



Chelating magnetic copolymer composite modified by click reaction for removal of heavy metal ions from aqueous solution



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HIGHLIGHTS

- Magnetic copolymer beads were functionalized by azide–alkyne click reaction.
- The chelating beads showed excellent adsorption capacity for heavy metal ions.
- The beads possessed a sensitive magnetic response and could be repeatedly used.

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ABSTRACT

Novel chelating magnetic copolymer beads in micron-size range were prepared by suspension polymerization and click reaction. The click chemistry was proposed as a tool for tuning the surface functionality of magnetic poly(vinylbenzyl chloride-co-styrene-co-divinyl benzene), M-PVBC, by a covalent attachment with propargyl alcohol via triazole formation. After click-coupling reaction, the changes in surface morphology and chemical functionality were examined by SEM–EDX and FT-IR, respectively. Adsorption characteristics for heavy metal were investigated by a batch adsorption in an aqueous system under different experimental conditions. The adsorption process was pH, concentration and time dependent. The maximum adsorption capacities of the chelating magnetic copolymer, M10-PVBC-C, for Zn(II), Cu(II) and Ni(II) in 500 ppm solutions were 67.29, 61.20 and 57.18 mg/g, respectively. Adsorption of Cu(II) ion, the model heavy metal ion, was well fitted to the Langmuir isotherm model. The magnetic chelating beads could be rapidly recovered from aqueous solution by an external magnetic field, regenerated and reused for 5 cycles without significant lost in adsorption capacity. The results of this work indicated that the surface functionalization by click reaction could be a simple and suitable method for the preparation of polymeric adsorbents for an effective removal of metal ions from aqueous solution.

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1. Introduction

Heavy metals are among the pollutants in aqueous waste effluents of many industries. Battery production, mining industry, oil refinery and paint production are just a number of examples. These toxic metals pose significant risks to the environment due to their non-biodegrading, carcinogenicity even at low concentration and tendency to accumulate, causing severe diseases in living organisms. Removal of heavy metals from wastewater has been a challenge in the field of environment protection and generally performed by traditional separation techniques including extraction, neutralization, precipitation/coagulation, membrane technology, biological treatment, and adsorption [1–5]. The application of adsorption technique has drawn enormous research attention over

the past years. Polymeric adsorbents have been used for this purpose because of their chemical functionality, adjustable surface area, dimension stability, easiness of handling and regeneration [6–8].

Recently, metal chelate adsorption combined with the use of magnetic nanoparticles is one of the promising techniques proposed due to its simplicity and fast separation in recovering adsorbent from wastewater under an appropriate magnetic field [9–12]. Several types of magnetic nanoparticles have been investigated including carbon-encapsulated magnetic, magnetite, maghemite and magnetic graphene nanoparticles [13–15]. These nanoparticles have attracted considerable attention because of their unique properties that make them very useful in different fields. They have at least one dimension smaller than 1 μm and are possible to be manipulated under an external magnetic field. Upon removal of the magnetic field, the superparamagnetic nanoparticles (usually diameter less than 15 nm) exhibit no

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magnetic properties and therefore have no attraction for each other, offering an advantage of reducing risk of particle aggregation and a possibility to be used for preparing polymeric composite [12,14]. The application of adsorption process based on the use of magnetic polymer composite involves the following steps: (i) adsorption, (ii) magnetic separation of the adsorbent from wastewater, (iii) adsorbent regeneration, and (iv) handling of the regeneration solution and the adsorbent. These magnetic polymer composites have been reported exhibiting good performance for the purpose of efficient removal owing to the choice of functionality and modification of the polymer matrix [16–18].

Different types of polymeric material have been chemically modified for the use of metal ion removal. The category of highly efficient organic reactions first described in 2001 by Sharpless and co-workers has emerged and become very popular in polymer chemistry [19]. The attention paid to the Cu-catalyzed “click” cycloaddition of azides and terminal alkynes has increased enormously in recent years as a useful and promising synthesis tool for functionalizing synthetic macromolecules and a wide range of polymer architectures [20–22]. These reactions proceed under mild conditions, generate inoffensive or no by products, and require simple purification techniques. One of the very important applications of the azide/alkyne click reaction is its high reactivity in heterogeneous reaction systems, which leads to the prospect of a high efficiency for the derivatization of surface and polymeric materials [23,24]. To the best of our knowledge, there has been no report on the preparation of chelating magnetic poly(vinylbenzyl chloride-co-styrene-co-divinyl benzene) by the effective click reaction for the application of heavy metal removal.

