

A Study of Polyacrylamide-Pumice Composite for Fast Removal of Copper Ions from Aqueous Solutions: Synthesis, Kinetics and Thermodynamics

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ABSTRACT: *In the present work, a polyacrylamide-pumice stone (PAAm-PMC) composite has been synthesized and used as an adsorbent for the fast removal of copper ions from wastewater. The PAAm-PMC composite was synthesized by the conventional free radical polymerization method and characterization has been done by Fourier Transform Infrared Spectroscopy (FT-IR) and Scanning Electron Microscope (SEM). Effects of various parameters on the adsorption capacity of the synthesized PAAm-PMC composite were studied and optimized. The optimized values of various parameters found were: contact time (60 minutes), pH value of solution (6.5), composite dose (0.05 g), Cu(II) concentration (1500 mg/L), and temperature (323 K). The kinetic studies reveal that the rate of adsorption of copper on the composite, increases with time and the maximum adsorption achieved for copper ions is ~ 96 %. The fast adsorption kinetics followed pseudo-second-order kinetics when modified composites were used. Among three different isotherm models, Langmuir adsorption isotherm model has been found to be the best-correlated model with experimental data-based on a higher correlation coefficient with a maximum Langmuir loading of 500 mg/g. The positive entropy during the adsorption process for both the materials ($\Delta S^0 = 55.6855 \text{ J}/(\text{mol}\cdot\text{K})$ for PAAm and $151.0737 \text{ J}/(\text{mol}\cdot\text{K})$ for PAAm-PMC at 303K) suggests, that the adsorption process is thermodynamically favorable and increases with the increase in temperature. Gibbs free energy values are found to be higher for composite material suggesting higher equilibrium constant values ($\Delta G^0 = -5.0191 \text{ kJ}/\text{mol}$ for PAAm vs $-8.0059 \text{ kJ}/\text{mol}$ PAAm-PMC at 303K). Structural strength and stability of the synthesized composite can be accessed, as modified composites were used up to three times for the adsorption removal of Cu(II) ions from waste-water, after regeneration. These investigations confirmed that the synthesized PAAm-PMC composite can work as an effective adsorbent for the economical and fast removal of Cu(II) ions from wastewater.*

KEYWORDS: *Polyacrylamide; Toxic metal pollution; Adsorption; Composite; Wastewater treatment.*

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INTRODUCTION

Toxic metal pollutants like copper, nickel, lead, mercury, arsenic, etc. enter water resources by consumer and industrial waste, which is ubiquitous in today's era. Although, the existence in wastewater is very essential for essential for plants, animals, and human health, but required in very minute amounts and beyond a certain limit these become toxic. These limits is time to time revised by World Health Organization depending on recent case studies and surveys on health. Some commonly found toxic heavy metals are lead, arsenic, mercury, cadmium, copper, nickel, cobalt, zinc, antimony, etc. The main polluting sources of heavy metal contamination are mining, electroplating, metal finishing, and smelting industries [1-3]. Copper (Cu) is one of the common metallic pollutants. Only a trace amount of copper (Cu) is good for health. Its ingestion beyond permissible limits may cause various types of chronic and acute diseases. Generally, the human body contains 50-120 mg of copper but in large quantity cause immunological, hematological, gastrointestinal, kidney, cornea, liver, brain and lung problems [4-5]. Copper is one of the most important metals for various industrial applications such as making alloys, electroplating industries, making wires, etc. Due to its huge application at the industrial level, copper ions pollute different water resources. Copper ion (Cu(II)) water pollution can cause serious problems for our environment because it is hazardous for all living beings may be due to the ability to form reactive species. It is non-biodegradable and long persists in our environment. Its prolonged ingestion causes Wilson disease in human beings [6-9].

Removal of hazardous metal pollutants from wastewater is a very important task for environmental safety. Different methods and techniques have been used for the removal of heavy metal pollutants from wastewater. Some important methods are reverse osmosis, lime coagulation, adsorption, solvent extraction, chemical precipitation, electrodialysis, and ion exchange. The adsorption process is an important method for the metal removal process due to several factors viz. lower cost, flexibility, reusability of adsorbent, and simple procedure, while in other processes either huge energy inputs are required in the form of pressure for membrane separation process where expensive materials also required for membrane, fouling is another big concern. Advanced oxidation processes like photodegradation, cavitation, and ultra

sonification have short life cycles of reactive species and, therefore limited to low initial concentration [10-15]. Adsorption process for wastewater treatment because of these aforesaid benefits over other methods of waste-water purification. Some other important waste-water treatment methods are photocatalysis [16], Electrochemical methods [17], membrane filtration [18], cementation [19], etc. In the photochemical method, the required time duration is long and applications are limited. The electrochemical method has high operating costs and also high energy consumption. Membrane filtration possess has a high operating cost. The disadvantage of the cementation process is its excessive consumption of sacrificial metal properties. All these disadvantages are not present in the adsorption method.

In recent years, the trends in research on low-cost adsorbents for waste-water treatment have escalated rapidly. Many researchers have reported work on low-cost materials such as clay minerals, wood waste, silica gel, fly ash, coal, zeolites, volcanic rocks etc. Volcanic rocks are porous, light, and non-toxic and due to their low cost, this material can be utilized as adsorbents for the removal of pollutants from water. Pumice is a low-cost volcanic natural rock which is porous, and nontoxic in nature therefore it can be utilized for the adsorption of various types of materials like metal, dyes, gases etc. It is chemically inert and insoluble in acid, base or water (except hydrofluoric acid). It contains surface functional groups like -OH groups and mono and polyvalent ions which are helpful in the formation of chemical bonds with organic and inorganic compounds [20-24].

A large number of polyacrylamide composites have been studied to develop effective and low-cost methods for the removal of toxic metal ions from wastewater [25-28]. The monomer acrylamide polymerizes to form three-dimensional crosslinked polyacrylamide ($-\text{CH}_2\text{CHCONH}_2-$)_n hydrogel. Metal ions are trapped by the amide groups (ionic functional group) of polyacrylamide. It is highly recommended for waste-water treatment due to having properties like non-toxic nature, high absorption capacity, flexibility, and retention of solute and water molecules. Pumice helps strengthen the hydrogel, increasing the adsorption of metal ions. It also provides stability during application, viz. makes loading easy, and prevents collapsing. Further pumice is reusable and supports the easy removal of trapped metal ions [29-30].

