

*Full Length Research Paper*

# **PHEMA magnetic nanogels for removal of Cu (II) ions from aqueous solution**

**Manar El-Sayed Abdel-Raouf<sup>1\*</sup>, Abdul-Raheim Mahmoud Abdul-Raheim<sup>1</sup>, Ahmed Fawzy El-Kafrawy<sup>2</sup>, Nermine El-Sayed Maysour<sup>1</sup>, Amany Khalil Ibraheim<sup>1</sup> and Abdel-Azim Ahmed Abdel-Azim<sup>1</sup>**

<sup>1</sup>Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt.

<sup>2</sup>Faculty of Science, Ain Shams University, Cairo, Egypt.

Accepted Date

Magnetic nanogels based on 2-hydroxyethyl methacrylate (HEMA) and N,N'-methylene-bis-(acrylamide)(MBA) were prepared via photochemical method under UV irradiation. The structure and compositions of magnetic nanogels are characterized by FTIR, TGA and TEM. TGA measurement indicates that magnetic nanogels contain about 85-92% magnetite. The prepared magnetic nanogels were used to remove copper ions from industrial water. The proposed mechanism was dependant on the interaction between the surface hydroxyl groups of polymer-Fe<sub>3</sub>O<sub>4</sub> composite and the copper ions present in the solution. Several factors affecting the absorption capability were studied. These include: structure of nanogels, % of MBA to HEMA, effect of pH and effect of temperature. The obtained data revealed that the maximum absorption capacity was attained at pH 6 and at 40°C. The efficiency decreased remarkably at acidic pH and at a temperature higher than 40°C. It was also found that the ratio of 10% HEMA : 20 mg MBA achieved maximum copper absorption. Furthermore, the reusability of the prepared nanogels was demonstrated.

**Key words:** Nanoparticles, magnetic, copper ions, removal.

## **INTRODUCTION**

The environment and all the life on earth face a very serious threat as a result of heavy metal pollution due to rapid industrialization and the increase in the world population. Unlike organic pollutants, the majority of which are susceptible to biological degradation, metal ions do not easily get converted into harmless end products. The metals that cause serious concern include Cr, Hg, Cu, Ni, Zn and Cd, which are commonly associated with pollution and toxicity problems.

The removal of heavy metals from wastewater is one of the most important issues due to dangerous effects that such metals have on human health and the environment (Mido and Satake, 1995). Traditional metal ion treatment processes included several methods such as chemical precipitation, ion exchange, electrolysis, reverse osmosis, adsorption, etc. Among these treatment methods, adsorption is considered to be an economical, efficient, and promising method for treating metal-ion-

contaminated wastewater (Savic et al., 2012). The interaction of the metal ions with the functional groups present on the surfaces of the adsorbents play an important role in determining the effectiveness, capacity, selectivity, and reusability of these adsorbents (Banerjee et al., 2004; Weltrowski et al., 1996). Magnetic separation is now widely used in many fields such as medicine, diagnostics, molecular biology (Siegel et al., 1999), bioinorganic chemistry, and catalysis (Ngomsik et al., 2005). Furthermore, magnetic separation method is also

---

\*Corresponding author. E-mail: [drmanar770@yahoo.com](mailto:drmanar770@yahoo.com).

**Abbreviations:** HEMA, Hydroxy methyl methacrylate; MBA, Methylene Bis-acrylamide; TGA, Thermogravimetric analysis; PCS, photo correlation spectroscopy; PHEMA, Poly hydroxy methyl methacrylate.

