

Synthesis and Characterisation of Polyacrylamide Hydrogel for the Adsorption of Heavy Metals

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ABSTRACT

Synthesis and characterization of polyacrylamide hydrogel for the adsorption of heavy metals was studied, the investigation being with regards to removal of cadmium from water sources. The polyacrylamide hydrogel used for the investigation was synthesized by solution polymerization of Acrylamide and N,N'-methylene bisacrylamide and initiated by ammonium persulfate. The hydrogel synthesized was characterized by Fourier Transform Infrared Spectroscopy (FTIR), by Scanning Electron Microscopy (SEM), as well as swelling behavior. The FTIR analysis showed the presence of N—H, —CH₂, C=O, —N—CH₂—, —C—N—, which corresponds to polyacrylamide hydrogel in literature. The SEM analysis revealed a less porous structure of the polyacrylamide hydrogel which implies more of surface adsorption. The adsorption of cadmium was carried out under the same conditions of temperature and pressure, with varying concentrations of Cadmium (as the heavy metal) and a slightly varying pH and varying hydrogel masses. In this, the synthesized hydrogel with less porous surface morphology was tested for applications as adsorbent for removal of cadmium pollution mainly from water sources. Cadmium adsorption unto the surface of the hydrogel was investigated first, by FT-IR, then Scanning Electron Microscopy (SEM), and its presence was confirmed by Atomic Adsorption Spectroscopy (AAS) of the resulting solutions after adsorption. The AAS analysis of solutions after adsorption experiment revealed that the hydrogel had high adsorption potential for cadmium removal, with 0.833g of the hydrogel removing as high as 1.738 mgL⁻¹ of cadmium at pH of 6.6, and thus, can be applied in the removal of cadmium pollution from water sources.

Keywords: Polyacrylamide, Hydrogel, Adsorption, Heavy metal.

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1.1 INTRODUCTION

A hydrogel is a three-dimensional (3D) network of hydrophilic polymers that can swell in water and hold a large amount of water while maintaining the structure due to chemical or physical cross-linking of individual polymer chains (Morteza *et al.*, 2016). Hydrogels are synthetic materials widely used to obtain realistic tissue constructs, as they resemble living tissues (Cristina *et al.*, 2017). Polymer hydrogels have been proposed for many applications such as the controlled delivery of medicinal drugs, artificial muscles, sensors systems and contact lenses, and they have potential applications in structural materials. In the polymeric network hydrophilic groups or domains are present which are hydrated in an aqueous environment thereby creating the hydrogel structure (We and Van, 2002).

Polyacrylamide hydrogel is formed by free radical polymerization reaction of acrylamide with N,N'-methylene bisacrylamide (which acts as a cross-linker) in the presence of redox initiators. Polyacrylamide hydrogel can be prepared by several methods such as solution polymerization, inverse emulsion polymerization, suspension polymerization and solid state polymerization. However, the scope of this work covers only solution polymerization.

Hydrogels also possess a degree of flexibility very similar to natural tissue due to their significant water content. The hydrophilicity of the network is due to the presence of hydrophilic groups such as —NH₂, —COOH, —OH, —CONH₂, —CONH—, and —SO₃H (Morteza *et al.*, 2016).

The viscoelastic behaviour of polymer gels near the sol–gel transition have been studied experimentally and theoretically (Richter *et al.*, 2005; Neamtu *et al.*, 2006). The sol-gel transition for a polyacrylamide gel during in situ preparation was investigated by dynamic rheology at constant frequency of 0.1 Hz and by means of temperature, pH and conductivity variation and conductivity determination. It was found the optimal weight ratio of the redox initiators pair from the viewpoint of elastic properties of the obtained hydrogel is 7/1 potassium persulfate/ascorbic acid (Neamtu *et al.*, 2006).

Dynamic swelling kinetics of the hydrogels shows that the rate of absorbency for porous hydrogels is higher than that of non-porous hydrogels. The effect of MBA concentration and CaCO₃ amount showed that the water absorbency of the hydrogels is increased with increasing of CaCO₃ amount but decreased with increasing MBA concentration (Mahdavinia *et al.*, 2009). Polyacrylamide hydrogels swell well when in media, but the influence of swelling on local elastic properties is poorly characterized (Ramesh *et al.*, 2020). Increase in starch content increase the rate of water uptake and the swelling degree at equilibrium (Ana *et al.*, 2020). Hydrogels exhibiting a high toughness, i.e., about 300% elongation ratio at break are obtained by modification of PAAm network chains with 10 mol% N-octylacrylamide (Suzan *et al.*, 2009).

Hydrogels with inorganic nanoparticles possessed excellent mechanical strengths and elasticities, and the compression strength of PAAM-SA-NS reached up to 1.3 MPa at $\epsilon = 60\%$ by adding only 0.036 g NS in a 30 g polymer matrix (Yiyang *et al.*, 2019). The viscous energy dissipation properties of the nanocomposite gel decreases by increasing the cross-linker concentration of the gelation system (Jamal and Ali, 2007).

The final properties of the hydrogels, especially when prepared in the presence of atmospheric oxygen depends on events during gel formation. Gelation features, including inhibition period, exothermic period and temperature increases, observed during the gelation, are dependent on the type and concentration of ingredients within the preparatory formulation (Hosseini and Kinam, 2002).