In recent years a large number of studies have been carried out by researchers towards the removal of toxic metal ions from water with the help of a variety of adsorbents. *J. Li et al.* prepared Fe_3O_4 nanoparticles decorated graphene oxide nanosheets for the removal of Cu(II) and fulvic acid [50]. *S. Yu* has shown the adsorption of Cu(II) ions on the composite of graphene oxide and titanium dioxide [51]. *M.M. Rao et al.* studied that activated carbon composites with *Phaseolus aureus* hulls and *ceiba pentandra* hulls can be used as good adsorbents for metal ion adsorption [52-53]. *T. Mishra et al.* studied the sorption properties of zeolite derived from Indian fly ash [54]. The use of Ag nanoparticle-loaded activated carbon has been studied by *S.A.R. Shahamirifard* as a good adsorbent for the removal of a variety of metal ions including Cu(II) [55]. *S. Xiao et al.* exhibited the use of zero-valent iron nanoparticle-immobilized hybrid electrospun polymer nanofibre mats as excellent adsorbent for Cu(II) ions [56]. *C. Ding et al.* studied the comparative sorption of Pb(II) , Cu(II) , and Ni(II) on carbonaceous nanofibers [57]. *C. Uzum et al.* have prepared kaolinite-supported zero-valent iron nanoparticles and studied their application for metal ion removal [58]. Chitosan-coated gauze has been shown to be a good alternative for the adsorption of copper ions by *F. Ferrero et al.* The physical structure of this Chitosan-coated gauze makes it useful in continuous flow filters owing to low-pressure drop [59]. *Z. Cao et al.* have prepared chitosan cross-linked by glutaraldehyde for the adsorption of Cu(II) ions. The cross-linking of chitosan by glutaraldehyde has been done by microwave irradiation [60]. Steel is one of the largest used materials in today's modern era. Huge amounts of steel by-products are generated by different industries. *F.A. Lopez et al.* have studied and confirmed that steel by-products can be utilized for the removal of copper ions from aqueous solutions [61]. *R. Ahmad et al.* have prepared iron oxide-coated eggshell powder for the adsorption of Cu(II) ions from aqueous solutions. This material is very useful for the adsorption of metal ions due to its low-cost and biodegradable nature [62]. Rose waste biomass is a unique type of material for metal ion adsorption. *A. R. Iftikhar et al.* have studied the kinetic and thermodynamic aspects of Cu(II) and Cr(III) removal from aqueous solutions using rose waste biomass as adsorbent [63]. *S.H. Huang et al.* prepared an amino-functionalized magnetic nano-adsorbent for the rapid removal of heavy metal ions from

aqueous solution [64]. *Spirogyra* can be a good material for the efficient and economic treatment of waste water. *V.K. Gupta et al.* have studied the biosorption efficiency of *spirogyra* through the study of the adsorption of copper ions [65]. *D. Karabelli et al.* have studied the adsorption of copper ions on the nanoparticles of zero-valent iron. They have studied the efficiency of the removal of Cu(II) ions and the mechanism of uptake using these nanoparticles [66]. *D. Feng et al.* studied that activated biomass derived from *E. maxima* can function as an efficient bio-sorbent for the adsorption of a variety of heavy metal ions. They selected Cu , Pb , and Cd metal ions for the study of adsorption and confirmed that *Ecklonia maxima* algae derivative can be used as a good adsorbent for these metal ions [67]. *M.J.A. Al-atabe* investigated a novel biological sorbent, Cane Papyrus for the adsorption of copper(II) ions from wastewater. The presence of acidic functional groups on the surface of the adsorbent makes it an effective adsorbent. It has good potential for use as an adsorbent due to its low cost and environment-friendly nature [68]. *M.J. Alatabe* prepared activated carbon from Cane Papyrus for the removal of Cu(II) from aqueous solutions. He has studied its effectiveness using various parameters like the effect of change in pH, contact time, metal ion concentration, and adsorbent dose. Results present its use as a novel, cheap, and eco-friendly adsorbent with having high potential for the removal of Cu(II) ions from wastewater [69].

Some researchers have studied polymer/pumice composites for wastewater treatment. *M. Vavuz et al.* [31] have synthesized polyacrylonitrile/pumice composite for the removal of Cu(II) and Cr(III) ions. Pumice as a low-cost adsorbent has been used for the removal of malachite green and crystal violet by *H. Shaysteh et al.* [32] *D. I. Cifci* and *S. Meric* [33] confirm that pumice is a good option for the removal of methylene blue from aqueous medium. *D. Turan et al.* synthesized a novel adsorbent, Chitosan-Immobilized pumice for the adsorption of As(V) from water. This adsorbent can also work in low pH environments [34]. Novel poly[2-(dimethylamino) ethyl methacrylate]/pumice stone hydrogel has been synthesized by *F. Taktak* and *Z. Ilbay* for the rapid adsorption of humic acid from aqueous solution. They also confirmed its reusability by conducting a reusability test and indicated that it is an efficient and cost-effective composite for humic acid adsorption [35]. *T. S. Anirudhan et al.* studied

humic acid immobilized amine-modified polyacrylamide/bentonite composite by direct intercalation polymerization technique for Cu(II) adsorption [36]. H. Chen *et al.* prepared polyacrylamide/attapulgite composite for Cu(II) from an aqueous solution [37].

Present work focused on making a low-cost biodegradable adsorbent for the effective removal of Cu(II) ions from aqueous solutions. This composite has been synthesized by using polyacrylamide and pumice particles, hence it is a low-cost composite. To the best of our knowledge, this composite has not been reported in literature. The effectiveness of the Polyacrylamide-Pumice (PAAm-PMC) composite has been investigated under different conditions, and it was found that it works as an effective adsorbent for the removal of copper ions from aqueous solutions.

EXPERIMENTAL SECTION

Materials

All the chemicals used were of analytical grade and have been purchased from SRL Pt. Ltd. (India) and used as such. The pumice sample was purchased through Amazon.com and sieved by a 100 mesh screen. The stock solution of Cu(II) ions (2000 mg/L) was prepared by dissolving $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in deionized water. The working solutions of Cu(II) ions (1000 mg/L or lower concentration) were prepared by the appropriate dilution of the stock solution just before its use. The pH of metal ion-containing aqueous solution was adjusted with dilute HCl or NaOH as per the need. Solutions for experiments were made by dissolving the appropriate quantity of chemicals of analytical reagent grade in deionized water.

Purification of pumice stone

The pumice sample may contain various types of extractable impurities, which can affect the adsorption of metal ions, hence the purification is necessary before its use. The pumice sample was washed with distilled water four times and then washed with 0.10 mol/l HCl solution. Again, it was washed two times with distilled water. After that, the pumice sample was dried at 120°C for 8 h in the oven. After purification, the pumice stone sample was ground and sieved with 100 mesh sieve and kept in an airtight jar for further use.

Synthesis of *N,N*-Methylenebisacrylamide crosslinker

The crosslinker *N,N*-Methylenebisacrylamide has been synthesized by common procedure given in the literature [38].

Acrylamide (4.5 g), paraformaldehyde (0.80 g) and copper(II) acetate (0.04 g) were taken in two neck round bottom flask. Subsequently conc. HCl (0.5 ml) was added to the flask and refluxed in water bath at 90°C for 90 mins. The yield of the crosslinker was 61%. The crosslinker was obtained in the form of solid precipitate and it has been crystallized with hexane-methanol system. After crystallization, it was dried at room temperature for 24 h. The purity of *N,N'*-Methylenebisacrylamide was confirmed by TLC. (Yield = 1.22 g, 61%).

Synthesis of polyacrylamide-pumice composite

The PAAm-PMC composite has been synthesized by conventional free radical polymerization method using pumice stone particles in aqueous medium [39]. The synthetic procedure has been as follows: Ground and sieved pumice particles (0.45 g) were added in 30 ml water in a two neck round bottom flask and the mixture was magnetically stirred for 15 minutes. After that acrylamide monomer (1.5 g), aqueous solution of potassium persulphate (0.038g dissolved in 5 ml water) and a crosslinker (0.045 g) were added slowly to the flask. The reaction mixture was stirred continuously with the help of magnetic stirring bar. The polymerization process was carried in nitrogen atmosphere at 70 °C for 2 h Fig. 1 shows the schematic representation of the synthesis of the crosslinked polyacrylamide matrix. The synthesized composite was removed from the flask and washed with deionized water. The composite was dried at 70 °C under vacuum for 48 h and sieved through 80 mesh screen. The yield of the synthesized PAAm-PMC composite was 98%.

