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An innovative method for preparation of nanometal hydroxide superabsorbent hydrogel

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ABSTRACT

A novel method for preparation of a conducting nanometal hydroxide hydrogel was undertaken. In situ accommodation of metal hydroxide nanoparticles within swollen hydrogel networks is developed. Thus, poly(acrylic acid/acrylate) hydrogel (PAAc/AC) was prepared by simultaneous polymerization of acrylic acid/acrylate (AAc/AC). Electrodeposition hydroxide of nanoiron and nanocopper into (PAAc/AC) hydrogel was performed. Swelling behaviour and swelling kinetics of prepared hydrogel were evaluated in media having different pH values. The conductivity of both PAAc/AC/nanocopper hydroxide and PAAc/AC/nanoiron hydroxide were measured in comparison with that for PAAc/AC hydrogel. An amelioration in conductance of PAAc/AC hydrogel having 0.8×10^3 μS after being incorporated with nanocopper hydroxide and nanoiron hydroxide to be 1.5×10^3 μS and 2.6×10^3 μS, respectively has been achieved. Distribution of the metal hydroxide nanoparticles penetrated within the hydrogel networks using transmission electron microscopy has been thoroughly elucidated.

1. Introduction

Superabsorbent polymers are characterized by a network structure with a suitable degree of crosslinking. They can absorb and retain huge amounts of water or aqueous solutions and are capable of absorbing hundreds to thousand times its own mass of water to form a stable hydrogel; however retained water is also hardly to be removed under some pressure (Lee & Chen, 2005). They are currently used in many areas of application including hygienic products (Singh, Sharma, Garg, & Garg, 2010), agriculture (Saxena, 2010), drug delivery systems (Singh et al., 2010), sealing (Singh et al., 2010), coal dewatering (Sun, Zhang, Shi, Tang, & Wu, 2002), and artificial snow (Singh et al., 2010), food additives (Chen et al., 1995), pharmaceuticals (Kashyap, Kumar, & Kumar, 2005), biomedical applications (Anton, 1990) tissue engineering and regenerative medicines (Ling Zhang et al., 2011), diagnostics (Van der Linden, Herber, Olthuis, & Bergveld, 2003), wound dressing (Sikareepaisan, Ruktanonchai, & Supaphol, 2011), separation of biomolecules or cells (Feng Wang et al., 2010) and barrier materials to regulate biological adhesions (Roy, Jennifer, & Brent, 2010), Biosensor (Peter Krsko et al., 2009).

Recently, many researchers pay much attention on the superabsorbent polymer for developing new applications, such as conducting materials, biomaterials, sensors, release matters and wave-absorbing materials (Qunwei Tang et al., 2008). However, researches on conducting polymer (or hydrogel) based on the superabsorbent polymer are rather few. A conducting hydrogel could be used in fuel cells, supercapacitor, dye sensitive solar cell and rechargeable lithium batteries (Lan et al., 2006; Lewandowski, Zajder, Frackowiak, & Beguin, 2001; Pissis and Kyritsis, 1997; Tang et al., 2008) due to a number of reasons including better conductivity character, colloid stability, low cost and simple preparation.

Since few decades, there has been a great deal of interest in biocomposites containing metal oxide nanoparticles dispersed in polymeric, glassy or ceramic matrices. Iron oxide nanoparticles display a great scientific interest in technological applications such as high density magnetic recording media (Cornell & Schwertmann, 2003), biosensors (Perez, Simeone, Saechi, Josephson, & Weissleder, 2003), ferrofluids (Anton, 1990), magnetic resonance imaging (Oswald, Clement, Chambon, Claeys, & Frija, 1997) and biomedicine (Fu, Dravid, & Jhonson, 2001).

Recently, detailed studies have been carried out on nanocomposites to gain advantages of their unique properties, and conducting polymer–metal nanocomposites will be typical of these kinds (Gaddy & McLain, 2004). Actually, there are many polymer/nanoparticle composite materials, and optimal control over the structure of the composite could be achieved by preassembling

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the inorganic nanoparticles with the organic polymer matrix (Wei, Luo, Zhang, Fan, & Chen, 2008).