When PAAm hydrogels are stored under alkaline conditions, they can undergo a hydrolysis reaction, which changes them from neutral hydrogels to polyelectrolyte hydrogels, resulting in significant volumetric increases (Yu and Lihua, 2020). Ions such as Cu and Cd are bound more strongly to copolymer hydrogel than the competing ions of Na, K, Ca and Mg, particularly at pH 5, largely due to the increased acidity of these transition metal ions (Li *et al.*, 2002)

1.2 Heavy Metals

Heavy metals are generally referred to as those metals which possess a specific density of more than 5 g/cm³ and adversely affect the environment and living organisms (Järup, 2003). Heavy metals are significant environmental pollutants and their toxicity is a problem of increasing significance for ecological, evolutionary, nutritional and environmental reasons (Jaishankar *et al.*, 2014; Nagajyoti *et al.*, 2010). Although it is acknowledged that heavy metals have many adverse health effects and last for a long period of time, heavy metal exposure continues and is increasing in many parts of the world (Jaishankar *et al.*, 2014).

1.2.1 Heavy Metal Pollution

Heavy metal pollution is commonly found in wastewater of many industrial processes and has been known to cause severe threats to the public health and ecological systems. Flora *et al.* (2008) found that oxidative deterioration of biological macromolecules is primarily due to binding of heavy metals to the DNA and nuclear proteins. Heavy metals enter the surroundings by natural means and through human activities (Jaishankar *et al.*, 2014). Various sources of heavy metals include soil erosion, natural weathering of the earth's crust, mining, industrial effluents, urban runoff, sewage discharge, insect or disease control agents applied to crops, and many others (Morais *et al.*, 2012). The most commonly found heavy metals in waste water include arsenic, cadmium, chromium, copper, lead, nickel, and zinc, all of which cause risks for human health and the environment (Lambert *et al.*, 2000).

Heavy metal toxicity can lower energy levels and damage the functioning of the brain, lungs, kidney, liver, blood composition and other important organs (Jaishanker *et al.*, 2014). Long-term exposure can lead to gradually progressing physical, muscular, and neurological degenerative processes that imitate diseases such as multiple sclerosis, Parkinson's disease, Alzheimer's disease and muscular dystrophy. Repeated long-term exposure of some metals and their compounds may even cause cancer (Jarup, 2003).

Lead poisoning was considered to be a classic disease and the signs that were seen in children and adults were mainly pertaining to the central nervous system and the gastrointestinal tract (Markowitz, 2000). The Environmental Protection Agency considers lead a carcinogen (Jaishanker *et al.*, 2014). Lead poisoning can also occur from drinking water. The pipes that carry the water may be made of lead and its compounds which can contaminate the water (Brochin *et al.*, 2008).

Mercury is considered the most toxic heavy metal in the environment (Jaishankar et al., 2014). Mercury poisoning is called pink disease. Exposure to elevated levels of metallic, organic and inorganic mercury can damage the brain, kidneys and the developing foetus (Alina et al., 2012). Exposure to metallic mercury vapors at higher levels for shorter periods of time can lead to lung damage, vomiting, diarrhea, nausea, skin rashes, increased heart rate or blood pressure (Jaishankar et al., 2014), and can also cause depression, fatigue, memory loss, tremours, headache, hair loss, etc.

Cadmium and its compounds are classified as Group 1 carcinogens for humans by the International Agency for Research on Cancer (Henson & Chedrese, 2004). Studies on humans and animals have shown that osteoporosis is a critical effect of cadmium exposure along with disturbances in calcium metabolism, formation of renal stones and hypercalciuria (Jaishankar et al., 2014). Inhalation of higher levels also damage the lungs and kidneys. Cadmium is the seventh most toxic heavy metal as per ATSDR ranking. It is a by-product of zinc production which humans or animals may get exposed to at work or in the environment. Once this metal gets absorbed by humans, it will accumulate inside the body throughout life. This metal was first used in World War I as a substitute for tin and in paint industries as a pigment. In today's scenario, it is also being used in rechargeable batteries, for special alloys production and also present in tobacco smoke. About three-fourths of cadmium is used in alkaline batteries as an electrode component, the remaining part is used in coatings, pigments and platings and as a plastic stabilizer. Humans may get exposed to this metal primarily by inhalation and ingestion and can suffer from acute and chronic intoxications. Cadmium distributed in the environment will remain in soils and sediments for several decades. Plants gradually take up these metals which get accumulated in them and concentrate along the food chain, reaching ultimately the human body. In the US, more than 500,000 workers get exposed to toxic cadmium each year as per The Agency for Toxic Substances and Disease Registry (Bernard, 2008; Mutlu et al., 2012). Researches have shown that in China the total area polluted by cadmium is more than 11,000 hectares and its annual amount of industrial waste of cadmium discharged into the environment is assessed to be more than 680 tons. In Japan and China, environmental cadmium exposure is comparatively higher than in any other country (Han et al., 2009). Cadmium is predominantly found in fruits and vegetables due to its high rate of soil-to-plant transfer (Satarug et al., 2011). Cadmium is a highly toxic nonessential heavy metal that is well recognized for its adverse influence on the enzymatic systems of cells, oxidative stress and for inducing nutritional deficiency in plants (Irfan et al., 2013).

Exposure to chromium compounds can result in formation of ulcers, which will persist for months and heal only slowly (Jaishankar et al., 2014). Chromate compounds can induce DNA damage in many different ways and can lead to the formation of DNA adducts, chromosomal aberrations, sister chromatid exchanges, alterations in replication and transcription of DNA (O'Brien et al., 2001; Matsumoto et al., 2006). Arsenic, manganese and other heavy metals have adverse effects as well.

1.2.2 Removal of Heavy Metals

Heavy metal pollution is commonly found in wastewater of many industrial processes and has been known to cause severe threats to the public health and ecological systems. Flora et al. (2008) found that oxidative deterioration of biological macromolecules is primarily due to binding of heavy metals to the DNA and nuclear proteins. Heavy metals enter the surroundings by natural means and through human activities (Jaishankar et al., 2014). Various sources of heavy metals include soil erosion, natural weathering of the earth's crust, mining, industrial effluents, urban runoff, sewage discharge, insect or disease control agents applied to crops, and many others (Morais et al., 2012). The most commonly found heavy metals in waste water include arsenic, cadmium, chromium, copper, lead, nickel, and zinc, all of which cause risks for human health and the environment (Lambert et al., 2000).