Adsorption of Cu(II) ions by PAAm-PMC composite

The synthesized composite sample has been added to the aqueous solution of copper ions for studying different factors such as the effect of contact time, pH of copper ion solution, composite dose, Cu(II) concentration and temperature. Each set of studies was conducted out using 0.05g of samples of the PAAm or composite and 25 ml of Cu(II) solution. The mixture was magnetically stirred on a magnetic stirrer at 150 rpm at 25 °C. For studying the effect of pH on adsorption metal solutions of different pH values from 2-7 were prepared with acetic acid and sodium hydroxide. The effect of time on the adsorption was studied in a time duration of 10-100 min. The images in Fig. 2 shows the photographs of the composite and Cu(II)

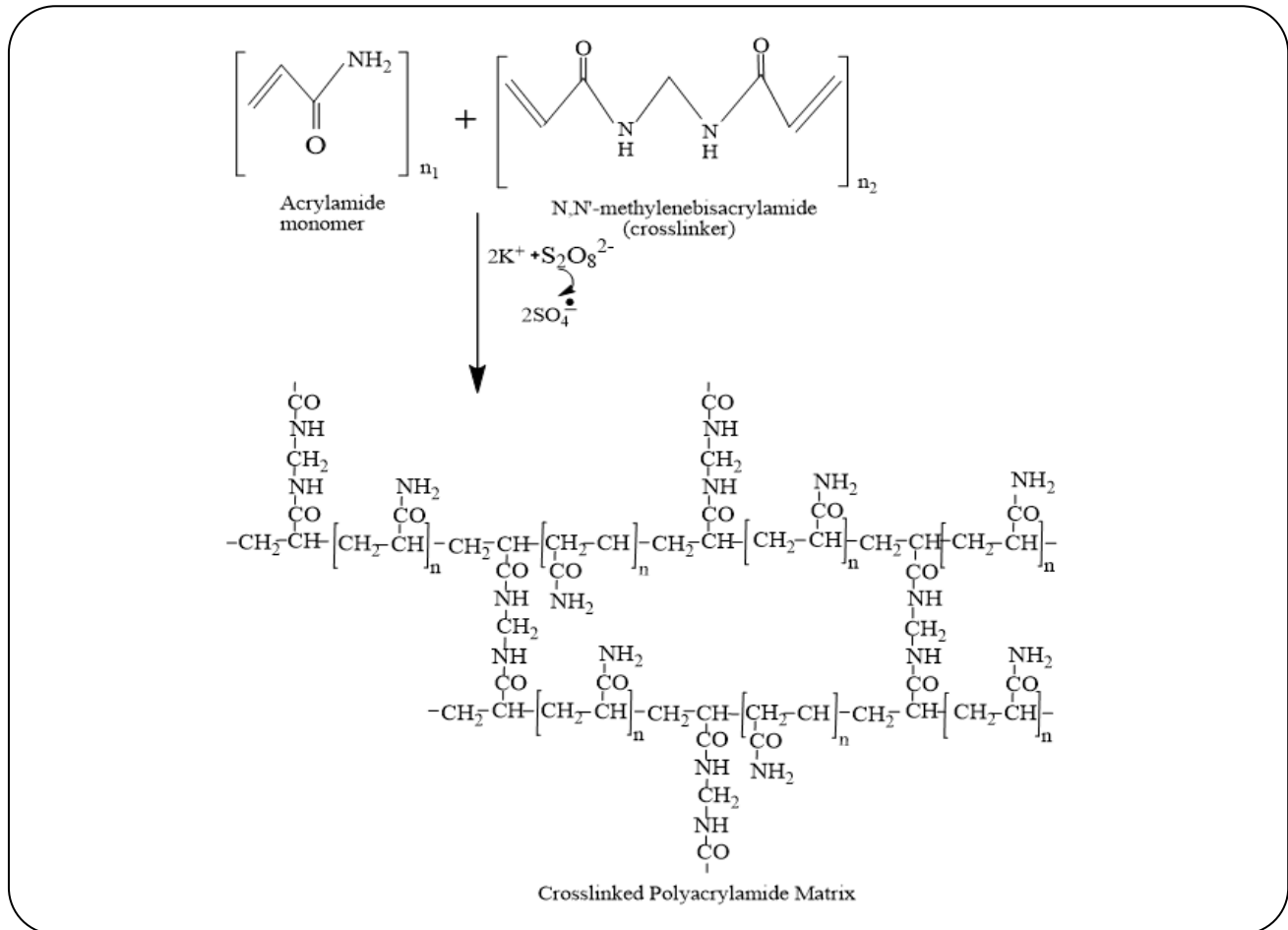


Fig. 1: Schematic representation of the synthesis of crosslinked polyacrylamide matrix.

solution before and after adsorption of Cu(II) from its solution. The amount of the adsorbed Cu(II) ions was determined quantitatively with the help of Lambda 19 (Perkin Elmer, U.S.A.) model UV-VIS spectrophotometer. The wavelength selected for the quantitative determination of Cu(II) was 380 nm. The concentration of Cu(II) ions in unknown samples was determined with the help of calibration curve (plotted using standard solutions of known concentration of Cu(II) ions). The removal percentage (R%) of Cu(II) and capacity of adsorption (q_e) in mg/g by PAAm-PMC composite was calculated by following equation [40].

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{C_0 - C_e}{w} \times V \quad (2)$$

W (mg/L) are the concentrations of Cu(II) at initial and equilibrium time. V (L) shows the volume of the Cu(II) solution, and w (g) is the adsorbent weight.

PAAm and PAAm-PMC isothermal adsorption

The values of adsorption at equilibrium were obtained from the experimental data and were applied to and fitted with different adsorption isotherm models. Freundlich, Langmuir, and Temkin adsorption isotherm models are some important models for adsorption study which were used for examining the plausible mechanism of Cu(II) ions adsorption [41-43]. All experiments for adsorption study were performed at pH 7, by varying the initial concentrations of Cu(II) ions from 200 to 2500 mg/L range. The Langmuir model explains the homogeneous uptake of Cu(II) ions by monolayer adsorption on PAAm and PAAm-PMC composite without interacting between Cu(II) ions and composite, and it is defined by Eq. (3):

$$q_e = q_{\max} \frac{bc_e}{(1+bc_e)} \quad (3)$$

Where q_{\max} denotes the maximum Cu(II) uptake per unit mass of adsorbent mg/g. The Langmuir equation can be linearized as Eq. (4), and related model constants

are determined from the slope and intercept values of the straight-line curve plotted between C_e/q_e versus C_e as Eq. (4) and the experimental data are calculated by Eq. (5) [44-45].

$$\frac{C_e}{q_e} = \frac{1}{bq_{\max}} + \frac{C_e}{q_{\max}} \quad (4)$$

$$r^2 = \frac{\sum(q_e, \text{exp} - q_e, \text{cal})^2}{\sum(q_e, \text{exp} - q_e, \text{cal})^2 + \sum(q_e, \text{exp} - q_e, \text{cal})^2} \quad (5)$$

Where q_e, exp is experimental values, q_e, cal is the isotherm model values, and q_e, cal is the mean values.