Progressive research has been carried out to synthesize various types of metal nanoparticles using different ways of preparation. These ways include sputtering, laser ablation, inert gas condensation, oven evaporation, spray conversion pyrolysis, flame hydrolysis, deposition, high energy milling, sol–gel deposition, and electrodeposition (Wei et al., 2008).

Traditionally, such a synthesis is carried out chemically making use of a reducing agent such as sodium borohydride or with irradiation to convert groups of metal ions into nanoparticles (Wei et al., 2008). Pileni et al. reported the synthesis of copper nanoparticles of varied shapes by using reverse micelles as micro-reactors and protecting shells (Pileni, Krzywicki, Tanori, Filankembo, & Dedieu, 1998). Gedanken and coworkers reported that excellent surface resonance can be observed for copper nanoparticles when prepared by a sonochemical technique (Dhas, Raj, & Gedanken, 1998).

Nanosized copper grains as conductive particles has a number of advantages over traditional copper conductive particles, for example, high surface activity, good electro-conductivity and heat-conductivity, ease of fabrication, as well as other nanosized effects (Fan, Zhang, Zhan, & Wu, 2006). They have found wide applications in mechanics, magnetics, electrical and chemical aspects.

It has been reported by Cioffi et al. for the first time the possibility of using copper/polymer nanocomposites as a bioactive coating against fungi (Cioffi & Torsi, 2005). However, examples dealing with copper/polymer composites as conductive composites for chemical vapour or gas sensors are very rare. Since agglomeration and oxidization are still two main disadvantages as nanoscale copper conductive particles, investigations into their preparation, fabrication and applications attracted much attention.

Conducting hydrogel is a novel functional material that has been developed recently. It is possible to be employed as conducting film, coating, sensor, conducting fiber, wave absorbing material and other applications (Ali, 2006; Li, Guo, Wei, Mac Diarmid, & Lelkes, 2006). The conducting hydrogel often was prepared by copolymerizing or doing conducting materials with/to hydrophilic monomers/polymers (Aouada et al., 2006).

Polymer hydrogel electrolyte was successfully prepared via high ionic conductivity close to that of 1 M H_2SO_4 aqueous solution (Wada et al., 2006). The high ionic/protonic conductivity of hydrogel is of prime importance in some applications as exemplified by cells and sensors.

The present work is based on a superabsorbent polymer polyacrylate, a scheme for developing a novel and simple method for preparation of a conducting nanometal hydroxide hydrogel is planned. In situ preparation of metal hydroxide nanoparticles within swollen hydrogel networks is undertaken. Thus, poly (acrylic acid/acrylate) hydrogel (PAAc/AC) was obtained. Electro deposition of nanoiron hydroxide and nanocopper hydroxide into superabsorbent hydrogel were investigated. Swelling behaviour and swelling kinetics of the so obtained hydrogels were evaluated. The conductivity of both PAAc/AC/nanoiron hydroxide and PAAc/AC/nanocopper hydroxide were measured and compared with that of PAAc/AC. Distribution of the metal hydroxide nanoparticles within the hydrogels using transmission electron microscopy (TEM) was thoroughly investigated.

2. Materials and methods

2.1. Materials

Acrylic acid (AAc) in the monomeric form was produced by Sisco Research Lab. Pvt. Ltd., India. N,N′-methylenebisacrylamide (MBA) as a crosslinking agent, potassium persulphate (KPS) as initiator and potassium hydroxide (KOH) were supplied by Sigma–Aldrich, Inc. These reagents were used as laboratory grade chemicals.