The removal of heavy metal ions from various water resources is of great scientific and practical interest. To solve the problem of heavy metal accumulation, toxicity and poisoning of heavy metals in the environment, several adsorbents have been used for the adsorption of heavy metal ions from the environment (water sources, sewage, soil, industrial wastes, etc) in order to minimize the effects that heavy metals pose to the environment. However, hydrogels are one of the most widely used and promising group of adsorbents that give better and efficient result with regards to the removal of heavy metals especially from water sources.

2.0 MATERIALS AND METHODS

2.1 Materials

Acrylamide (LOBA Chemie Pvt Ltd, Mumbai, India), N,N'-Methylenebisacrylamide (LOBA Chemie Pvt Ltd, Mumbai, India), Ammonium persulphate (Guangshua Sci—Tech Co., Ltd. Shoutou, Guangdong, China), Sodium metabisulphide (Guangdong Guagshua Sci—Tech Co., Ltd, China), Nitrogen gas (Multi—User Science Research Laboratory, Ahmadu Bello University, Zaria, Kaduna State, Nigeria), Distilled water, Beakers (4 beakers of 100ml, 1 beaker of 200ml, and 1 beaker of 2000ml), Glass plates, Table knife, Weighing balance (analytical: AM1530, top loading balance), Magnetic stirrer, Spatula, Pair of surgical gloves, Measuring cylinders (1 cylinder of 100ml and 1 cylinder of 200ml), and pH meter (HANNA pH Instrument calibrated using buffer pH-7 tablet)

2.2 Methods

2.2.1 Weighing and Sample Preparation

N,N'-Methylene bisacrylamide solution was prepared by dissolving weighed 0.5g N,N'-methylene bisacrylamide in 10ml distilled water in a 100ml beaker. Ammonium peroxydisulphate solution was prepared by dissolving 0.5g ammonium peroxydisulphate in 10ml distilled water in a 100ml beaker. Sodium metabisulfite solution was prepared by dissolving 0.5g sodium metabisulfite in 10ml distilled water in a 100ml beaker. About 30g Acrylamide was weighed and transferred into a 2000ml beaker for further synthesis.

2.2.2 Synthesis of Polyacrylamide Hydrogel

The polyacrylamide gel was prepared by redox solution copolymerization of Acrylamide and N,N'-methylene bisacrylamide in distilled water. About 30g of Acrylamide was weighed in an analytical weighing balance and transferred into a 2000ml beaker. About 150ml distilled water was measured in a measuring cylinder and transferred into the beaker containing the acrylamide. The mixture was placed on a magnetic stirrer and the bar was placed inside the beaker and stirred for about 10 minutes under nitrogen gas to achieve homogeneity. The N,N'-Methylene bisacrylamide (in 10ml distilled water) solution was added and stirred continuously for another 10 minutes under nitrogen gas to achieve and eliminate oxygen gas and achieve inert atmosphere for the polymerization reaction to take place. The prepared solution of Ammonium persulfate (in 10ml distilled water) was then added into the reaction mixture as a redox reaction initiator to initiate the polymerization reaction of acrylamide and N,N'-Methylene bisacrylamide by supplying free radicals. The stirring continued for another 2 minutes under nitrogen gas. Because the polymerization reaction is slow, the prepared solution of sodium metabisulfite (in 10ml distilled water) was added to the reaction mixture as an activator to hasten the polymerization reaction. The reaction mixture was further stirred to for about 20 more minutes to complete the polymerization reaction process. The magnetic stirrer was switched off and the nitrogen gas nozzle was put off. The highly viscous solution was allowed to stand for about 5 minutes to ensure total gelling. The polyacrylamide hydrogel obtained was peeled off the containing beaker and cut into pieces of desired sizes with a knife for further treatment. The gel was observed to be sticky. The whole synthesis process was carried out at room temperature.

2.2.3 Determination of Bulk Density

The bulk density of the synthesized polyacrylamide hydrogel was determined by weighing a certain mass (m) on an analytical weighing balance and inserting into a beaker containing a certain volume of water V_0 . The volume of water rose to a new volume V_1 . The data obtained was used to calculate the bulk density using the equation below:

$$\text{Bulk density} = \frac{\text{Mass of substance}}{\text{Volume of water displaced}}$$

$$\text{Bulk density} = \frac{m}{(V_1 - V_0)}$$

The bulk density of the polyacrylamide hydrogel was determined at room temperature.

2.2.4 Swelling Property of Polyacrylamide Hydrogel

The degree of swelling (S_0) was obtained by first sun-drying the polyacrylamide hydrogel. The dry gel was weighed and recorded as W_0 on the analytical weighing balance. A certain volume of water was measured in a measuring cylinder and transferred into a beaker. The pH of the water was measured using pH meter calibrated with solution of buffer tablet, pH 7 prepared in 100ml distilled de-ionized water. The weighed sun-dried polyacrylamide hydrogel was inserted into the water in the beaker and allowed to stand for 24 hours at room temperature and pressure so as to enable it absorb as much water as it can hold at that temperature.

The polyacrylamide hydrogel was removed from the water after about 24 hours and wrapped with a filter paper to remove surface water and weighed again on an analytical weighing balance to obtain a second weight recorded as W_1 . The swelling degree, S_0 was calculated using the following equation:

$$S_0 = \frac{\text{Weight of water absorbed by hydrogel (in the swollen state)}}{\text{Weight of hydrogel (in the dry state)}}$$

$$S_0 = \frac{W_1 - W_0}{W_0}$$

Where, W_0 = Weight of hydrogel (in the dry state).

