understand mechanism of adsorption process and to estimate the performance of the adsorbents used for adsorbate adsorbed. Therefore the pseudo-first order kinetic and the pseudo-second order kinetic models were used to analyze the experimental data obtained.

Lagergren pseudo-first order⁴³ and Ho and McKay's pseudo-second order kinetics model⁴⁴ are two widely applied models used for solid-liquid adsorption.

The Lagergren pseudo-first order can be expressed as

$$\log(q_e - q_t) = \log q_e - k_t t / 2.303 \quad (16)$$

Table II. Thermodynamic Parameters for Adsorption of Phosphate Ions on Poly(AAc/AM/SH)-Cu Superabsorbent Hydrogels at Various Temperatures

Temperature (K)	Phosphate ion			
	$\ln K_e$	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/mol K)
303.15	2.52	-6.351		10.78
318.15	2.46	-6.506	-3.081	10.76
333.15	2.41	-6.675		10.79

Table III. Estimated Adsorption Kinetic Parameters for the Adsorption of Phosphate Ions on Poly(AAc/AM/SH)-Cu Superabsorbent Hydrogels in Aqueous Solutions

Temperature (K)	Pseudo-first-order model				Pseudo-second-order model			
	q_e exp (mg/g)	q_e cal (mg/g)	$k_1 \times 10^3$ (1/min)	R^2	q_e exp (mg/g)	q_e cal (mg/g)	$k_2 \times 10^5$ (g/mg min)	R^2
303.15	87.62	100.25	5.98	0.944	87.62	92.59	11.48	0.999
318.15	79.70	63.38	6.21	0.939	79.70	90.29	10.47	0.997
333.15	70.23	91.20	5.06	0.926	70.23	87.77	6.16	0.998

where q_e (mg/g), and q_t (mg/g) represent the amount of phosphate ions adsorbed (mg/g) at equilibrium and at any time t , respectively. k_1 (min^{-1}) is the rate constant of the pseudo-first-order model. Values of k_1 and q_e can be calculated from the slope and intercept of the plot of $\log(q_e - q_t)$ versus t , and were listed in Table III.

This model has been applied extensively to give account of the adsorption of metal ions on the adsorbents, however pseudo first-order-kinetic equation poor fit for the whole range of the contact time, and generally applicable over the initial phase of adsorption process. The chief disadvantage of pseudo first-order model are (i) the plots are only linear to the first 5 h, approximately. After this initial 5-h period the theoretical and experimental data do not correlate well, and (ii) the equilibrium removal capacities determined from the linear equation were not agree well with the experimental q_e values.

It was observed that there are large differences between the calculated q_e values and experimental q_e values ($q_{e,exp}$). In addition, the linear regression coefficients (R^2) for the pseudo-first order kinetic model were obtained between 0.92 and 0.94, thus suggesting that phosphate adsorption process does not fit well to pseudo-first-order model.

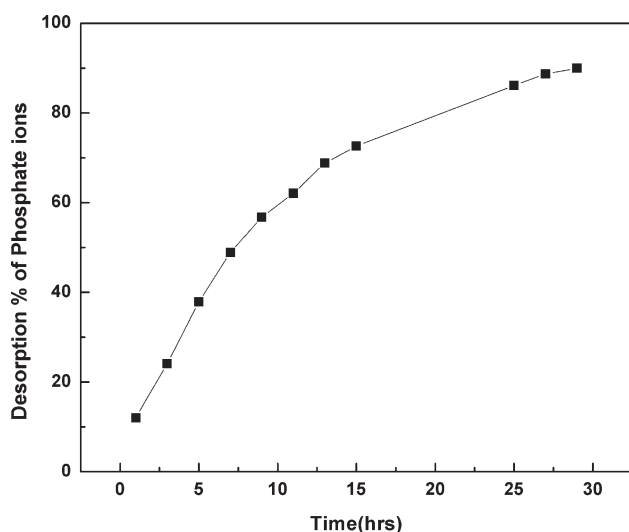


Figure 9. Plot of desorption ratio for phosphate ion from poly(AAc/AM/SH)-Cu hydrogels as a function of time.