The Freundlich equation's empirical form is shown in Eq. (6),

$$\log(q_e) = \log(K_F) + \frac{1}{n} \log(C_e) \quad (6)$$

Where, C_e is the equilibrium concentration of Cu(II) ions in the solution (mg/L), K_F and n are the Freundlich isotherm model constants, which clarify the adsorption capacity and intensity, respectively. The Freundlich isotherm model constants K_F and n can be determined by a linear plot between $\ln(q_e)$ versus $\ln(C_e)$. q_e is the amount of Cu(II) ions adsorbed at equilibrium on adsorbent (mg/g). The Temkin adsorption model is expressed as given in Eq. (7),

$$q_e = B_1 \ln(K_T) + B_1 \ln(C_e) \quad (7)$$

Where, $B_1 = \frac{RT}{b}$; b is the Temkin constant (J/mole), K_T denotes the interaction value of adsorbate and adsorbent.

The average relative errors (ARE%) are determined by using equation 8

$$\text{ARE \%} = \frac{100}{N} \sum_1^N \frac{|q_{\text{cal}} - q_{\text{exp}}|}{q_{\text{exp}}} \quad (8)$$

This Average Relative Errors (ARE%) equation has been determined relative goodness of fitting of the data (experimental) with equations of different models. Where N denotes the experimental data point's number. The equilibrium values (q_{exp}) and the models are denoted as q_{cal} and both have similar units (mg/g).

Adsorption Kinetics

The standard kinetic models like pseudo-first order and pseudo-second order are chosen for study of PAAm and PAAm-PMC adsorption kinetics and linearized form of

these models are presented [46]. Eq. (9) shows pseudo-first order model in linear form

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (9)$$

Where, q_e and q_t are the amount of Cu(II) adsorbed in mg/g on the composite at equilibrium and at instantaneous time, respectively. Pseudo-first order kinetic rate constant k_1 has been determined from the slope obtained from $\log(q_e - q_t)$ versus $t(\text{min})$ plot. The linear form of the pseudo-second order kinetic model is shown in Eq. (10).

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e} \quad (10)$$

Where, k_2 is pseudo-second-order rate constant (g/mg/min) and q_e values are obtained from the slope of plot of the t/q_t versus t .

Nonlinear models are determined from these rate-constant values for all the different models, and the correlation coefficient is determined for each model with the help of the experimental data.

Thermodynamic analysis of Cu(II) ion adsorption

The adsorption mechanism of Cu(II) ion on PAAm and PAAm-PMC was studied thoroughly by different adsorption thermodynamic parameters such as Gibbs free energy change (ΔG_0), enthalpy change (ΔH_0), and entropy change (ΔS_0) [47]. The Gibbs free energy change (ΔG_0) evaluated and could be expressed by the Van't Hoff Eq. (11),

$$\Delta G^0 = -RT \ln K \quad (11)$$

where, K is equilibrium constant and can be calculated from Eq. (12)

$$K = \frac{C_s}{C_e} \quad (12)$$

Where, C_s (mg/L) is the amount Cu(II) ions on the PAAm and PAAm-PMC composite at equilibrium and R (8.314 J/mol K) is the universal gas constant. The change in entropy evaluated in kJ/mol K and the heat of adsorption in kJ/mol, at a constant temperature T (K) from Eqs. (13) and (14), and values were determined from slope and intercept of the plot between $\ln(K)$ versus $1/T$.

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

$$\ln K = \frac{-1}{RT} \Delta H^0 + \frac{1}{R} \Delta S^0 \quad (14)$$

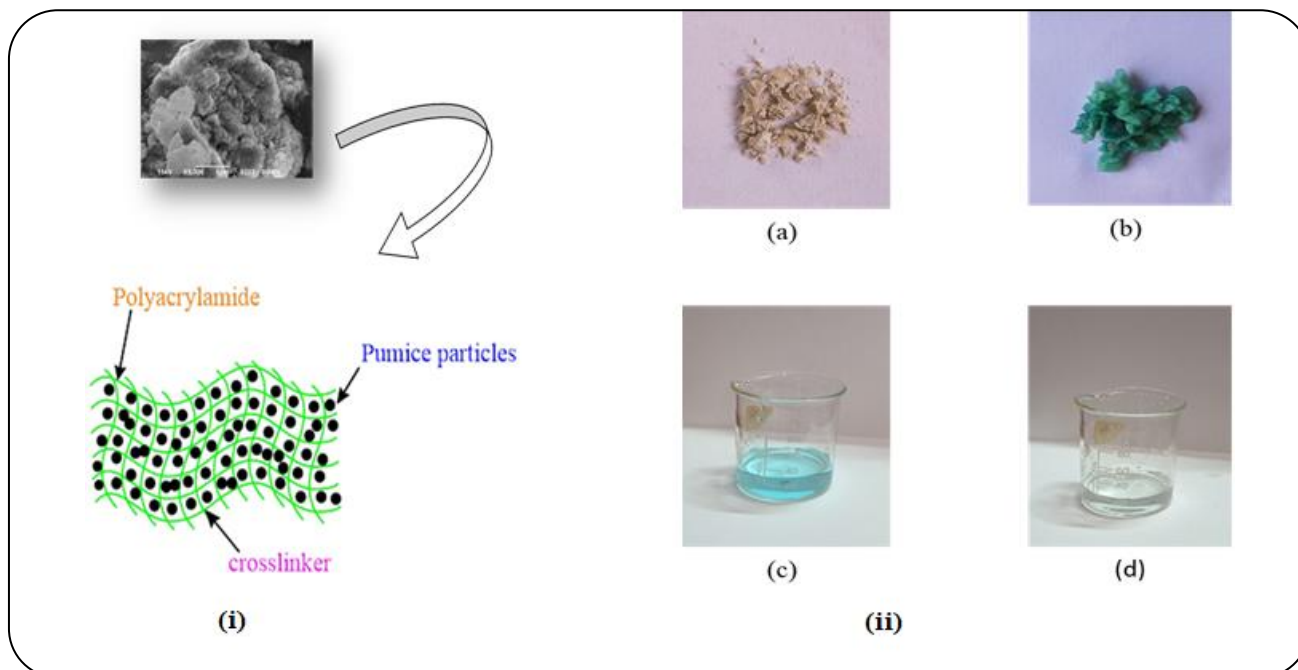


Fig. 2: (i) Schematic representation of PAAm-PMC Composite and (ii) PAAm-PMC (a) before adsorption (b) after adsorption and Cu(II) solution (c) before adsorption (d) after adsorption of Cu(II) ions.

Chemical and physical characterization of the composite

The pumice composition of sample was determined by X-Ray Fluorescence Spectrometers (XRF) technique (Panalytical Axios MAX). Fourier transform infrared spectra (FT-IR) of composite before and after Cu(II) adsorption were obtained using Perkin-Elmer GX FT-IR Spectrometer in range $4000-400\text{ cm}^{-1}$. The KBr pressed pellet method was used for the preparation of samples for testing. The Field emission Scanning Electron Microscopy (Fe-SEM) images of PAAm-PMC composite obtained by instrument type Fe-SEM coupled with Energy Dispersive Spectroscopy (EDAX) XL-30, Philips, Netherlands. For samples analysis were coated with a thin film of platinum *via* sputter coater. The elemental analysis has been done by EDAX. A digital pH-meter (Orion 900S2 model) was used for measuring the pH values.

RESULTS AND DISCUSSION

Physical appearance of the prepared adsorbent

The Fig. 2(i). shows schematic structure of PAAm-PMC composite. The pumice particles are present between crosslinked structure of polyacrylamide hydrogel. Fig. 2(ii) shows the digital images of prepared composites before and after the adsorption process. The colour of composite

after adsorption indicate successful removal of Cu(II) from solution.