W_1 = weight of hydrogel (in water-swollen state).

2.2.5 Characterization of the Structure and Composition of the Polyacrylamide Hydrogel

The FTIR spectra of the Acrylamide and the polyacrylamide hydrogels (before and after adsorption) were obtained using an FTIR spectrophotometer to determine the change in functional groups present (from the acrylamide to polyacrylamide). The hydrogels were dewatered in air and placed each directly in the instrument. Each spectrum was collected after 30 sample scans and 16 background scans at a resolution of 8 (Agilent technologies, Multi-User Science Research Laboratory, Ahmadu Bello University, zaria, Kaduna State, Nigeria). The first sample was scanned while it remained dewatered right before the adsorption of cadmium from its solution of salt. The FTIR for the second sample was obtained after the adsorption of cadmium from solution of its salt, and after moderate drying at room temperature.

2.2.6 Morphological study of the Polyacrylamide Hydrogel Using Scanning Electron Microscopy (SEM).

The purified hydrogels were dewatered by wrapping with filter paper. The morphology of the dewatered hydrogel samples was analyzed using scanning electron microscopy (Phenom World, Federal university Dutsin-Ma, Katsina State, Nigeria) at an accelerating voltage of 15.0 kV. The SEM was taken twice on the same sample of polyacrylamide hydrogel once each before and after adsorption of the heavy metal cadmium from a solution of its salt. The first was taken to study the morphological properties before adsorption, whereas the second, taken after adsorption was meant to check its metal binding property.

2.2.7 Preparation of Solution of Cadmium Salt (Cadmium (ii) Chloride, CdCl_2) For Adsorption Experiment

The solution of Cadmium used for the adsorption analysis was synthetically prepared in the laboratory using a highly soluble compound of cadmium (cadmium chloride) at room temperature. About 2.4g, 2.0g, 1.6g and 1.2g each of cadmium (ii) chloride were weighed in an analytical weighing balance and placed in 250ml beakers each and filled to mark of 100ml with distilled water. The resulting mixtures were each stirred with glass stirring rod and allowed to stand a few minutes to homogenize the solutions. The resulting mixtures were then divided into two parts by transferring about 60ml each of the prepared solutions to other clean beakers and leaving 30ml of the solutions on the original beakers. Both the beakers for each prepared solution were labelled and the pH for each of the solution was taken and noted from the pH meter and kept on the cupboard for latter adsorption experiment.

2.2.7 Adsorption Experiment of Cadmium on the Polyacrylamide Hydrogel

Four different samples of polyacrylamide hydrogel were weighed each on analytical weighing balance and placed one in each of the beakers containing the 60ml prepared solutions. The beakers containing the 30ml solutions were labelled with numbers showing they were noted before adsorption experiment while those containing the hydrogels were labelled with numbers differentiating them from the former. All the beakers containing the hydrogels and the prepared solutions were placed in cupboard for about 118 hours to ensure adsorption of the metal ions (Cd^{2+}) from the solution on the hydrogel surface.

The gels were removed from the solutions after about 118 hours and exposed to air in order to ensure dehydration/drying of the gels for further FTIR and SEM analysis after adsorption experiment.

Adsorbed amounts of cadmium on the polyacrylamide hydrogels were computed using by subtracting the equilibrium concentrations from the initial concentrations of cadmium from the sample solutions by the equation below:

$$q_e = (C_o - C_e)$$

q_e = Concentration of cadmium adsorbed/removed by hydrogel, C_o = Initial concentration, C_e = Equilibrium concentration.

3.0 RESULTS AND DISCUSSION

3.1 Bulk Density

The bulk density of the prepared polyacrylamide hydrogel was obtained by inserting a measured mass of 39.76g of the hydrogel in a beaker containing about 100ml of water. The water level rose to a new volume of about 129ml. The bulk density was computed as a ratio of the mass of hydrogel to its change in volume as 1.371gcm^{-3} .

3.2 Polyacrylamide Hydrogel Swelling Property

The swelling properties of hydrogels are of interest in many applications (Osada *et al.*, 1994; Brazel and Peppas, 1995). The characteristic hydrogel swelling behaviour depends on functional groups present. For a given hydrogel, the degree of swelling depends on pH and ionic strength of the solution (Durmaz and Okay, 2000; Cohen *et al.*, 1992). In order to efficiently use the polyacrylamide hydrogel for adsorption, characterizing the swelling properties of the hydrogel is needed. This is because the pore size of the hydrogel network as well as its volume are both dependent on its swelling properties. These (pore size and volume) in turn affect the ease of handling of the hydrogel and other practical considerations for its use for adsorption.

The swelling properties of the polyacrylamide was determined by inserting a measured weight of the hydrogel in distilled water at pH 7 (measured by HANNA pH meter calibrated using buffer solution prepared using buffer pH-7 tablet) for 24 hours. The hydrogel was then removed from the water and wrapped in paper to remove surface water and reweighed again to obtain a new weight from which the swelling ratio was calculated as 13.39 under room conditions of temperature and pressure.

3.3 Composition of Polyacrylamide Hydrogel

FTIR of acrylamide and polyacrylamide hydrogel (both before and adsorption of cadmium) were carried out to ensure that the polymerization reaction had proceeded as expected and to elucidate the composition of the newly prepared polyacrylamide hydrogel.

The FTIR of acrylamide had adsorption peaks at 3336.0, 3168.2, 2814.1, 1988.0, 1923.3, 1654.9, 1610.2, 1423.8, 1349.3, 1278.5, 1136.0, 1051.1 cm^{-1} and several other peaks in the finger print region ($< 1000\text{ cm}^{-1}$). The absorption peaks between 3000cm^{-1} and 3600cm^{-1} are assigned to N—H and C—H, while the band at $2800 - 2900\text{ cm}^{-1}$ is due to C—C—H. The absorption bands between 1600 and 1800 are attributed to C=C and C=O bands of the acrylamide monomer as depicted in figure 3.1 (a).