In this study, we reported the combination of facile suspension copolymerization between vinylbenzyl chloride, styrene and divinyl benzene in the presence of magnetic nanoparticles and the “click” 1, 3-dipolar cycloaddition reaction of azide and propargyl alcohol. Adsorption property and efficiency for the removal of Ni(II), Cu(II) and Zn(II) ions from aqueous solutions were investigated by a batch adsorption experiment. The influences of initial ion concentration, pH, and adsorption time on the adsorption capacity were studied. Adsorption isotherms, their parameters and correlation factors were also reported. Furthermore, the regeneration and reusability of these chelating magnetic beads were also studied to evaluate their effectiveness as an adsorbent.

2. Experimental

2.1. Materials

The materials used in organic phase for suspension polymerization, benzoyl peroxide (BPO), styrene (ST), vinylbenzyl chloride (VBC) and divinyl benzene (DVB) were purchased from Merck. The monomers were passed through activated alumina to remove inhibitors before use. Sodium azide, dimethylformamide, propargyl alcohol, dimethylsulfoxide, diethylenetriamine (99% grade) and chemicals used for nanoparticles preparation were purchased from Aldrich and used as received. Sodium chloride, sodium hydroxide, copper iodide and magnesium chloride were of reagent grade. The following chemicals, copper nitrate trihydrate, zinc chloride and nickel chloride hexahydrate (Ajax Finechem) were used for the adsorption study.

2.2. Synthesis of Fe_3O_4 nanoparticles

The magnetic Fe_3O_4 nanoparticles were synthesized via chemical co-precipitation between an aqueous mixture of ferric and ferrous salts. 4.00 g $FeCl_3 \cdot 6H_2O$ and 2.00 g $FeCl_2 \cdot 4H_2O$ were dissolved in 75 mL deionized water with a mechanical stirring

under nitrogen atmosphere at 50 °C for 30 min. 40 mL of ammonia was then added into the mixture and stirred for 3 h. The obtained nanoparticles were separated from the reaction mixture by a magnet, washed with deionized water for several times to neutrality, and dried in a vacuum oven.

2.3. Synthesis of magnetic copolymer beads

Poly(vinylbenzyl chloride-co-styrene-co-divinyl benzene), PVBC, and magnetic-PVBC, M-PVBC, beads were synthesized by a radical suspension polymerization from the reaction mixture given in Table 1. A three-necked glass reactor equipped with a mechanical stirrer and a reflux condenser was used. Dissolved oxygen in the reaction mixture was removed by bubbling nitrogen through a gas inlet tube and then the reactor content was covered with a nitrogen blanket. Suspension was achieved by stirring and sonication of the monomer mixture with magnetic nanoparticles. The mixture was added dropwise to an aqueous phase in the glass reactor with 250 rpm stirring. The contents of magnetic nanoparticles in monomer phase were varied at 1, 5, and 10% wt/v of monomer. The polymerization was carried out at 85 °C for 8 h using a thermostated water bath. The resulting copolymer beads were then washed, sequentially with water and methanol to remove any unreacted monomers. The beads were then dried under vacuum. Using this procedure, a series of magnetic copolymer beads was produced with a constant degree of crosslinking (10 mol% DVB). The obtained composite beads were named M1-PVBC, M5-PVBC and M10-PVBC according to the content of magnetic nanoparticles added into the monomer mixture.