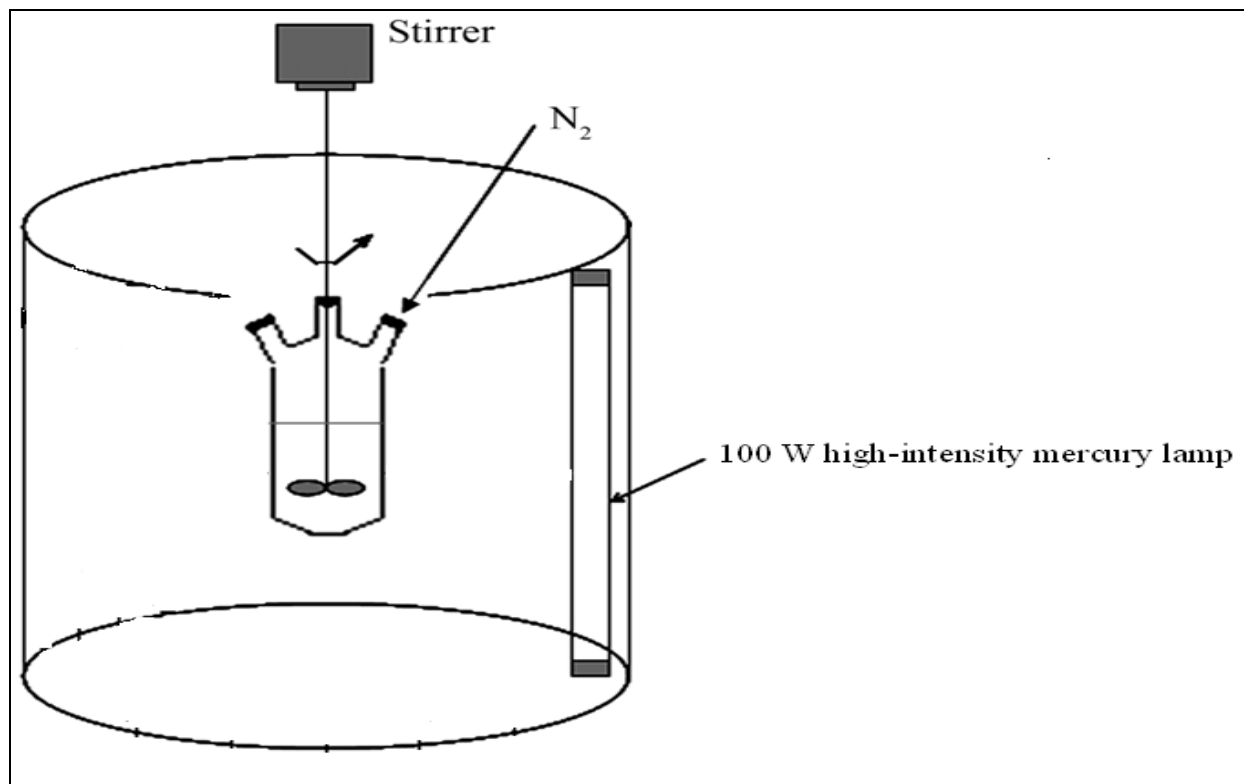


Figure 1. Photo-reactor for the polymerization process.

beneficial with regard to the environment because it does not result in the production of contaminants such as flocculants (Goya et al., 2003). Conventional polymeric adsorbents are generally known (Liao and Chen, 2002; Groman et al., 1996; Leong et al., 2001; Mak and Chen, 2005; Reis et al., 2006; Chang and Chen, 2005; Butterworth et al., 2001), in which suitable functional groups are present on the adsorbent surface. In this study, some magnetic adsorbents were developed for the adsorption of copper ions from industrial water as an important step in water de-toxication. The adsorbents were synthesized by the surface modification of  $\text{Fe}_3\text{O}_4$  with PHEMA. The sizes, structures, and surface charges of these magnetic adsorbents were characterized by transmission electron microscopy (TEM), particle size analyzer with photo correlation spectroscopy (PCS) and Fourier transforms infrared (FT-IR) spectroscopy. Furthermore, their adsorption behavior and mechanism were examined under various conditions.

## EXPERIMENTAL

### Materials and apparatus

All the chemicals were of analytical grade and were obtained from Sigma-Aldrich, and used as received. They are: 2-hydroxyethyl methacrylate (HEMA) monomer,

*N,N'*-methylene-bis- acrylamide (MBA) which served as cross-linker, Ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), sodium sulfite ( $\text{Na}_2\text{SO}_3$ ), Copper nitrate pentahydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ ) and ammonium hydroxide (25% [w/w]). Doubly distilled water and  $\text{N}_2$  (99.99%) were used in the experiments. Stirrer (Metrohm, Germany) was used to synthesize the ferrofluid and magnetic nanogels. The photo-polymerization process took place in a specially designed photo-reactor equipped with a 365 nm, 100 W high-intensity mercury lamp as a source of UV (model Black-Ray B100A) (Figure 1).

### Preparation of $\text{Fe}_3\text{O}_4$ nanoparticles

$\text{Fe}_3\text{O}_4$  nanoparticles were synthesized by reduction-coprecipitation method. In a 500 ml three-necked flask, 6.49 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was dissolved in 100 ml of distilled water and the solution was blushed with  $\text{N}_2$ . Then, 50 ml of  $0.16 \text{ mol. L}^{-1} \text{ Na}_2\text{SO}_3$  solution was slowly added into the flask. After the solution turned from red to yellow, 50 ml of diluted  $\text{NH}_3 \cdot \text{H}_2\text{O}$  (5%) was rapidly injected into the flask with vigorous stirring. The reaction was kept at  $70^\circ\text{C}$  for 30 min, and matured for 2 h at room temperature. The black precipitate was separated by a magnet and washed several times with pure water until pH 7.0. The slurry was at last dispersed in a certain volume of pure water. The concentration of the ferrofluid was determined

**Table 1.** Codes and composition of the prepared PHEMA magnetic nanogels.

Samples	Composition	
	HEMA (%)	MBA (mg)
H <sub>a</sub> M <sub>a</sub>	10	5
H <sub>a</sub> M <sub>b</sub>	10	10
H <sub>a</sub> M <sub>c</sub>	10	20
H <sub>b</sub> M <sub>a</sub>	15	5
H <sub>b</sub> M <sub>b</sub>	15	10
H <sub>b</sub> M <sub>c</sub>	15	20

as 9.8 mg/ml. An average size of Fe<sub>3</sub>O<sub>4</sub> nanoparticles obtained from TEM images was 11±1 nm.

### Preparation of PHEMA magnetic nanogels

Different PHEMA hydrogels were prepared by placing about 100 ml of aqueous solution containing HEMA (10, 15%) and MBA (5, 10 and 20 mg) into a three-necked cylindrical quartz flask. The system was stirred and bubbled with N<sub>2</sub> for 30 min. Then 1 ml of ferrofluid sonicated for 30 s was introduced into the flask. After the ferrofluid was dispersed homogeneously, the mixture was exposed to UV irradiation for 10 min. The pure PHEMA magnetic nanogels were at last recovered from the reaction system by placing the flask on a permanent magnet, washed several times with pure water and re-dispersed in water (15%). Composition of this process is shown in Table 1. An average size of PHEMA magnetic nanogels obtained from TEM images was 20±7 nm.