The spectrum of the polyacrylamide hydrogel (before adsorption) had absorption peaks at 3433, 2926, 2856, 1707, 1664 and 1537cm^{-1} . The absorption peak at 3433 cm^{-1} corresponds to the N-H group vibration from crosslinking bridges, while valence vibration peak at 2926 is attributed to CH_2 groups in the chain and crosslinking bridges. The band of absorption at 2856 corresponds to —N— CH_2 — bonds from the crosslinking

bridges. The stretching and deformation attributed to the C=O and N—H links from the amide group appeared at 1664 cm^{-1} and 1537 cm^{-1} . The deformation vibrations of —C—N— and CH_2 groups had peaks in the wavenumber range 1400 to 1000 cm^{-1} . The absorption bands were in agreement with values given in literature (Turan *et al.*, 2009; Dumitrescu *et al.*, 2015). The FTIR spectra of polyacrylamide hydrogel showing all its bands as well as their absorption peaks in their wavenumber ranges is as seen in the figure 3.1 (b).

The spectrum of polyacrylamide hydrogel (after adsorption of cadmium from solution of its salt, CdCl_2) had absorption peaks which were lower than the absorption peaks of polyacrylamide hydrogel before adsorption due to the presence of cadmium on the hydrogel surface. The N—H absorption band at 3433 shown in the hydrogel before adsorption of cadmium decreased to 3175.7 due to presence of cadmium after adsorption took place. The absorption band at 1664 due to C=O decreased to 1651.2 , while the band 1537 cm^{-1} which should correspond to N—H link from the amide group increased to 1599.0 with the presence of cadmium. Other bands in the region 1400 to 1000 cm^{-1} also showed little changes. Stretches above 1500 cm^{-1} were observed to have their peaks decreasing whereas, those below 1500 cm^{-1} tends to have increased peaks after adsorption of cadmium as seen in figure 3.1 (c).