2.2. Preparation of polyacrylate superabsorbent polymer

Preparation of polyacrylate superabsorbent polymer was carried out according to a modified procedure (Wu, Zhong, Lin, Wei, & Xie, 2006). A mixed solution of acrylic acid monomer and potassium acrylate was prepared by agitating the monomer with (N,N′-methylene bisacrylamide) as a crosslinker in presence of potassium hydroxide in distilled water under ambient conditions. Under a nitrogen atmosphere, the mixture solution was stirred and heated to 80 °C in a water bath for 15 min., followed by addition of the initiator. The reaction mixture was kept under stirring for few minutes to complete polymerization reaction.

2.3. Electro-deposition of nanometal hydroxides into superabsorbent hydrogel

The electro-deposition was carried out using two electrodes system, where iron or copper was fixed as anodes and graphite plate as cathode into a glass cell 15 cm × 7.5 cm × 8 cm using a Power Supply (GW Lab DC GPR-3030).

A known weight of the swollen superabsorbent hydrogel was prepared and filled into the cell between two electrodes. It has been considered that the distance between the electrodes was kept constant throughout the experiments of using different types of iron and copper anodes. The anodic dissolution of iron and copper was carried out at room temperature and duration of 15 min, while electric potential varied to study the amount of metal ion dissolved. Conductivity meter (D8120 Weilhein WTW LF-6) was employed to measure the conductance of swollen superabsorbent hydrogel before and after the anodic dissolution of iron and copper into the eletrolytic cell.

2.4. Measurements and characterization

2.4.1. Transmission electron microscopy (TEM)

TEM images for the prepared superabsorbent hydrogel and nanometal hydrogel composites were recorded by a JEOL JEM-1230 electron microscope operating at an acceleration voltage of 100 kV. Specimens for TEM were prepared by placement of a swollen sample of superabsorbent hydrogel on a 400-mesh copper grid and the evaporation of excess water in air at room temperature.

2.4.2. Swelling studies

The swelling characteristics of the prepared hydrogel were measured via gravimetric analysis (Li et al., 2006). The swelling ratio is the criterion of describing water absorption capacity. Measurement of the swelling ratio of the prepared hydrogel was conducted by the so-called tea-bag method (Zhao, Kang & Tan, 2006), and using distilled water as liquid to be absorbed. The bags used were made of nonwoven polypropylene. The dried samples confined in nonwoven polypropylene bags were placed in different swelling media with different pH values under ambient conditions and taken from swelling media at regular periods of time. The surface water on the swollen hydrogel was removed by soft pressing the bag sample between the folds of a filter paper; an increase in weight was determined.

The equilibrium swelling of the gels was determined as follows: gels were dried for 3 days at room temperature and were then dried under vacuum at 80 °C. After the weight of the dried samples was determined, the samples were equilibrated in swelling media for a day at room temperature and then weighed again. The

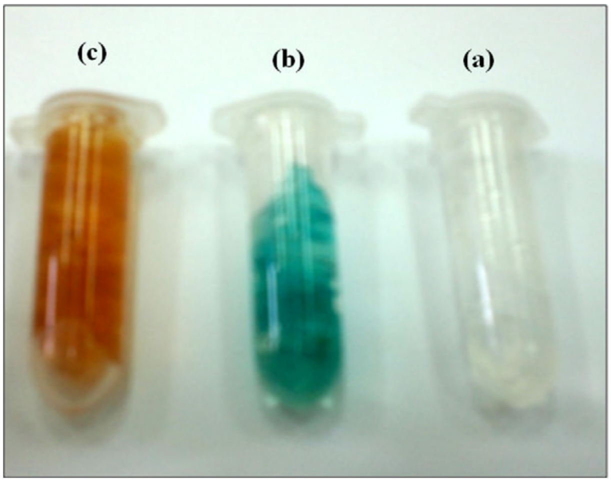

Fig. 1. Photographs of the PAAc/AC superabsorbent hydrogel (a), PAAc/AC superabsorbent hydrogel loaded with copper oxide nanoparticles (b) and iron oxide nanoparticles (c).

swelling ratio (S) and equilibrium swelling ratio (S_{eq}) were obtained by application in the following equations (Ahmed & Aggor, 2010):

$$S\left(\frac{g}{g}\right)=\frac{W_t-W_0}{W_0} \tag{1}$$

$$S_{eq}\left(\frac{g}{g}\right)=\frac{W_{eq}-W_0}{W_0} \tag{2}$$

where W_0, W_t and W_{eq} are the weights of the samples in the dry state, the swollen state at a certain time, and the completely (equilibrium) swollen state, respectively.