### Characterization

Chemical compositions of magnetic nanogels were analyzed by Fourier transform infrared spectroscopy (FTIR) (Perkin-Elmer720) with a KBr pellet. Thermogravimetric analysis (TGA) was done on a thermal analyzer (model Q600 SDT simultaneous DSC-TGA) to determine the magnetic content and thermal stability of the prepared PHEMA. The morphologies of magnetic nanogels were observed using transmission electron microscope (TEM, Jeol2100, 200Kv). An aliquot part of 7 µL of the diluted sample was dropped on a copper grid for TEM and freeze-dried in vacuum at -197°C (liquid N<sub>2</sub>). Mean hydrodynamic diameters and diameter distributions were measured by a particle size analyzer (Kruss) with photo correlation spectroscopy (PCS) analysis. Samples for FTIR and TGA measurements were dried in vacuum for 48 h prior to use whereas those for TEM and PCS were dispersed in water.

### Adsorption and desorption studies

The adsorption of copper ions by the magnetic nano-adsorbents was investigated in aqueous solutions at

pH 2, 4 and 6 and at temperatures of 30, 40 and 50°C. A copper nitrate solution of initial copper ion concentration (250 mg/L) and the desired pH was prepared. The solution pH was adjusted by NaOH or HCl. Then 25 mg of magnetic nano-adsorbent was added to 10 ml of copper nitrate solution. After mixing by a shaker (200 rpm) for 15 min, the magnetic nano-adsorbent was removed magnetically from the solution. The concentrations of copper ions were measured using a Flame Atomic Absorption Spectrometer; model Zeenit 700P, obtained from Analytikjena Co., Germany. Desorption of copper ions was studied by placing 25 mg of copper ions-loaded PHEMA in 10 ml of HCL solution (pH 1) concentration. After stirring at 200 rpm for 30 min, the PHEMA was removed and the concentration of copper ions in liquid solution was measured to estimate the amount of copper ions desorbed.

## RESULTS AND DISCUSSION

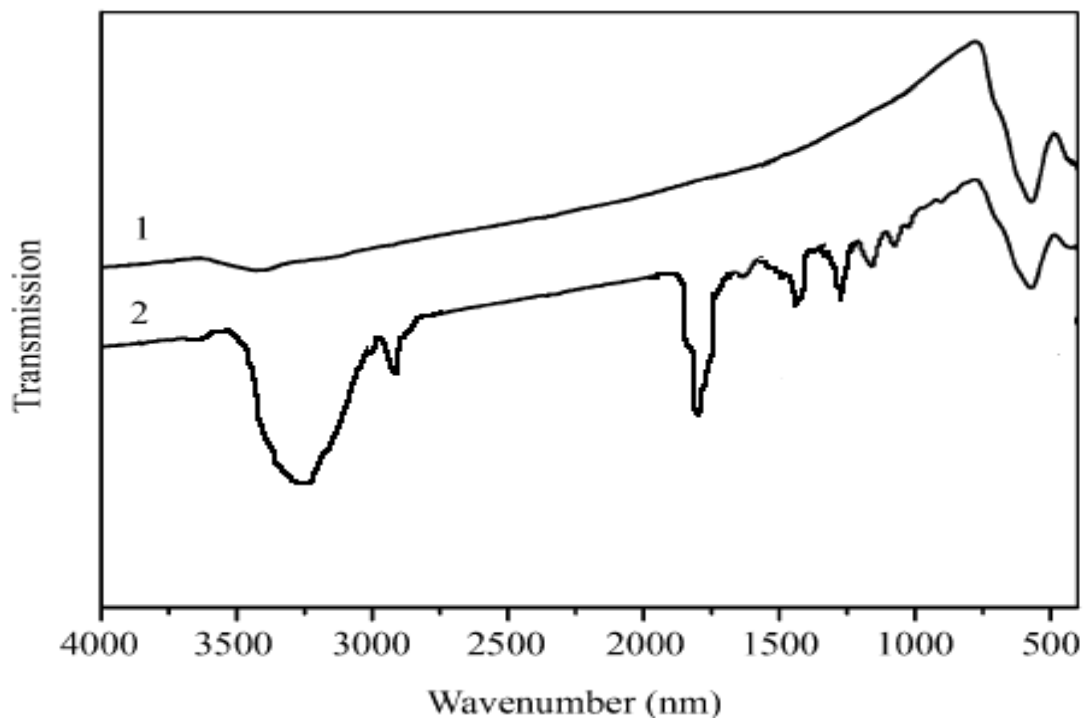
### Chemical compositions of magnetic nanogels

Figure 2 shows FTIR spectra of the ferro-fluid and magnetic nanogels. From the comparison between Curves 1 and 2, the characteristic band for Fe<sub>3</sub>O<sub>4</sub> strongly appeared at 590 cm<sup>-1</sup> in Curve 1. In Curve 2, the bands of 1719 and 1130 cm<sup>-1</sup> were respectively assigned to the C=O and C—O stretching vibrations of carbonyl group of carboxylic ester (Chang and Chen, 2005), the wide band of 3000-3500 cm<sup>-1</sup> is due to the O—H stretching vibration, and the bands of 2990-2870 and 1470-1380 cm<sup>-1</sup> to the vibrations of methylene (CH<sub>2</sub>). Furthermore, the peak of 1640 cm<sup>-1</sup> corresponds to the characteristic band of amido group (CONH) of MBA, and the band of 3300-3100 cm<sup>-1</sup> which indicates the presence of amido group is indistinct due to the overlapping with the wide O-H band. It can be concluded that the prepared magnetic nanogels are composed of Fe<sub>3</sub>O<sub>4</sub> covered with the copolymer formed from HEMA and MBA.