FT-IR (Fourier transformed infrared spectra) of PAAm-PMC composite

The FT-IR spectra of PAAm-PMC composite and after Cu(II) adsorption is shown in Fig. 3 (a) and (b). Spectroscopic data of the adsorbent surface from the range of $4000-400\text{ cm}^{-1}$ has been obtained by FT-IR analysis. In the spectrum of PAAm-PMC before adsorption [Fig. 3 (a)], the Broad band at 3426 cm^{-1} is due to the N-H vibration of acrylamide. The C-H structure vibration at $2935, 2173\text{ cm}^{-1}$ and the stretching vibration peak of carbonyl group at 1656 cm^{-1} is observed. Bands at 1423 is due to carboxylate group stretching of acrylate. The band around 1000 cm^{-1} are due to deformations of N-H and CH_2 groups and band around $456, 666$ and 784 cm^{-1} are due to the bending and deformation of the Si-O bond. These characteristic peaks confirms the presence of PAAm and PMC in the sample. In Fig. 3(b) the spectrum of PAAm-PMC all the functional groups are involved in Cu(II) adsorption and it has been confirmed by broadening of the spectrum of composite after adsorption [48-49].

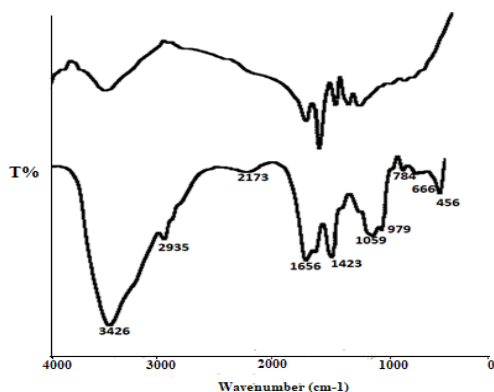


Fig. 3: FT-IR spectrum of PAAm-PMC composite (a) before and (b) after adsorption of Cu(II) ions

SEM analysis of PAAm-PMC composite

The surface morphology of the PAAm-PMC composite before and after the adsorption of Cu(II) ions has been shown in SEM images and indicated in Fig. 4. As shown in Fig. 4, it was found that the composite has a highly porous microstructure having an uneven surface. The highly porous and rough surface results in an increase in the surface area of the composite. The large surface area of the composite is responsible for the fast adsorption of Cu(II) from the aqueous solution. The highly porous and rough surface is beneficial for the adsorption of metal ions and easy and fast bonding of ions to the functional groups of composite. The elemental distribution in composite has been determined by EDAX analysis and shown in Fig. 4(d). The Pt on the surface of the composite was found due to the coating of Platinum on the surface of the sample.

Table 1 includes the elemental compositions of composites, determined from XRF analysis.

Adsorption and Kinetics Studies

Effect of contact time

Effect of contact time on adsorption of Cu(II) ions on PAAm and PAAm-PMC composite adsorbent was studied in the range of 10-100 min and shown in Fig. 5(a). It is an important adsorption parameter because it gives the kinetics of adsorption of the synthesized composite. The experiments were conducted using 25 ml of Cu(II) solution of 1000 mg/L concentration, 0.05 g of adsorbent at pH 7 with a stirring speed 200 rpm at room temperature. Results indicate that the rate of adsorption increased rapidly in the

first 20 min, thereafter adsorption rate decreases gradually and at last equilibrium is achieved. PAAm and PAAm-PMC removed 87% and 96% Cu(II) ion respectively. This confirm that PAAm-PMC composite has more affinity for Cu(II) adsorption than PAAm.

Effect of pH

The Cu(II) adsorption is highly affected by pH value of the solution. The surface polarity of composite and degree of ionization of Cu(II) is dependent upon the pH value of solution. At low pH value all the active sites were ionized and presented in positive charged form. The electrostatic repulsion occurs between these positive charged sites and Cu(II) ion which inhibits the adsorption process. When pH of solution is higher the active sites of adsorbent gets negative charge and enhance the Cu(II) adsorption. The result shown in Fig. 5(b) confirm that the adsorption value increased from 13 to 87% for PAAm and 16 to 96% for PAAm-PMC composite. The maximum adsorption value of Cu(II) on PAAm and PAAm-PMC composite was investigated as 87 and 96 % respectively at pH value of 6.5.

Effect of dose

Different dose of both adsorbents PAAm and PAAm-PMC has different adsorption affinity. The adsorption percentage of Cu(II) ion at different adsorbent dose is shown in Fig.5(c). Increase in Cu(II) ion adsorption with increase in composite dose can be attributed to the more binding sites availability. After particular dose, the percentage removal remains constant and further increase in adsorbent dose do not increase the adsorption of Cu(II). This happens because most of the Cu(II) ions present in the solution have already been removed at a particular dose level and further removal of the copper ions from very low concentration is not a favourable process. This is the reason for the insignificant increase in the percentage of copper adsorption by the adsorbent from 0.05 g to 0.08 g in Fig. 5 (c). This confirm that the maximum adsorption has taken place and the Cu(II) concentration has been reduced to its minimum level at a dose of 0.05 g. The experimental results showed that 0.05 g was sufficient adsorbent dose for maximum Cu(II) adsorption. The concentration of copper ions (Cu(II)) taken for experiment was 1000mg/L and volume 25 mL.

Table 1: Chemical composition of the pumice sample determined by X-ray fluorescence technique.

Metal	Concentration (%)
Na ₂ O	0.38
MgO	0.728
Al ₂ O ₃	1.734
SiO ₂	40.02
SO ₃	18.668
K ₂ O	0.179
CaO	18.832
TiO ₂	0.546
MnO	0.358
Fe ₂ O ₃	11.496
SrO	0.816
ZrO ₂	0.566
SnO ₂	2.184