3. Results and discussion

The introduction of nanoparticles in the hydrogel network systems was considered as the most important approach because of its feasibility in various areas of application. The free network spaces between hydrogel networks accomodate and stabilize nanoparticles. Fig. 1 displays the formation of metal nanoparticles embedded in swollen PAAc/AC hydrogel network. The formation of metal hydroxide nanoparticles in the hydrogel networks was confirmed by the appearance of reddish brown and bluish green colours for nanoparticles of hydroxides of iron and copper, respectively. This was ascribed to the presence of nanometal hydroxides in the hydrogel matrix whereas the PAAc/AC hydrogel was found to be colourless.

3.1. Swelling behaviour

Swelling experiments were carried out with a view of evaluation the swelling capacity of the prepared hydrogel under investigation in distilled water and at different pH values. Results of these experiments indicated that the increase in weight of the swollen hydrogels is directly related to the duration of swelling. The swelling behaviour observed could be associated with the absorption mechanism, which, in turn, is determined by the diffusion process.

Fig. 2 represents the effect of variation in pH values on the swelling characteristics of the prepared hydrogel. It is evident that the swelling ratio increases sharply upon prolongation of swelling time up to 45 min then levels off. Moreover, decreasing alkalinity of the swelling media enhanced the swellability of the prepared hydrogel and followed the order pH 8 > pH 10 > pH 12. While as the swellability of superabsorbent hydrogel at pH 3 was not different when compared with that observed at pH 8. It was also noted that good swellability properties of the prepared superabsorbent hydrogel obtained when distilled water was used.

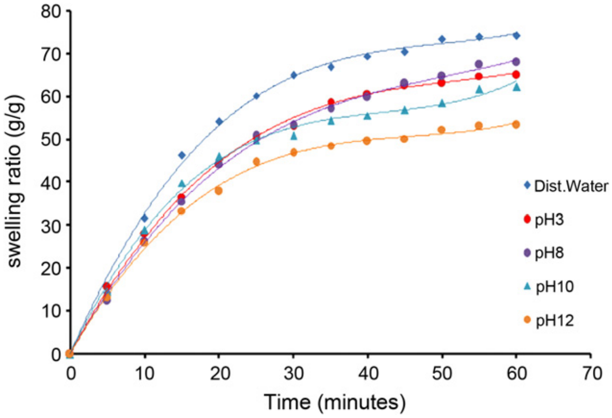

Fig. 2. Swelling behaviour of PAAc/AC hydrogel at different pH values.

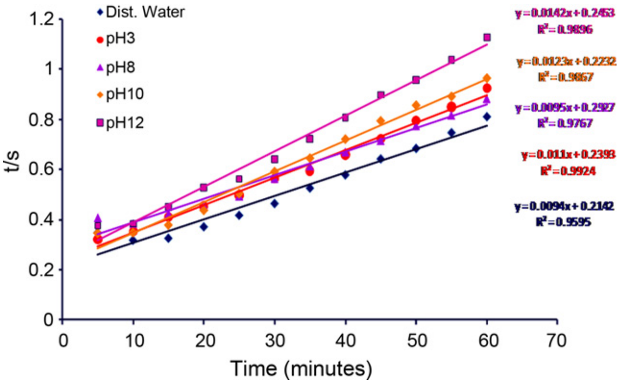

Fig. 3. Swelling rate relations of PAAc/AC hydrogel.