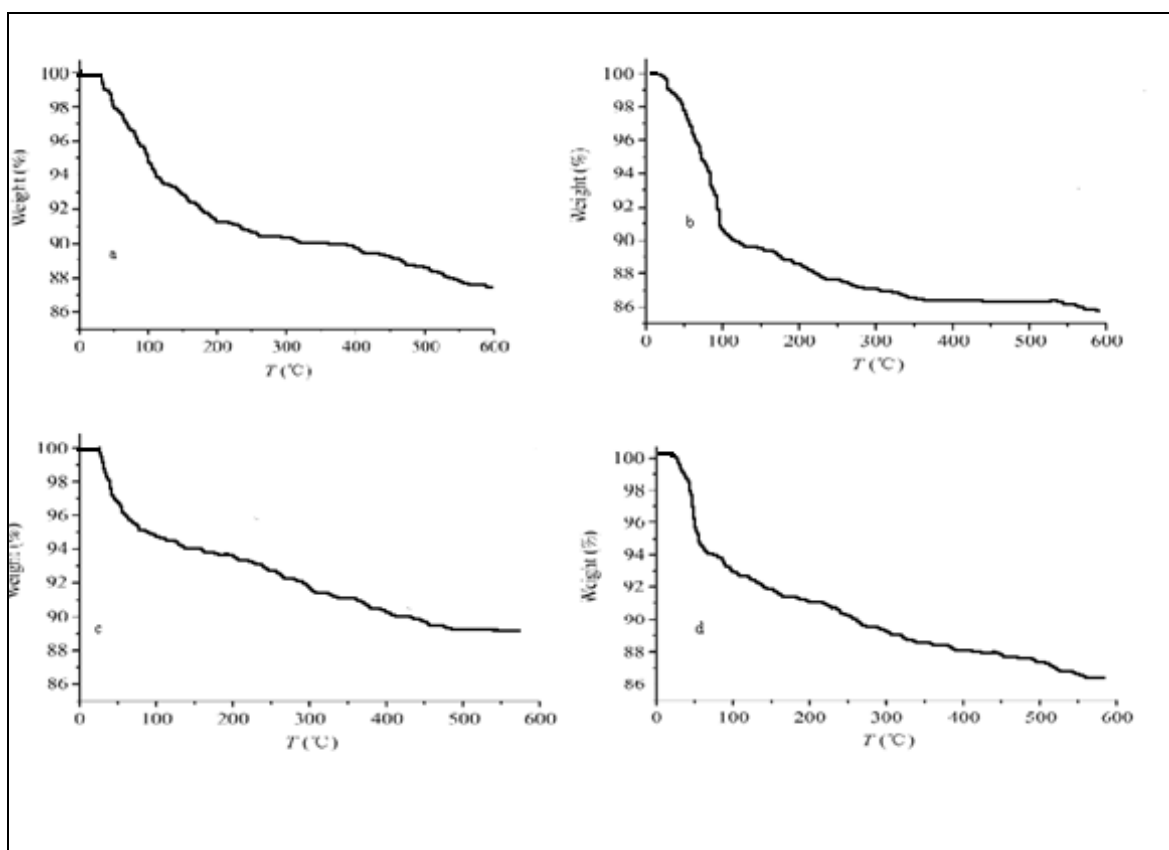
### TGA of magnetic nanogels

The TGA curves of four magnetic nanogels are shown in Figure 3, namely H<sub>a</sub>M<sub>a</sub>, H<sub>a</sub>M<sub>c</sub>, H<sub>b</sub>M<sub>a</sub> and H<sub>b</sub>M<sub>c</sub>. The % mass loss of magnetic nanogels that was observed when the temperature rose from room temperature to 120°C implies that a small amount of associated water still exists in magnetic nanogels dried in vacuum at room temperature. This amount differs according to the monomer ratio. It can be observed from a careful inspection of Figure 3 that the amount of water rose from 8 to 10.2% in H<sub>a</sub>M<sub>a</sub> and H<sub>a</sub>M<sub>c</sub> and from 4 to 6.1% in H<sub>b</sub>M<sub>a</sub> and H<sub>b</sub>M<sub>c</sub> respectively when the concentration of MBA increased from 5 to 20 mg.