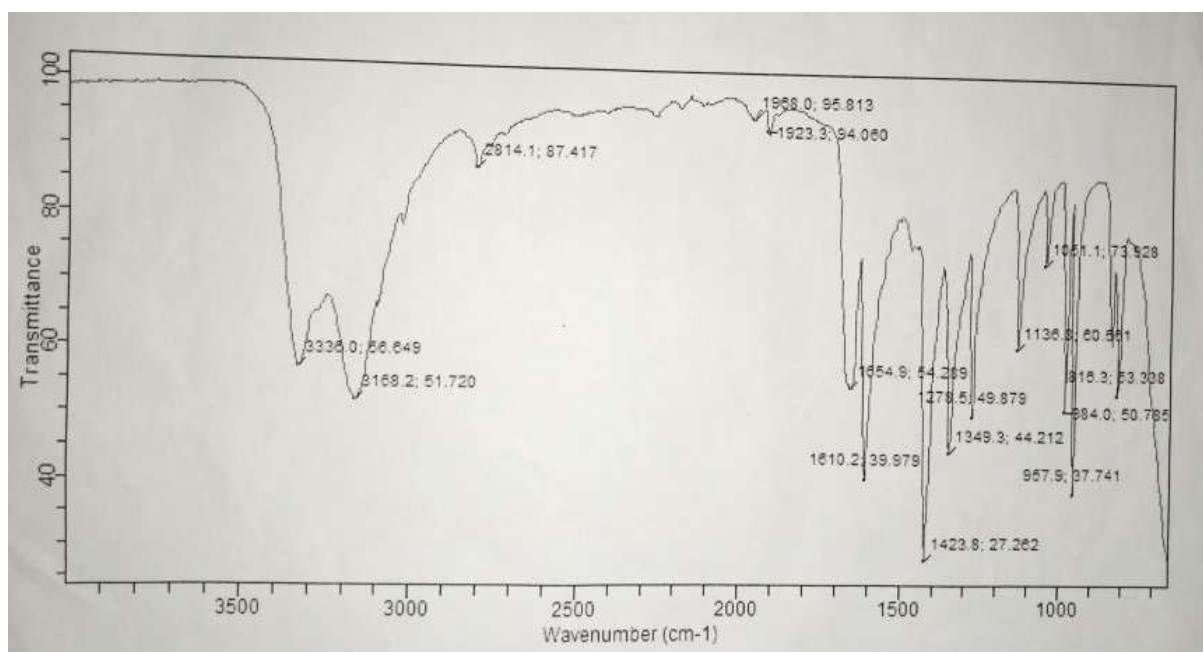


Figure 3.1(a): FTIR spectrum of Acrylamide monomer

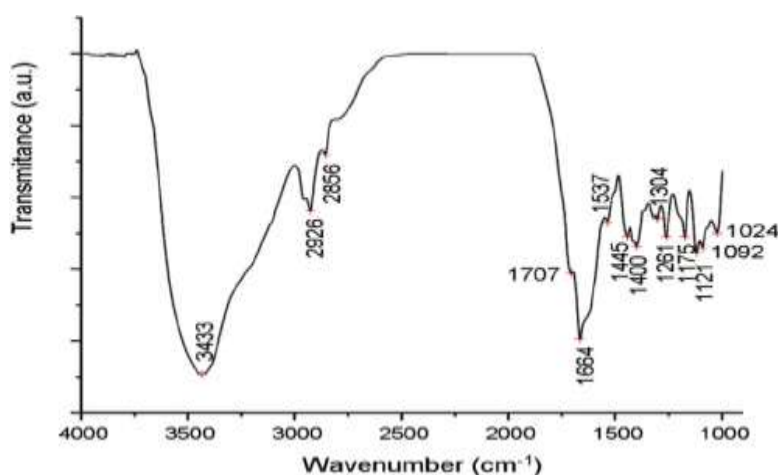


Figure 3.1(b): FTIR spectrum of polyacrylamide hydrogel

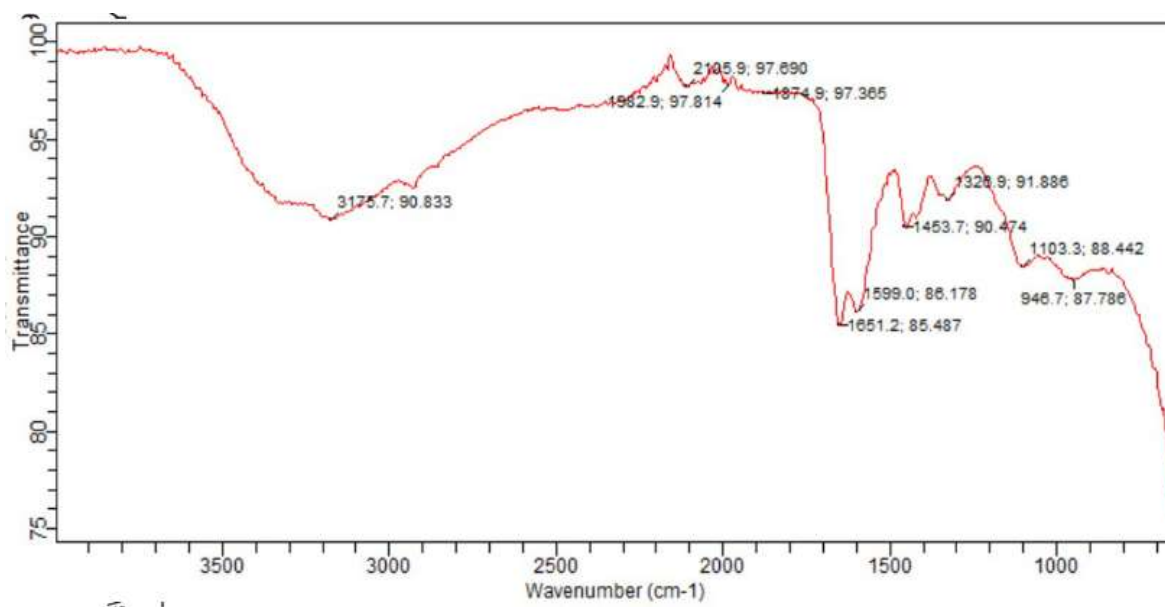


Figure 3.1(C): FTIR spectrum of polyacrylamide hydrogel after adsorption of cadmium.

In general, each absorption band changed its peak value due to the presence of cadmium in the hydrogel, and can be concluded with certainty that the polyacrylamide hydrogel had adsorbed cadmium (ions) onto its surface, which account for the slight changes in absorption bands of the hydrogel after adsorption of the metallic ions (cadmium) had taken place.

All FTIR spectra were registered in the mid infrared range ($4000 - 1000 \text{ cm}^{-1}$) which is more significant to this research as other bands in the finger print region are of less significance here.

3.4 Morphology of Polyacrylamide Hydrogel

Figure 4.2, illustrating the SEM micrograph of the polyacrylamide hydrogel presents a less porous microstructure when magnified about 320 times as shown in (a), whereas, (b) shows the presence of some particles (of cadmium ions) adsorbed onto the hydrogel surface when magnified about 300 times after adsorption had been carried out. The adsorption shows that the acrylamide-based synthesized hydrogel had some great impact on the adsorption of cadmium ions from a solution of its salt. This indicates that the polyacrylamide-based hydrogel will serve well in the environmental treatment of industrial and municipal waste containing cadmium or any of its soluble compounds in water sources, the effectiveness of which will be confirmed by latter Atomic Adsorption Spectroscopic (AAS) analysis.