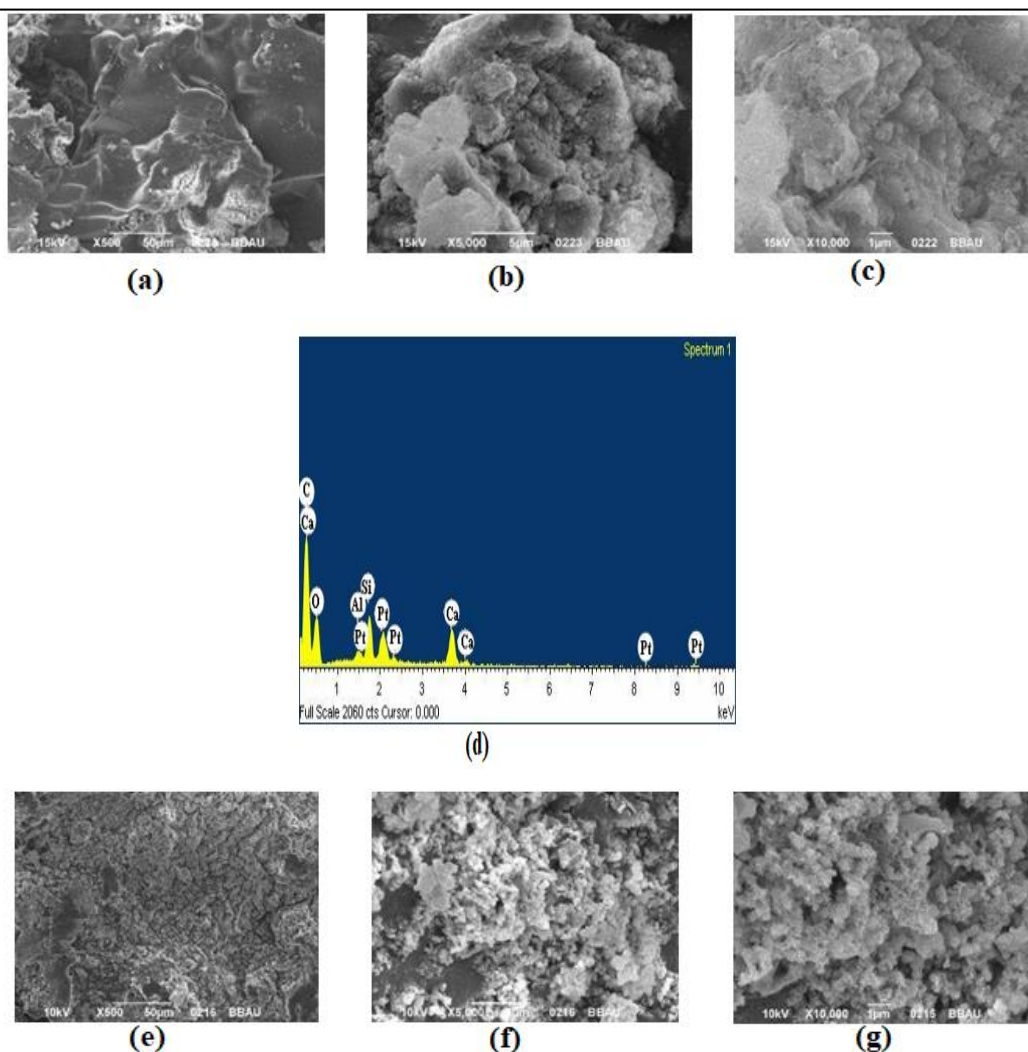


Fig. 4.: SEM micrographs of PAAM-PMC composite before Cu(II) adsorption at (a) 500 (b) 5000 (c) 10000 magnification (d) EDAX elemental analysis and SEM after adsorption of Cu (II) ions at (e) 500 (f) 5000 (g) 10000 magnification.

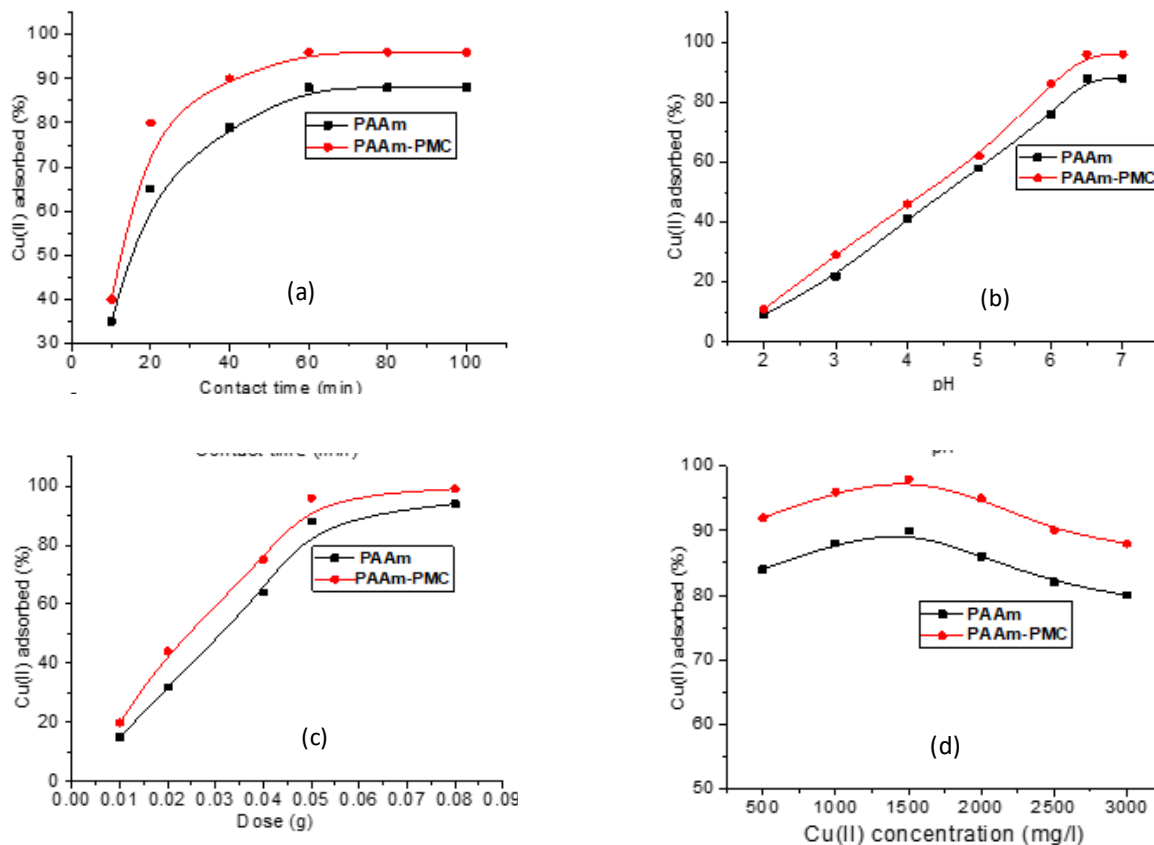


Fig. 5: (a) Effect on adsorption capacity of PAAm and PAAm-PMC composite by contact time variation (b) Effect of pH on adsorption capacity of PAAm and PAAm-PMC composite (c) Effect of PAAm and PAAm-PMC dose on adsorption (d) Effect of Cu(II) concentration on adsorption capacity of PAAm and PAAm-PMC.

Effect of concentration of metal ion

The Cu(II) removal from aqueous solution on PAAm, PAAm-PMC adsorbents at different initial Cu(II) (500-3000 ppm) has been studied. Result have been shown in Fig. 5(d). It has been found that percentage removal of Cu(II) from its aqueous solution depends upon the initial concentration of Cu(II) ions. The percentage removal versus initial Cu(II) concentration study showed that the percentage of Cu(II) adsorption decreased with increase in initial Cu(II) concentration. The numbers of ions present in the aqueous solution are less at lower Cu(II) concentration as compared to the adsorption sites available on the composite. Hence the adsorption of Cu(II) ions increases upto a concentration of 1500 mg/L. However, in higher concentration of Cu(II) ions the number of adsorption sites present on composite become less than the number of Cu(II) ions available, causing the saturation of adsorption sites, due to which the percentage adsorption of Cu(II) decreases.

Effect of temperature

The graph in Fig. 6 shows the temperature effect on Cu(II) adsorption on PAAm and PAAm-PMC composite. The study was carried out at three different temperatures viz. 303 K, 313 K, 323 K. It was found that adsorption of Cu(II) on PAAm, and PAAm-PMC adsorbents increases with increase in temperature, which shows that the process is endothermic in nature. The value of ΔH , which is positive also support the endothermic nature of Cu(II) adsorption on both adsorbents.