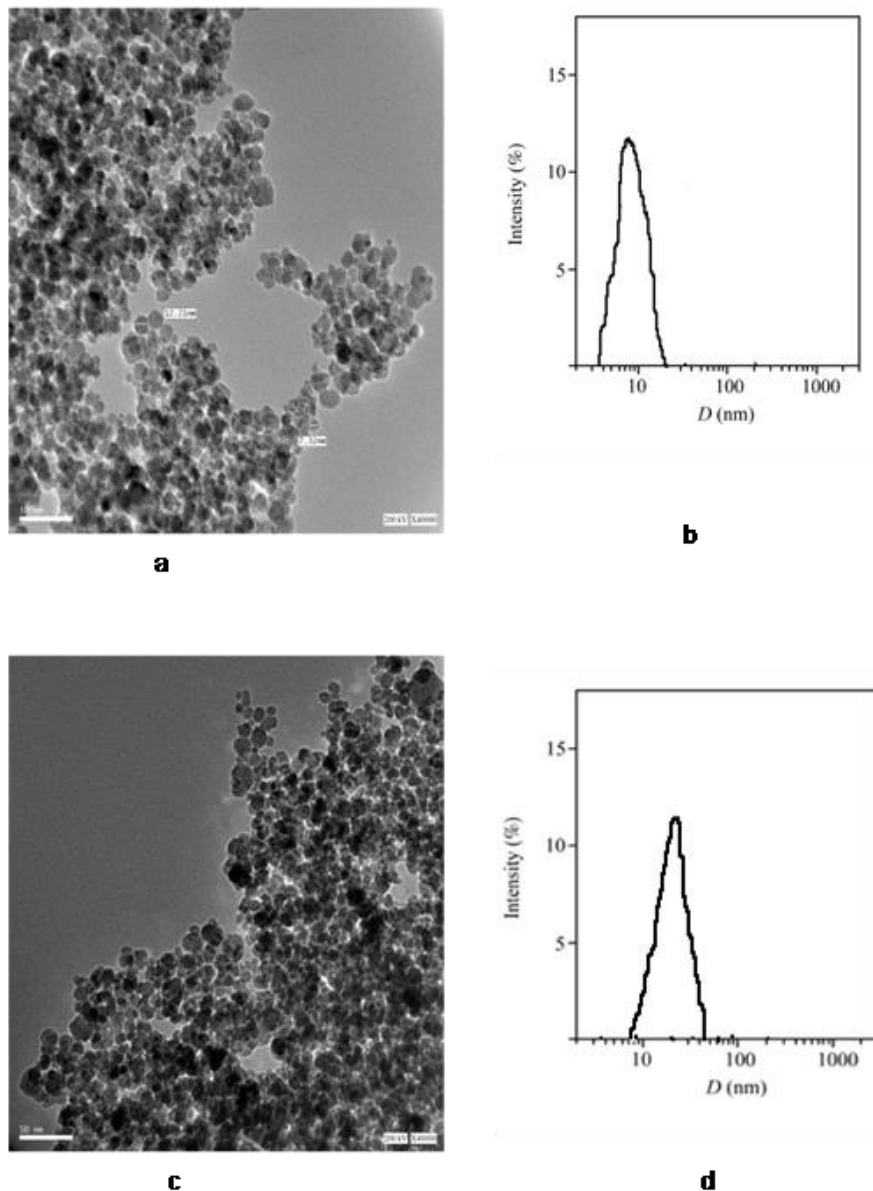
In contrast to that, the amount of associated water decreased from 8 to 4% in H<sub>a</sub>M<sub>a</sub> and H<sub>b</sub>M<sub>a</sub> and from 10.2 to 6.1% in H<sub>a</sub>M<sub>c</sub> and H<sub>b</sub>M<sub>c</sub> respectively when the HEMA



**Figure 2.** FTIR spectra of samples. 1, Fe<sub>3</sub>O<sub>4</sub> nanoparticles; 2, PHEMA magnetic nanogels.



**Figure 3.** TGA of PHEMA magnetic nanogels. a - H<sub>a</sub>M<sub>a</sub>, b - H<sub>a</sub>M<sub>c</sub>, c - H<sub>b</sub>M<sub>a</sub> and d - H<sub>b</sub>M<sub>c</sub>.



**Figure 4.** Particle size of PHEMA magnetic nanogels. a - TEM image of ( $H_aM_a$ ); b - PCS of ( $H_aM_a$ ); c - TEM image of ( $H_aM_c$ ); d - PCS of ( $H_aM_c$ ).

concentration increased from 10 to 15%. This may explain why the increase in MBA expands the spaces between chains whereas the increase in HEMA elongates the chain but decreases the inter-space between chains. The finding of this study runs in harmony with that of Gong et al. (2007). This structure change may affect their absorption capability. Furthermore, it can be concluded that the prepared PHEMAs have very high thermal and oxidative stabilities as shown from their decomposition patterns. It is also clear that the  $Fe_3O_4$  content of magnetic nanogels in dry state ranged from 85 to 92%. This high content is very close to that obtained by Liao and Chen (2002).

## Factors affecting the morphology and size of magnetic nanogels

### Structure of nanogels

Figure 4a to d shows a TEM image of  $H_aM_a$  and its particle size distribution by PCS and a TEM image of  $H_aM_c$  and its particle size distribution by PCS respectively. The TEM images show that the prepared nanogel particles having approximately spherical morphology and with uniform size aggregate due to the magnetic interactions. It can also be shown that each magnetic nanogel which contains several  $Fe_3O_4$

**Table 2.** Absorbance efficiency of the prepared PHEMA magnetic nanogels.

Samples	Initial Cu concentration (blank), mg/L*	Cu in tested samples (ppm)	The amount of Cu absorbed**	% Removal effectiveness***
H <sub>a</sub> M <sub>a</sub>	250	32.74	217.26	86.9
H <sub>a</sub> M <sub>b</sub>	250	9.821	240.18	96.1
H <sub>a</sub> M <sub>c</sub>	250	4.360	245.64	98.2
H <sub>b</sub> M <sub>a</sub>	250	54.30	195.40	78.2
H <sub>b</sub> M <sub>b</sub>	250	44.68	205.32	82.1
H <sub>b</sub> M <sub>c</sub>	250	4.817	245.18	98.0

\*1 mg/L is equivalent to 1 ppm. \*\* The amount of Cu Absorbed= Initial Cu Concentration (blank) - Cu in tested samples. \*\*\* %

$$\text{Absorbance efficiency} = \frac{\text{The amount of Cu Absorbed}}{\text{Initial Cu Concentration}} \times 100.$$

nanoparticles appeared as dark points embedded by the highly cross-linked polymer networks in the centre and the light hairy polymer chains build up the outer shell. The remarkable discrepancy indicates the high swelling capability of magnetic nanogels which may have potential application in absorbing metals from aqueous solutions.