3.2. Swelling kinetic study

The swelling kinetics of the prepared hydrogel was thoroughly investigated. The controlling mechanism of the swelling processes was visualized through kinetic models. The latter were used to examine the data arrived at from the experimental work and the kinetic analysis is represented by a second-order equation, as given below (Ahmed & Aggor, 2010):

$$\frac{dS}{dt}=k_s\left(S_{eq}-S\right)^2 \tag{3}$$

where k_s is the swelling rate constant and S_{eq} is the degree of swelling at the state of equilibrium. After integration, when the initial conditions $S=0$ at $t=0$ and $S=S$ at $t=t$, was applicable, Eq. (3) would be in the form:

$$\frac{t}{S}=A+Bt \tag{4}$$

where $B=1/S_{eq}$ is the inverse of the maximum or equilibrium swelling, $A=1/k_s(S_{eq})^2$ is the reciprocal of the rate of swelling at the initial state $[(\mathrm{d}S/\mathrm{d}t)_0]$ of the hydrogel, and k_s represents the swelling rate constant. The kinetic models were examined by plotting t/S vs. t for the distilled water, pH 3, pH 8, pH 10 and pH 12. The swelling parameters such as initial swelling rate (r), swelling rate constant (k_s) and maximum equilibrium swelling $(S_{eq})_{max}$ were calculated from the equations of the straight lines given in Fig. 3. The calculated values are listed in Table 1. Also Fig. 3 shows that the swelling kinetic model was found to be in agreement with experimental data.

Table 1
Some swelling parameters of PAAc/AC hydrogel.

Swelling parameter	Swelling media				
	Dist. water	pH 3	pH 8	pH 10	pH 12
$S_{exp.}$	80.8	66.8	69.3	63.2	54.1
S_{eq}	106.26	80.8	105.3	81.3	70.4
$k_s \times 10^4$	0.4125	0.5056	0.3083	0.6778	0.8220
r	4.67	4.18	3.42	4.48	4.08
n	0.6057	0.558	0.6472	0.5281	0.5185

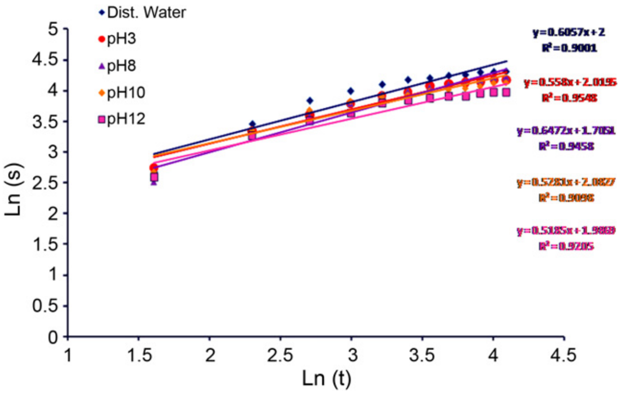

Fig. 4. Swelling kinetic relations of PAAc/AC hydrogel.

Mechanism of water diffusion in swellable polymeric hydrogels has attracted much attention due to its several biomedical, environmental, pharmaceutical and agricultural applications. Diffusion of water interred the hydrogel can be evaluated by applying the following equation (Ahmed & Aggor, 2010).

$$S\left(\frac{g}{g}\right) = \frac{[W_t - W_0]}{W_0} = Kt^n \tag{5}$$

where K is the swelling constant and (n) is the swelling exponent calculated from the slopes of the lines of Ln (swelling ratio)–Ln t plots. For cylindrical shapes, $n = 0.45–0.50$ and corresponds to Fickian diffusion, whereas $0.50 < n < 1.0$ indicates that diffusion is non-Fickian type. As represented by Fig. 4, the values of n were found to be between 0.5185 and 0.6472 indicating that the diffusion is of the non-Fickian type. Values of n higher than 0.5 indicating diffusion of water to the interior of all the hydrogels, follows an anomalous mechanism. This behaviour reported with the hydrogel is due to the regularity of the chain and strong interaction via formation of hydrogen bonding, leading to a compact structure which would be in accordance with anomalous aspects of diffusion even for a molecule as small as water (Srivastava, Rai, Singh, & Chandra, 1998).