Adsorption isotherm results

Out of three adsorption isotherm models, Langmuir adsorption isotherm model gives the best fitting of the experimental data. The values of R^2 (nonlinear) for PAAm-PMC in Langmuir adsorption isotherm model are greater than that of Freundlich and Temkin adsorption isotherms shown in Table 2. This result suggest about monolayer adsorption and presence of finite number

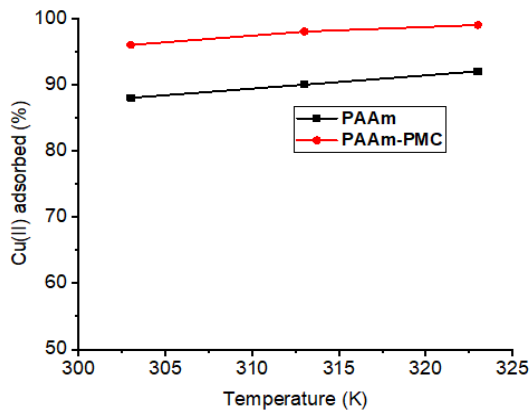


Fig. 6: Temperature effect on Cu(II) adsorption on PAAm and PAAm-PMC composite.

of sites of adsorption. Fig. 7(a) represents the adsorption data q_e versus C_e plots where the experimental data has been shown with black square dots while the adsorption isotherm model values have been shown with dotted lines (right side figure for PAAm and left side figure for PAAm-PMC composite). As observed from Fig. 7(a) Langmuir isotherm model data lines (red dotted line) are fitted closely with experimental data points, while the data obtained from Freundlich model (blue dotted line) is showing deviation from experimental values. Fig. 7(b) show the Langmuir isotherm fitting of PAAm-PMC composite. Temkin data is not included as it deviates a lot from experimental data (R^2 (nonlinear) and ARE %) included in Table 2. The Table 2 shows the error function values of ARE% and the small value of error function is considered as prime criteria of following with nonlinear adsorption model. Therefore, less ARE% shown by Langmuir model also confirm that it is the best fitted model for this experiment. Thus, it confirms that PAAm-PMC can effectively work for Cu(II) adsorption for wastewater treatment.

Kinetic study of PAAm-PMC composite

Different standard kinetics models are applied with experimental kinetics data and shown in Fig. 8 and Table 3. The nonlinear model equation and linear correlation coefficients (R^2) are determined from all models. The pseudo second order gives highest value of linear correlation coefficient (R^2). This confirms that the adsorption kinetics following pseudo-second order equation.

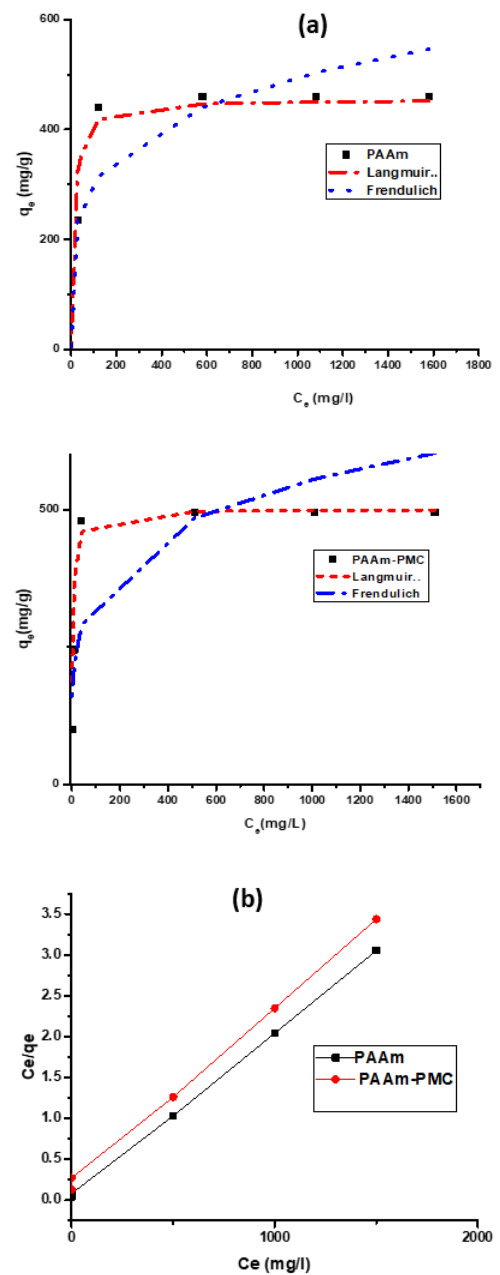


Fig. 7: (a) Adsorption isotherm and (b) Langmuir isotherm fitting of PAAm and PAAm-PMC composite.

Thermodynamic studies

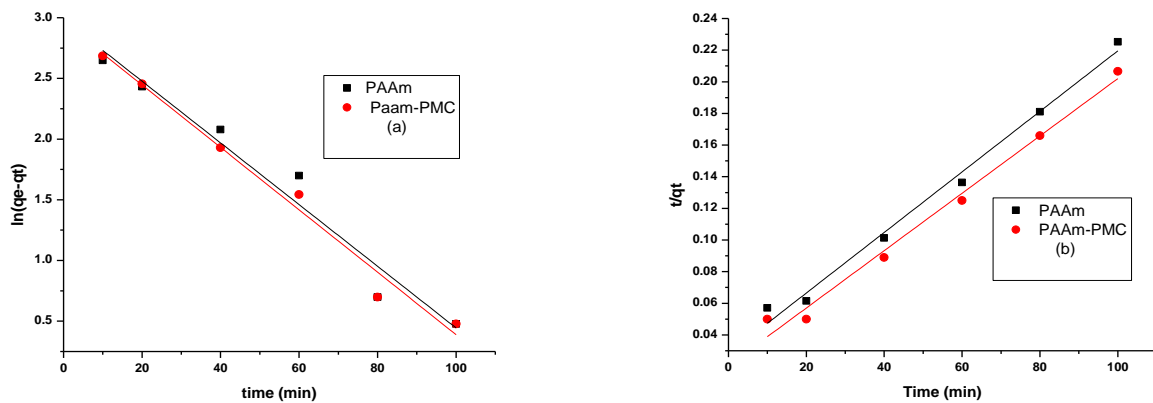
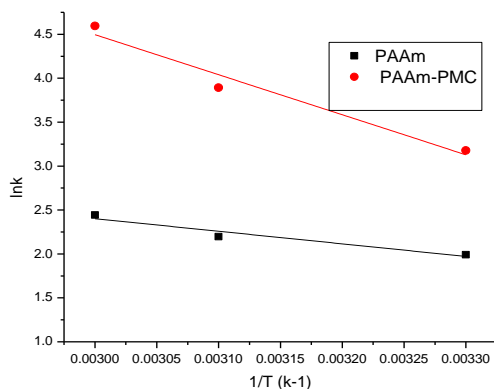
Different thermodynamic parameters (ΔH , ΔS and ΔG) were obtained from the slope and intercept values calculated from $\ln K$ versus T plot by the linear fitting of the experimental data. The linear fitting and regression coefficient value of PAAm and PAAm-PMC composite is 0.943 and 0.966 respectively for adsorption and shown

Table 2: Parameters of Langmuir, Freundlich and Temkin adsorption isotherm model for PAAm and PAAm-PMC.