#### **Effect of monomer concentration**

Recalling Figure 4a to d, it can be seen that the mean hydrodynamic diameter of H<sub>a</sub>M<sub>a</sub> is 23.2 nm and is larger when compared with the results of the TEM images because of the hydrated layer around magnetites in aqueous suspension. The mean hydrodynamic diameter of H<sub>a</sub>M<sub>c</sub> is bigger than that of H<sub>a</sub>M<sub>a</sub>, indicating that the increase in MBA increases the polymer shield around the Fe<sub>3</sub>O<sub>4</sub> nanoparticles because the photopolymerization of monomer and cross-linker on the surface of Fe<sub>3</sub>O<sub>4</sub> is a free radical reaction. With a higher monomer reactant concentration, the probability of the collision between HEMA molecules and reactive free radicals on magnetic nanogels is bigger during the reaction, and the chain propagation will take place at a higher speed. In addition, at a higher concentration of HEMA, the ratio of cross-linker to monomer is lower, which leads to the polymer shell with a lower degree of cross-linking and a bigger swelling capability. As a result, the diameter of magnetic nanogels became bigger. This structure change will essentially affect their effectiveness in removing the Cu metal from industrial water. The findings of this study match the results obtained by Atia et al. (2003).

#### **Factors affecting the absorption efficiency of magnetic nanogels**

##### **Effect of nanogel structure on adsorption of copper ions**

The feasibility magnetic of using PHEMA as a magnetic nano-adsorbent for the removal of heavy metal ions from aqueous solutions was demonstrated using copper ions

as a model compound. The typical experiments were conducted at pH 6, 303 K, 15 min contact time and an initial copper ion concentration of 250 mg/L. The data are listed in Table 2. The data revealed that the prepared PHEMA magnetic nanogels are very effective in removing copper ions from aqueous medium under the test conditions and the maximum adsorption was achieved by H<sub>a</sub>M<sub>c</sub>. One can observe that the efficiency increases by increasing MBA and decreases by an increase in the % of HEMA. These findings can be correlated with the data obtained from TGA. The increase of the associated water enhances the absorption process and the efficiency increases when the number of the inter-spaces found in the gel increases. The findings of this study are very close to those obtained by Albornoz et al. (2004).

##### **Effect of temperature on adsorption of copper ions**

The effects of temperature on the adsorption of Copper ions by PHEMA magnetic nanogels were investigated at aqueous solution of pH 6 and at three temperatures, namely 303, 313 and 323 K, and an initial copper ion concentration of 250 mg/L. As shown in Figure 5, the % adsorption efficiency for all the prepared nanogels increased with the increase in temperature from 303 to 313 K, revealing that the adsorption process was endothermic. But it decreased when the temperature rose from 313 to 323 K. One possible explanation was that the metal ions were well hydrated. They have to lose part of the hydration sheath in order to be adsorbed. This dehydration process of metal ions needed energy (Campo et al., 2005). At higher temperatures, the gel may shrink and release some of the adsorbed copper resulting in increasing the copper concentration in the solution again.

##### **Effect of pH on adsorption of copper ions**

The effects of solution pH on the adsorption of copper ions by PHEMA magnetic nanogels were studied at pH

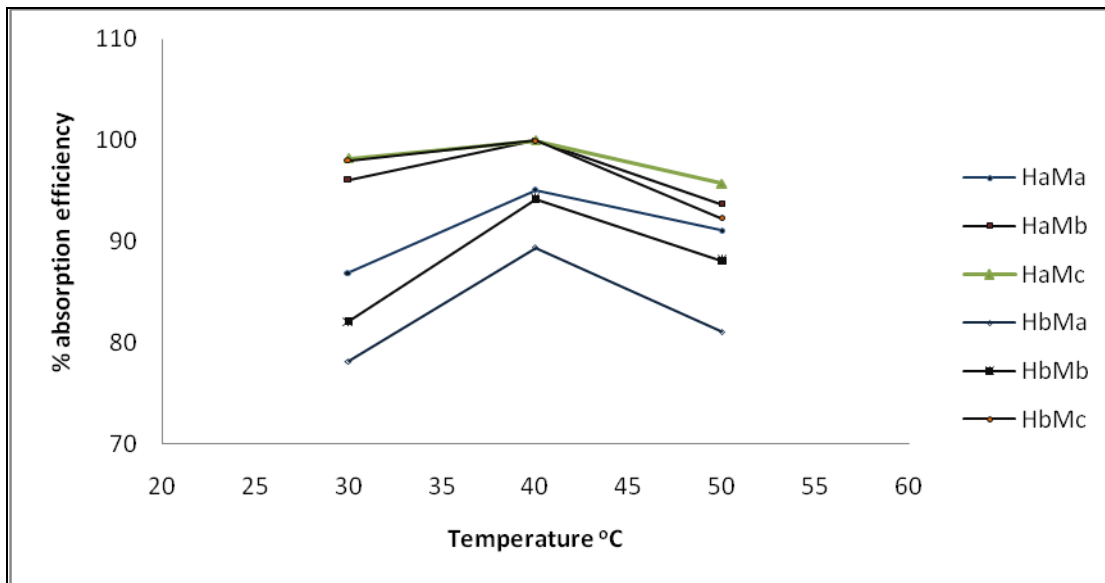


Figure 5. Effect of temperature on the absorption efficiency of PHEMA magnetic nanogels.