3.3. *Anodic dissolution of iron and copper*

Hydrogels are macroscopically solid materials and they are microscopic liquid-like due to the presence of large numbers of water molecules filled micropores and mesopores in gels, and they conduct electricity due to the transport of anionic and cationic species (Aouada et al., 2006).

Conductivity measurements indicated that the conductance of PAAc/AC hydrogel was 8 μS due to the presence of water through the network of hydrogel, so it permits the ionic penetration and mobility by diffusion and migration as the electrolyte behaviour. In addition, chemical structure and mechanical bending of network improve the penetration of Fe and Cu ions into the network structure of hydrogel.

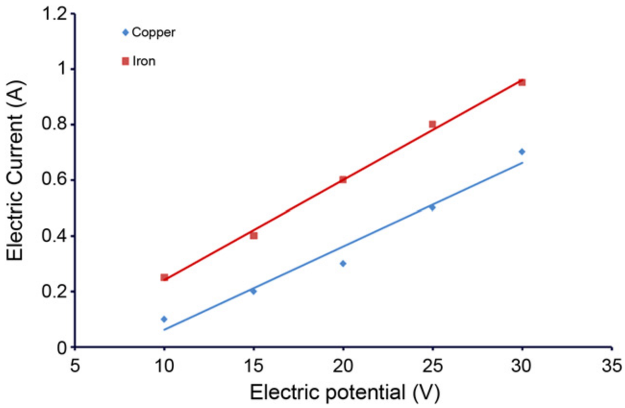

Fig. 5. Effect of electric potential on the electric current response using different metals as anode iron, copper and graphite.

Electrolytic characteristics of PAAc/AC hydrogel were achieved and found to be adequate for the passage of electric current. The response of electric current against electric potential in the electrolytic cell containing PAAc/AC hydrogel as electrolyte indicates the passage of electric current and conductance of the prepared PAAc/AC hydrogel electrolyte. As shown in Fig. 5, the electric current was increased from 0.25 to 0.95 A by increasing of electric potential from 10 to 30 V due to the anodic dissolution of iron. Also, the same conditions were used with the replacement of iron electrode by copper electrode, where the electric current response was increased from 0.1 to 0.7 A.

It can be observed that a high current was obtained in case of using iron as anode, than copper, where the anodic dissolution rate and the density of ions released depends on the electrode potential. So, it can be expected that the presence of Fe ions penetrated into the PAAc/AC hydrogel network are more than Cu and the sequence of ionic density in the hydrogel:

$$Fe^{3+} > Cu^{2+}$$

3.4. *Conductivity of nanometal into PAAc/AC hydrogel*

The characteristics of PAAc/AC hydrogel such as colour and conductivity have been altered due to impregnation of nanometal hydroxide into the hydrogel network. Metal ions of iron and copper are less electropositive than those of potassium present in chemical composition of PAAc/AC hydrogel (see the experimental section). So it can be expected that iron and copper ions are penetrated into the hydrogel network forming the corresponding hydroxides.

It has been observed that PAAc/AC hydrogel was colourless. Penetration of nanoiron and nanocopper hydroxides into the hydrogel network followed by anodic dissolution turned the medium reddish brown and bluish green in colour due to conversion of iron and copper ions to nanoiron and nanocopper hydroxides respectively.

On the other hand, the conductivity of PAAc/AC hydrogel was improved after the electrolytic process as shown in Fig. 6. The conductivity was ameliorated from 0.8×10^3 μS of PAAc/AC hydrogel to 1.5×10^3 μS of PAAc/AC hydrogel impregnated with copper