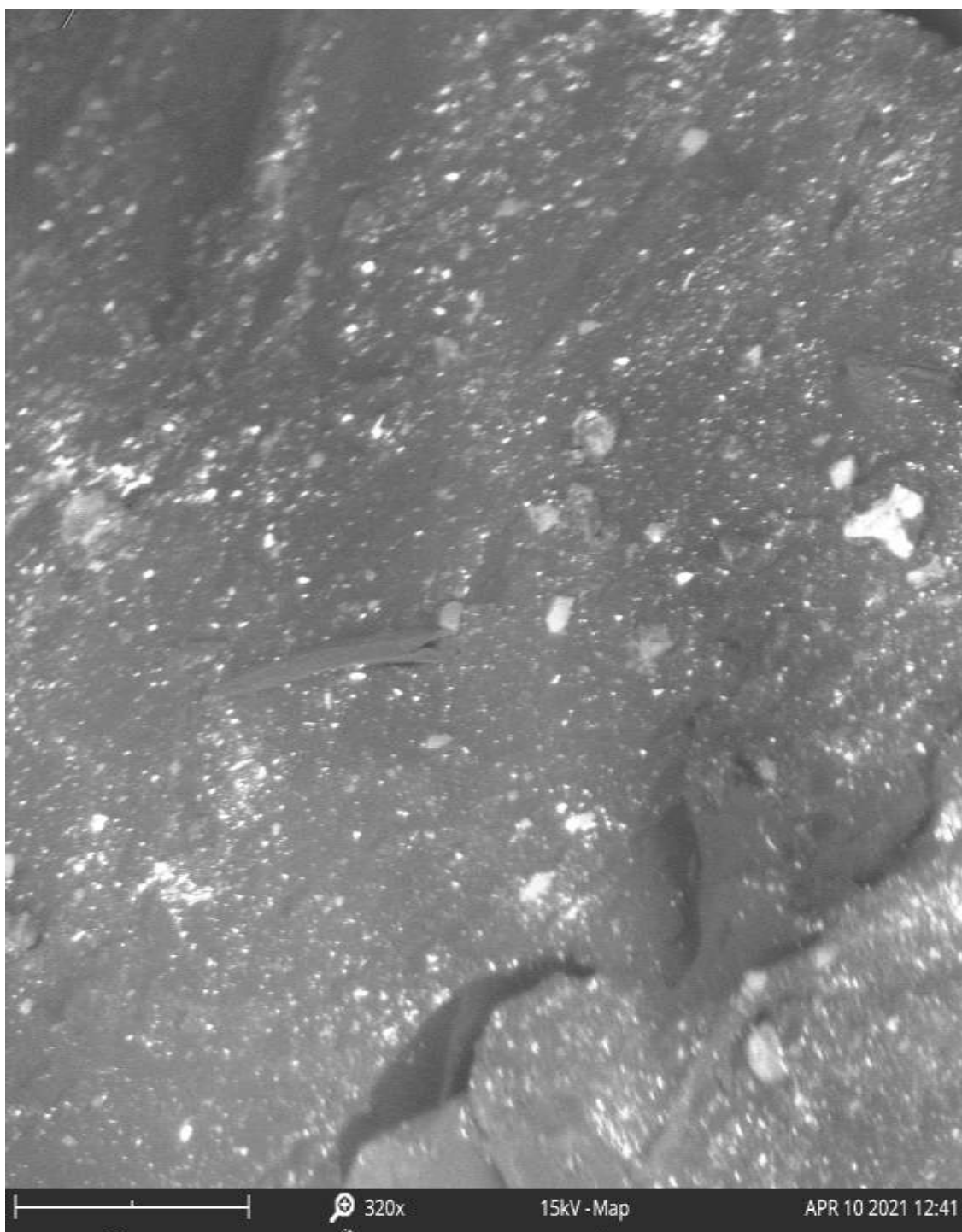


Figure 3.2 (a): SEM micrograph (X320) of polyacrylamide hydrogel before adsorption of cadmium (from a solution of its salt)

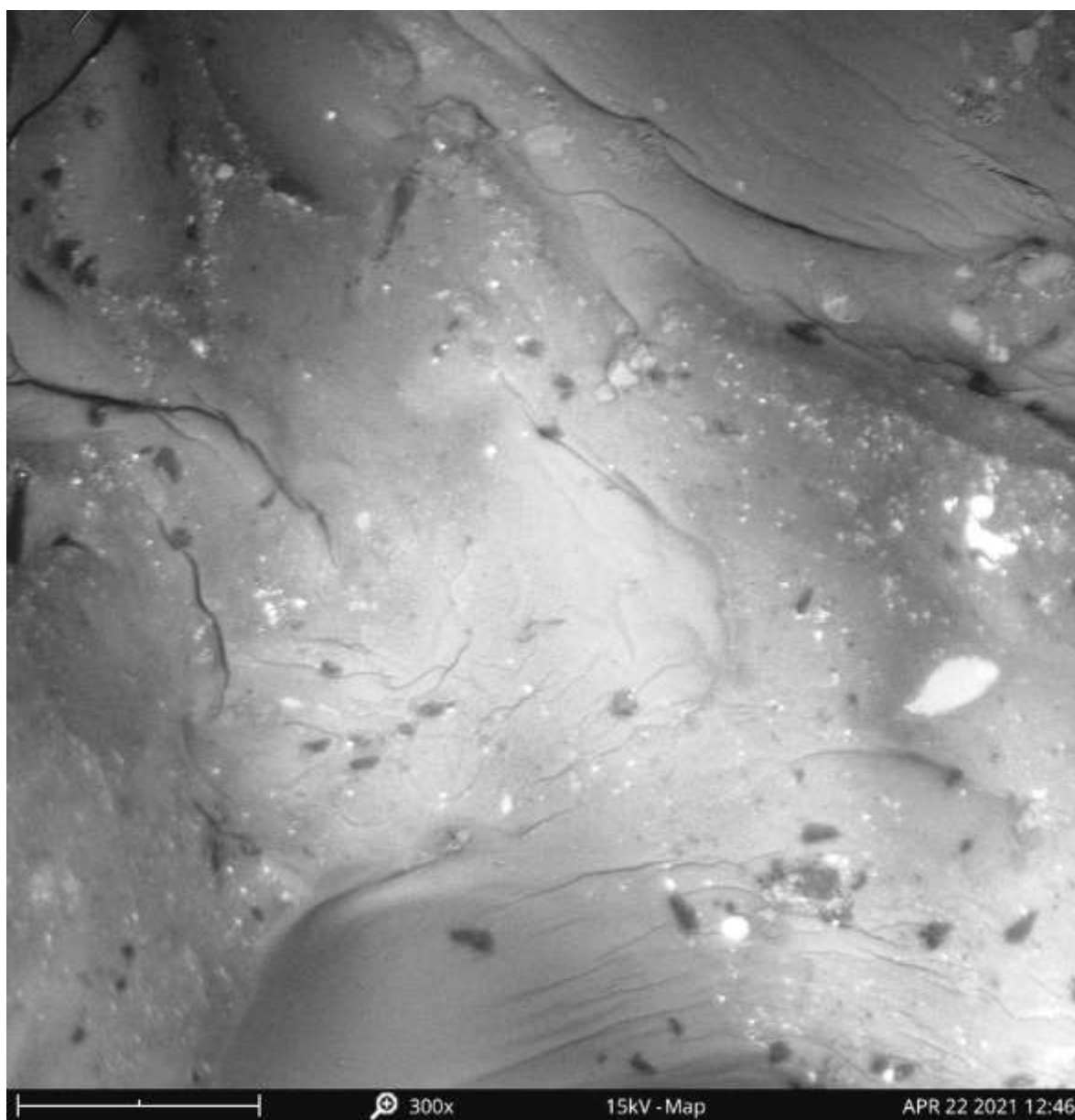


Figure 3.2 (b): SEM micrograph (X 300) of polyacrylamide hydrogel after adsorption of cadmium (from solution of its salt) showing adsorbed particles of the heavy metal on the gel surface