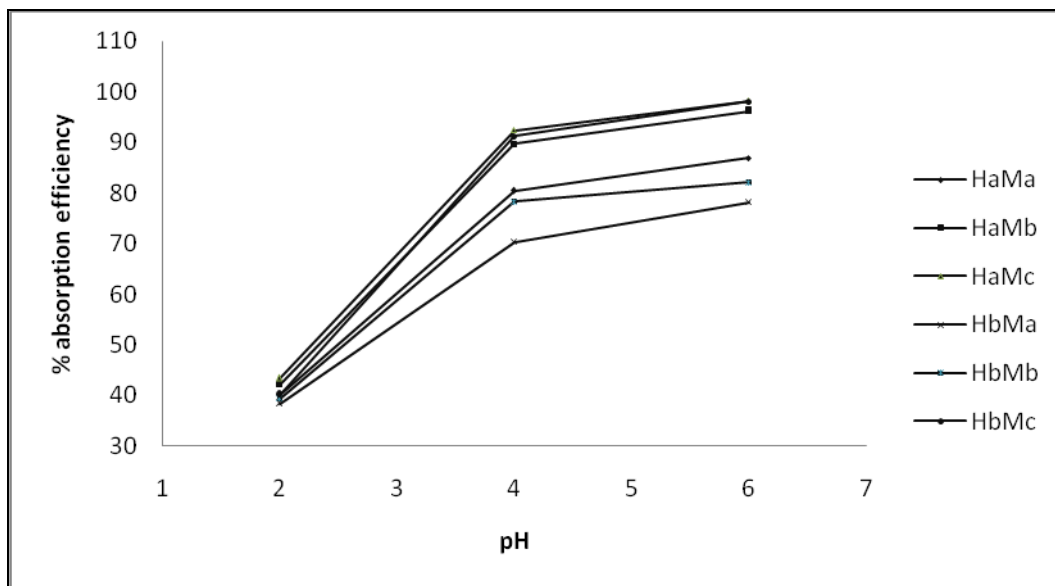


Figure 6. Effect of pH on the absorption efficiency of PHEMA magnetic nanogels.

values 2, 4 and 6, temperature 303 K, and an initial copper ion concentration of 250 mg/L. The adsorption studies at pH > 6 were not conducted because of the precipitation of Cu (OH)<sub>2</sub> from the solution. As shown in Figure 6, there is an obvious decrease in the adsorption effectiveness when the acidity of the solution increases, that is, from pH 6 to pH 4 to pH 2. This may be due to the reaction between the H<sup>+</sup> of the acids and the O-H groups present in the PHEMA structure. This low adsorption efficiency at lower pH value could refer to the sufficiently

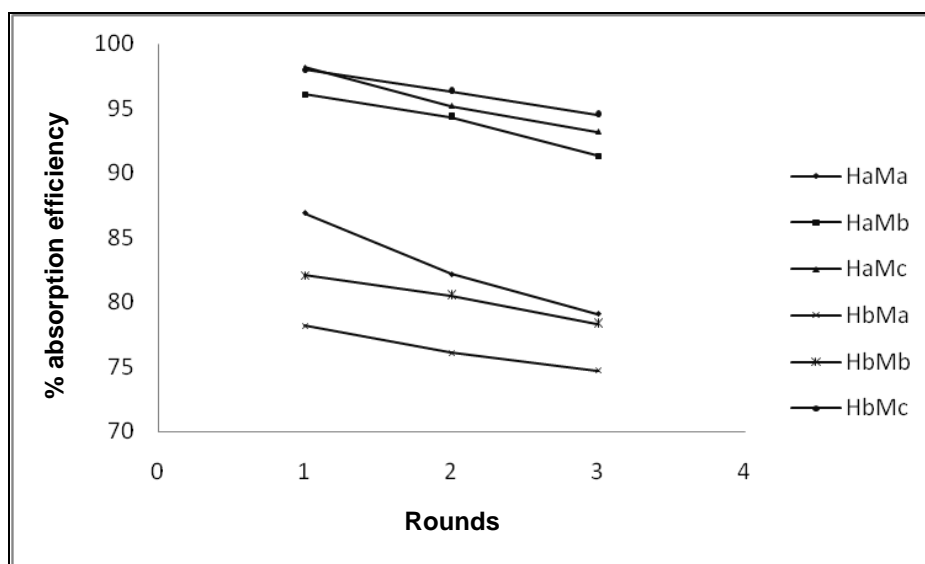
high hydrogen ion concentration, which led to the strong competitive adsorption (Liao et al., 2002). The findings of this study match those obtained by Chang and Cheng (2005).

#### Desorption and reusability studies

From the pH study, it has been found that the adsorption of copper ions on PHEMA magnetic nanogels decreased remarkably. This suggested that desorption of copper

**Table 3.** Adsorption-desorption studies of the prepared PHEMA magnetic nanogels.

Samples	% Removal effectiveness in the first cycle	% Removal effectiveness in the second cycle	% Removal effectiveness in the third cycle
H <sub>a</sub> M <sub>a</sub>	86.9	82.2	79.1
H <sub>a</sub> M <sub>b</sub>	96.1	94.3	91.3
H <sub>a</sub> M <sub>c</sub>	98.2	95.2	93.2
H <sub>b</sub> M <sub>a</sub>	78.2	76.1	74.7
H <sub>b</sub> M <sub>b</sub>	82.1	80.5	78.3
H <sub>b</sub> M <sub>c</sub>	98.0	96.3	94.5

**Figure 7.** Absorption-desorption rounds of PHEMA magnetic nanogels.

ions from these nanogels was possible at pH < 2.0. Therefore, HCl solution of pH 1 was used to examine the desorption study. The adsorption-desorption experiments were conducted three times. The data are given in Table 3 and illustrated in Figure 7. It was found that there is a slight % adsorption decrease after each desorption for all the prepared nanogels. Thus, the prepared adsorbents can be reused almost with very slight loss in the adsorption performance.