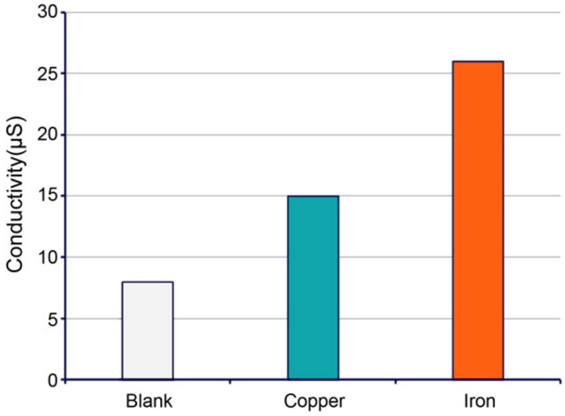

Fig. 6. Variation of electric conductivity (µS) of PAAc/AC hydrogel by impregnation of new metals into swelled water.

hydroxide by using copper anode, and to 2.6×10^3 µS of PAAc/AC hydrogel impregnated with iron hydroxide by using iron anode.

It should be stated that the conductivity properties of PAAc/AC hydrogel bearing nanoiron hydroxide are superior to those of the same hydrogel after addition of polyaniline as reported elsewhere (Tang, Lin, Wu, Zhang, & Hao, 2007).

3.5. Transmission Electron Microscopy

It is known that electric conductivity of copper is higher than that for iron (Rajasekharan & Seshubai, 2011), while PAAc/AC hydrogel impregnated with nanoiron hydroxide showed higher electric conductivity as compared with PAAc/AC hydrogel impregnated with nanocopper hydroxide as shown in Fig. 7. This can be attributed to the higher anodic dissolutions of iron than that for copper and, in turn, the abundance of ironions penetrated into the PAAc/AC hydrogel network was higher than those for copper.

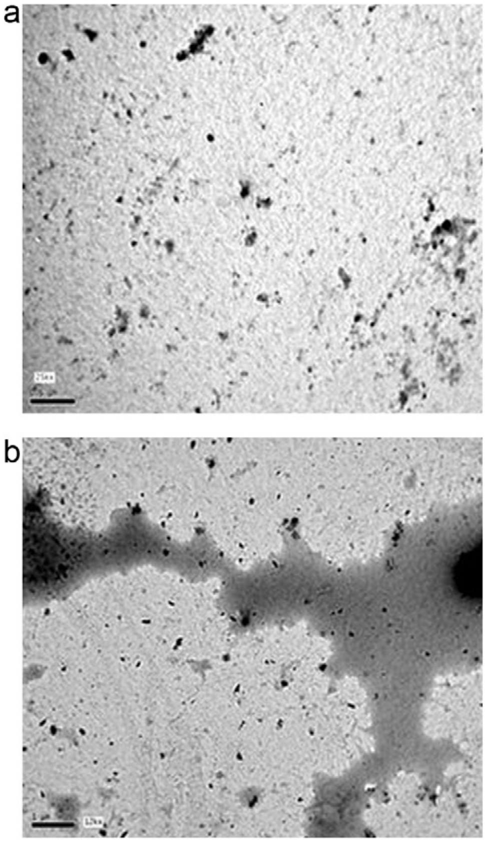

Fig. 7. TEM images of the PAAc/AC hydrogel impregnated with copper hydroxide nanoparticles (a) and iron hydroxide nanoparticles (b).

The size distributions derived from the TEM image are shown in Fig. 7(a and b). Particle size of copper hydroxide nanoparticles are ranging from 8 to 26 nm (Fig. 7a) while those for iron hydroxide nanoparticles are ranging from 4 to 16 nm (Fig. 7b).

4. Conclusion

A novel preparation of conducting nanometal hydroxide hydrogel is undertaken. A superabsorbent hydrogel was prepared through polymerization of acrylic acid/acrylate under potassium persulphate initiation and crosslinking. Electro-deposition of nanometal hydroxides of copper and iron in the network structure of the prepared hydrogel has been developed. Swelling characteristics and kinetics in different media has been investigated in some details. Conductivity measurements indicated an improvement in conductance of the resulting hydrogel due to incorporation with nanocopper and nanoiron hydroxides. A study of the distribution of metal hydroxide nanoparticles within the hydrogel network using transmission electron microscopy has also been achieved.

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