PAAm	adsorption parameters						R ² (nonlinear)	ARE%
Langmuir	Q _m	476.19	b	0.043			0.880	5.61
Freundlich	1/n	0.26	k _f	78.27			0.772	18.55
Temkin	B	159.49	b	15.01	A _t	0.993	0.123	115.89
PAAm/PMC								
Langmuir	Q _m	500	b	0.28			0.968	11.52
Freundlich	1/n	0.20	k _f	138.01			0.753	17.24
Temkin	B	123.55	b	19.38	A _t	3.32	0.051	157.40

Table 3: The values of k₁, k₂ and their R² of PAAm and PAAm-PMC/

Adsorbent	Pseudo first order		Pseudo second order	
	k ₁ min ⁻¹	R ² (linear)	k ₂ /L(mg.min ⁻¹)	R ²
PAAm	0.0254	0.9648	0.0021	0.9840
PAAm-PMC	0.0273	0.9796	0.0019	0.9806

**Fig. 8: Kinetic model of (a) Pseudo first order (b) Pseudo second order for removal of Cu(II) ion with PAAm and PAAm-PMC.****Fig. 9: Van't Hoff plot of adsorption equilibrium constants for Cu(II) adsorption on PAAm and PAAm-PMC composite.**

in Fig. 9. The negative values for the change in Gibbs free energy (ΔG) determined that the adsorption process is spontaneous in nature. The positive ΔS° values confirmed that the liquid and solid interphase phase adsorption is thermodynamic favourable process; it also explains the increase in the favourability of reaction with the increase in temperature. Furthermore, the positive ΔH value gives information about the endothermic nature of process.

Reusability of synthesized composite

The reusability of a promising adsorbent is very much demanded with its high adsorption capacity. We investigated its reusability with three times adsorption-desorption process. For analysing reusability of PAAm

Table 4: Tabular parameters of Cu(II) adsorption isotherm.

Adsorbent	Heavy metal ion	Temperature (K)	ΔG^0 (kJ/mol)	R^2	ΔH^0 (kJ/mol)	ΔS^0 (J/(mol.K))
PAAm	Cu(II) 1000 mg/L, 25 mL	303	-5.0191	0.9427	11.9065	55.6855
		313	-5.7178			
		323	-6.5587			
PAAm-PMC		303	-8.0059	0.9659	37.8985	151.0737
		313	-10.1276			
		323	-12.3398			

Table 5: Different Low-cost adsorbents for Cu(II) removal.

S No.	Type of adsorbent	pH	Maximum Adsorption Capacity (mg/g)	Reference
1	Graphene oxide	5	45.20	50
2	Graphene oxide/Fe ₃ O ₄	5.3	18.26	51
3	Activated carbon prepared from Phaseolus aureus hulls(ACPAH)	7	20.00	52
4	Activated carbon prepared from Ceiba pentandra hulls	6	21	53
5	Zeolite derived from fly ash	3.5	147.7	54
6	Ag nanoparticle-loadedactivated carbon(Ag-NP-AC)	4.7	60	55
7	MVCNT-reinforced nanofibrous matssupported NZVI	5.5	107.80	56
8	Carbonaceous nanofibers	6.4	204.10	57
9	Kaolinite-supported zerovalent iron nanoparticles	6.0	49.0	58
10	Non-crosslinked chitosan	5	85.00	59
11	Crosslinked chitosan	5	200.00	60
12	Steel-making by-product	6	40.00	61
13	Iron oxide coated eggshell powder	6	44.00	62
14	Rose water biomass	5	56.00	63
15	Amino-functionalization of PAA-coated Fe ₃ O ₄ nanaoparticles	5	12	64
16	Spirogyra (green alga)	5	133.00	65
17	Bare NZVI (FeCl ₂ .4H ₂ O+NaBH ₄)	6.5	250.00	66
18	Ecklonia maxima-marine alga	6	90.00	67
19	Cane Papyrus	6.5	116	68
20	Activated carbon prepared from Cane Papyrus	6	40	69
21	Polyacrylamide-Pumice composite(short nomenclature)	6.5	480	This study

and PAAm-PMC composite, 0.05 g of Cu (II) adsorbed samples were added in 25 ml of 0.05 mol/l of HCl solution for 100 min at room temperature. The pH of the solution was maintained at 2. Both desorbed samples were removed from HCl solution and centrifuged then washed with distilled water and dried in oven at 70 °C for 12 h. The more acidic medium was helpful for breaking bond between composite active sites and Cu(II). In comparison to PAAm, the composite shows good adsorption capacity even after three times of reuse. The adsorption-desorption shows that adsorption capacity was decreased by 28%

for PAAm and only by 7 % for the PAAm-PMC composite respectively and results are shown in Fig. 10.

Comparison of the synthesized composite with other adsorbents reported in literature

In recent years a large number of studies have been carried out by researchers towards the removal of toxic metal ions from water with the help of a variety of adsorbents. A list of different adsorbents and their efficiency for the removal of Cu (II) ions has been presented in Table 5. From this table it is clear that the

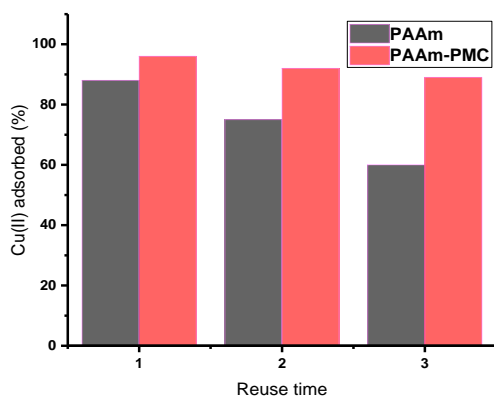


Fig. 10: Relation between the reuse frequency and adsorption capacity of PAAm and PAAm-PMC composite.

composite synthesized by us has excellent adsorption capacity towards the removal of copper ions.

CONCLUSIONS

In present paper, the adsorption of copper ions Cu(II) from aqueous solutions on synthesized PAAm-PMC composite has been investigated with different experimental conditions *viz.* contact time, pH value of metal ion solution, composite dose, Cu(II) concentration, and temperature. It was observed that 96% of copper ions were adsorbed by the PAAm-PMC composite in a single step in about 60 minutes. The PAAm-PMC composite is highly stable in water and reusable than PAAm due to this composite PAAm-PMC performs better than only PAAm because PAAm is soluble in an aqueous medium. FT-IR, SEM, EDX, and TGA were used for the characterization of the composite. The Langmuir adsorption isotherm model has been found to be the best-correlated model with experimental data based on a higher correlation coefficient with a maximum Langmuir loading of 500 mg/g. The positive entropy during the adsorption process for both materials suggests that the adsorption process is thermodynamically favorable and it explains the increase in the favourability of the adsorption process with the increase in temperature ($\Delta S^0 = 55.6855 \text{ J}/(\text{mol}\cdot\text{K})$ for PAAm vs $151.0737 \text{ J}/(\text{mol}\cdot\text{K})$ PAAm-PMC at 303K). Gibbs free energy values are found to be higher for composite material suggesting higher equilibrium constant values ($\Delta G^0 = -5.0191 \text{ J}/\text{mol}$ for PAAm vs $-8.0059 \text{ kJ}/\text{mol}$ PAAm-PMC at 303K). The negative values for the change

in Gibbs free energy (ΔG) values determined that the adsorption process is spontaneous in nature. The positive ΔS^0 values confirmed that the liquid and solid interphase phase adsorption is thermodynamic favourable process; it also explains the increase in the favourability of reaction with the increase in temperature. This composite can be used in treating waste-water generated by mining and electroplating industry. From the study it can be concluded that the PAAm-PMC composite has been found to be a good option for the fast removal of Cu(II) from aqueous solution. It can be a good alternative for various expensive synthetic adsorbents for wastewater treatment as it is a low cost, biodegradable, reusable, nontoxic and easy to synthesize composite material.

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