### Conclusions

PHEMA magnetic nanogels could be prepared and used as absorbents for copper ions from aqueous solutions. Different factors affecting the absorption effectiveness were studied. These factors include: % of reactants, structure of nanogels, pH of the aqueous solution and the temperature at which the nanogels were applied. The data reveal that the maximum % effectiveness was attained at 10% HEMA, 20 mg MBA, pH 6 and a temperature of 40°C. The reusability studies

demonstrated that the prepared nanogels are effective in absorption of copper after three times of application.

### REFERENCES

- Albornoz C, Sileo EE, Jacobo SE (2004). Magnetic polymers of maghemite (γ-Fe<sub>2</sub>O<sub>3</sub>) and polyvinyl alcohol. *Physica B: Condensed Matter*, 354: 149–153.
- Atia AA, Donia AM, Abou-El-Enein SA, Yousif AM (2003). Studies on uptake behavior of copper (II) and lead(II) by amine chelating resins with different textural properties. *Sep. Pur. Technol.*, 33: 295–301.
- Banerjee SS, Jayaram RV, Joshi MV (2004). Removal of Cr(VI) and Hg(II) from aqueous solutions using fly ash and impregnated fly ash, *Sep. Sci. Technol.*, 39: 1611–1629.
- Butterworth MD, Illum L, Davis SS (2001). Preparation of ultrafine silica- and PEG-coated magnetite nanoparticles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 179: 93–102.



- Campo A, Sena T, Lellouchec JP, Bruce IJ (2005). Multifunctional magnetite and silica-magnetite nanoparticles: Synthesis, surface activation and applications in life sciences. *J. Magn. Magn. Mat.*, 293: 33–40.
- Chang YC, Chen DH (2005). Adsorption kinetics and thermodynamics of acid dyes on a carboxymethylated chitosan-conjugated magnetic nano-adsorbent, *Macromol. Biosci.*, 5: 254–261.
- Chang YC, Chen DH (2005). Preparation and adsorption properties of monodisperse chitosan-bound  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles for removal of  $\text{Cu}(\text{II})$  ions, *J. Colloid Interface Sci.*, 283: 446–451.
- Gong PJ, Sun HW, Hong J, Xu DM, Yao SD (2007). *In-situ* synthesis of PHEMA magnetic nanogels via photochemical method, *Sci. China Ser. B-Chem*, April, 50(2): 217-223.
- Goya GF, Berquo TS, Fonseca FC (2003). Static and dynamic magnetic properties of spherical magnetite nanoparticles, *J. Appl. Phys.*, 94: 3520–3528.
- Groman ET, Menz PM, Enriquez C, Jung LJM, Josephson L (1996). Delivery of therapeutic agents to receptors using polysaccharides, United States Patent, 5554386.
- Leong YK, Seah U, Chu SY, Ong BC (2001). Effect of gum arabic macromolecules on surface forces in oxide dispersion, *Coll. Surface*, 182: 263–268.
- Liao MH, Chen DH (2004). Preparation and characterization of modified magnetic nano-adsorbents, *J. Mater. Chem.*, 14: 5001-5007.
- Liao MH, Chen DH (2002). Preparation and characterization of novel magnetic nano-adsorbents, *J. Mater. Chem.*, 12: 3654–3659.
- Mak SY, Chen DH (2005). Binding and sulfonation of poly(acrylic acid) on iron oxide nanoparticles: a novel, magnetic, strong acid cation nano-adsorbent, *Macromol. Rapid Commun.* 26: 1567–1571.
- Mido Y, Satake M (1995). *Chemicals in the Environment*, Discovery Publishing House, New Delhi, 1995.
- Ngomsik A, Bee A, Draye M, Cote G, Cabuil V (2005). Magnetic nano and microparticles for metal removal and environmental applications: a review, *C. R. Chimie*, 8: 963–970.
- Reis AV, Guilherme MR, Cavalcanti OA, Rubira AF, Muniz EC (2006). Synthesis and characterization of pH-responsive hydrogels based on chemically modified arabic gum polysaccharide. *Polymer*, 47: 2023–2029.
- Savic IM, Stojiljkovic ST, Savic IM, Stojanovic SB, Moder K (2012). Modeling and Optimization of  $\text{Fe}(\text{III})$  Adsorption from Water using Bentonite Clay: Comparison of Central Composite Design and Artificial Neural Network. *Chem. Eng. Technol.*, 35: 2007–2014. doi: 10.1002/ceat.201200085.
- Siegel RW, Hu E, Roco MC (1999). *Nanostructure Science and Technology, A Worldwide Study*, WTEC, Loyola College Kluwer Academic, Baltimore, MD, 1999.
- Weltrowski M, Martel B, Morcellet M (1996). Chitosan *N*-benzyl sulfonate derivatives as sorbents for removal of metal ions in an acidic medium, *J. Appl. Polym. Sci.*, 59: 647–654.