3.5 Adsorption and Elution of Heavy Metal (Cadmium) By Polyacrylamide Hydrogel

The metal binding capacity of the hydrogel was determined by the adsorption experiment. Four different samples containing different amounts of the metal in solution were prepared using 2.4g, 2.0g, 1.6g and 1.2g each of the salt of the heavy metal, cadmium chloride (CdCl_2) in 100ml distilled water in a 250ml beaker. The solutions were divided in two parts of 30ml and 60ml. About 0.965g, 0.602g, 0.833g and 1.673g each of the polyacrylamide hydrogel were measured and inserted into the gel for about 118 hours. The 0.965g hydrogel removed about 0.441 mgL^{-1} of cadmium ions from a solution of its salt containing 16.839 mgL^{-1} of cadmium ions by adsorption unto its surface at pH 6.5. The 0.602 g hydrogel removed 0.765 mgL^{-1} from solution of CdCl_2 containing about 16.664 mgL^{-1} of cadmium ions at pH 6.5. The 0.833g hydrogel removed about 1.738 mgL^{-1} of cadmium at pH of 6.6 from solution of its salt containing about 16.580 mgL^{-1} of cadmium ions, and the 1.673g removed 2.630 mgL^{-1} of cadmium from solution of its salt (CdCl_2) containing 17.643 mgL^{-1} cadmium ions at pH of 6.6

TABLE 3.1: Relationship between Initial Concentration (C_o), Equilibrium Concentration (C_e) and Concentration of cadmium adsorbed/removed by hydrogel (q_e).

S/N	Mass(g)	pH	Volume(ml)	C_o (mg/L)	C_e (mg/L)	q_e (mg/L)	Gel mass (g)	Sample
1	2.000	6.5	60	16.389	16.398	0.441	0.965	A
2	1.600	6.5	60	16.664	15.899	0.765	0.602	B
3	0.800	6.6	60	16.580	14.842	1.738	0.833	C
4	2.400	6.6	60	17.643	16.751	2.630	1.673	D

The adsorption experiment was carried out at room conditions of temperature and pressure, and the adsorbed quantities of the cadmium ions were determined by Atomic Adsorption Spectrometry (AAS). The result shows that the hydrogel has high adsorption capacity to remove the heavy metal cadmium from solutions and water containing the heavy metal, though morphological studies by SEM microscopy revealed that it has less porosity at magnification up to about 320 times.

4.0 CONCLUSION

Polyacrylamide hydrogel was synthesized by solution polymerization of acrylamide. The crosslinking agent used was N,N' -methylene bisacrylamide (99%).

The synthesis of hydrogel by this method is economical as few chemicals are involved and hence, less spending but shows a high adsorption capacity which is mainly due to chemisorption rather than absorption as lesser porosity is observed by morphological studies using scanning electron microscopy technique at magnifications up to 320 times.

The bulk density of the polyacrylamide hydrogel was computed to be about 1.371gcm^{-3} .

The swelling properties of the hydrogel was studied by inserting a measured mass in distilled water for 24 hours, and its swelling ratio was determined to be 13.39 at pH 7 and under room conditions of temperature and pressure.

FTIR was used to study the crosslinking bond formation. Blending was observed between the polyacrylamide hydrogel synthesized and the acrylamide monomer from which it was synthesized by the presence of peaks in the polyacrylamide hydrogel which are similar with those in the acrylamide monomer. These peaks include the N-H, C=O absorption peaks among others, present in the polyacrylamide hydrogel that is believed to be derived from similar peaks present in the acrylamide monomer.

The FTIR spectrometry can also trace the presence of cadmium in the hydrogel. This is indicated by changes in wavelength of maximum absorption peaks of the polyacrylamide hydrogel after adsorption of cadmium (ions) such as the slight decrease in absorption peak of the N-H stretching in the polyacrylamide from 3433 to 3175.7 and from 1664 to 1651.2 for C=O stretch. The presence of cadmium in the polyacrylamide hydrogel accounts for these changes in the IR bands.

SEM analysis shows that the microstructure of the polyacrylamide based hydrogel synthesized by this method had less porosity at magnifications up to 320 times. Also, SEM analysis of the polyacrylamide hydrogel after inserting in solutions cadmium salt revealed the presence of new particles adsorbed on the surface of the hydrogel. These particles were confirmed to be particles of cadmium by AAS analysis of the solution before and after.

AAS analysis revealed that the hydrogel has high (surface) adsorption capacity for the heavy metal, cadmium. A small mass of 0.833g of the polyacrylamide hydrogel synthesized by this method removed adsorbed and removed about 1.738mgL^{-1} cadmium from a solution of CdCl_2 containing 15.580mgL^{-1} cadmium, 1.673g of the polyacrylamide hydrogel adsorbed and removed about 2.63mgL^{-1} cadmium from a solution of the same salt containing 17.643mgL^{-1} of cadmium ions. Due to the high adsorption capacities of this hydrogel, it can be used in the environmental, municipal and industrial treatment of sewage and waste water where the presence of heavy metals, mainly cadmium is present in order to ensure safe and healthy water for domestic, industrial, recreational and other uses as hydrogels are environmentally friendly and biodegradable as well.

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