Pseudo-second order kinetic models was depicted by the following equation

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \quad (17)$$

where k_2 ($\text{g}/(\text{mg min})$) is the rate constant of the pseudo-second order model. The parameters q_e and k_2 were obtained from slope and intercept of the plot of t/q_t against t , and shown in Table III.

It can be observed from Table III that the q_e values for the pseudo-second order kinetic model were in perfect agreement with the $q_{e,exp}$ values. Moreover, linear regression coefficients (R^2) for the pseudo-second-order kinetic model studied are over 0.997, which indicate that the pseudo-second-order model can be used for the whole adsorption process. The results suggested that the studied adsorption process belongs to pseudo-second-order adsorption model, which indicate that the adsorption behavior of the poly(AAc/AM/SH)-Cu was chemical adsorption.

Desorption/Regeneration of Adsorbent

A good solid adsorbent in addition to its high adsorption capacity should also exhibit a good regeneration capacity for potential application. The recovery of phosphate ions is an important factor to characterize the economics of the process. Desorption studies can help to recover the phosphate ions from the adsorbent and regenerate the hydrogel, so that it can be used again and again. The poly(AAc/AM/SH)-Cu hydrogels that were applied for the adsorption of phosphate ions were placed in 0.1M NaOH solution for 48 h and the amount of phosphate ions desorbed to the elution medium was measured. Figure 9 displays the desorption ratio of poly(AAc/AM/SH)-Cu hydrogels (having 87.62 mg/g phosphate ion) as a function of time. The desorption process reached equilibrium at about

Table IV. Adsorption Amount of Phosphate Ions After Repeated Adsorption-Desorption Cycle

Cycle no.	Adsorption capacity (mg/g)	Desorption (%)
1	87.62	94.28
2	86.45	94.10
3	85.37	93.57
4	85.01	92.91
5	83.14	92.33

29 h and the desorption ratio was ~90%. Table IV shows the experimental results for the adsorption capacity and times for reuse for the sample. The adsorption capacities did not show any significant decrease after the fourth reuse cycle. After five cycles of adsorption–desorption operations, adsorption capacity of phosphate ions were around 83.14 mg/g. Phosphate ions were desorbed approximately in alkaline medium. Higher desorption is because of the competing of the OH⁻ ions for the adsorption sites at the higher pH, as well as the poly(AAc/AM/SH)-Cu hydrogel was stable at higher pH and due to that no Cu²⁺ ion was desorbed to the elution medium. Therefore, it can be concluded that, poly(AAc/AM/SH)-Cu hydrogel showed stable phosphate ions removal capacities after repeated regeneration and thus qualified for multiple practical application.

CONCLUSIONS

In this study we attempt to provide a cost efficient and effective method to reuse a waste adsorbent poly(AAc/AM/SH)-Cu hydrogel for the phosphate ion adsorption from aqueous solution. The concentration of Cu²⁺ ions released from poly(AAc/AM/SH)-Cu hydrogel decreased gradually on increasing the pH and can not be observed at pH higher than 4.5. Therefore the poly(AAc/AM/SH) hydrogel after the adsorption of Cu²⁺ ions can be used directly for the removal of phosphate ion at pH > 4.5. Adsorption capacity was found to be maximum (87.62 mg/g) at pH 6.1. Increase in temperature caused decrease in adsorption capacity. Addition of equimolar concentration (0.01M) of chloride, nitrate and bicarbonate influenced little, whereas sulfate and citrate affect adversely on the phosphate adsorption and the effects follow the order nitrate < chloride < bicarbonate < sulfate < citrate. The adsorption isotherm agrees well with the Langmuir model as confirmed by linear fit of the plots to Langmuir equation. The thermodynamic analysis suggests that the adsorption process was exothermic and spontaneous in nature. Adsorption kinetics follows satisfactorily to the pseudo second-order kinetics. The results of five time consecutive adsorption–desorption cycle indicate that the poly(AAc/AM/SH)-Cu superabsorbent hydrogels have high adsorption and desorption efficiency for the phosphate ions. The results confirmed that poly (AAc/AM/SH)-Cu superabsorbent hydrogels can be applied as effective solid adsorbent for the removal of phosphate ions from waste water and aqueous effluents, which seems the most efficient method to treat an already used adsorbent.

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