2.4. Surface modification of the copolymer by click reaction

In order to run the reaction, the initial key procedure involves a covalently attachment of $-N_3$ onto the PVBC and M-PVBC beads. The copolymer beads (1.0 g) were agitated with NaN_3 (3.0 g) in DMF (30.0 mL) at 50 °C for 7 h. After cooling to room temperature, the obtained beads were rinsed with distilled water and methanol, and dried under vacuum. Next, clicking of propargyl alcohol onto the azide functionalized beads was performed. 1.0 g of PVBC- N_3 (or M-PVBC- N_3) was dispersed in a solution of DMSO (10.0 mL) and diethylenetriamine (0.5 mL) at room temperature for 10 min. Then, propargyl alcohol (2.5 mL) and CuI (0.05 g) were added and stirred in the reaction mixture at 50 °C for 1 h. At the end of reaction, the resulted chelating magnetic copolymers, M-PVBC-C, were washed several times with DMSO, distilled water and methanol, then dried under vacuum at 55 °C for 24 h.

2.5. Characterization

2.5.1. TEM analysis

Transmission electron micrographs of the magnetic nanoparticles were obtained using a transmission electron microscope, Phillip-Tecnai20.

Table 1
Standard recipe for M-PVBC microsphere preparation.

Monomer mixture	Aqueous phase
50% mole ST	8.6 g $MgCl_2 \cdot 6H_2O$
40% mole VBC	90 mL, 20% NaCl
10% mole DVB	40 mL, 2 M NaOH
1% mole BPO of monomer	
Total volume of monomers = 30 mL	
Magnetic nanoparticles at 1,5 and 10% wt/v of monomer	

2.5.2. Average size and size distribution of the copolymer beads

The copolymer beads were fractionated by sieve analysis using 300, 425, 500, 600, 710 and 850 μm Tyler standard sieves to yield fractions of the beads. The fraction having diameter between 600 and 709 μm was used for the adsorption study.

2.5.3. FTIR study

In order to confirm the effectiveness of surface modification procedure, FTIR spectra of the copolymer beads before and after the click reaction were obtained using Fourier transform infrared spectroscope (FT-IR, Perkin Elmer system 2000). The dry beads were blended with KBr, ground and pressed into disks. The spectra were then recorded.

2.5.4. Swelling test

Swelling behavior of the beads was determined in hexane and toluene to examine their resistance to organic solvents. Dry beads were weighed and placed in a 50 mL vial containing a solvent at room temperature. After a desired period of time, the sample was taken out from the solvent, wiped with a filter paper, and weighed. The swelling ratio was calculated by the following expression:

$$\text{Swelling ratio} = [(W_s - W_o)/W_o] \times 100 \quad (1)$$

where W_o and W_s are the weights of beads before and after uptake of solvent, respectively.

2.5.5. SEM analysis

Surface morphology of the beads was observed by a scanning electron microscope (SEM, LEO 1450VP). Representative samples of the beads before and after surface modification were attached with double-side conductive tapes onto the steel stubs and coated with gold before SEM observation.

2.6. Batch adsorption

Cu(II), Ni(II) and Zn(II) ions were selected as model ions to test the heavy metal ion adsorption characteristics of the beads modified by click reaction. The effects of solution pH (1–5), initial concentration (100–3000 ppm), and adsorption time (15–240 min) on adsorption behavior were investigated. The Cu(II) adsorption isotherm was derived using 0.05 g of chemically modified beads as an adsorbent in copper nitrate solutions (50 mL) with an equilibrium time of 120 min. The adsorption capacity was calculated by Eq. (2):

$$q = [(C_o - C)V]/m \quad (2)$$

where C_o and C are the concentrations of metal ions in the aqueous solution (mg/L) before and after the interaction with copolymer beads for a certain period of time, respectively; V is the volume of solution (L); and m is the amount of the copolymer (g).

3. Results and discussion

3.1. Characterization of magnetic nanoparticles

The magnetic nanoparticles were synthesized via chemical coprecipitation between an aqueous mixture of ferric and ferrous salts in an alkali solution. The chemical reaction can be expressed by the following equation:



It has been known that the co-precipitation reaction usually produces a mixture of magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$). Both forms of crystalline iron oxides show the same

X-ray diffraction pattern in the 30–65 $2\theta^\circ$ interval, but only maghemite shows a signal at $2\theta^\circ$ of 18.2. Fig. 1 shows XRD pattern of the prepared nanoparticles and confirms the majority product of crystalline Fe_3O_4 . Six typical peaks observed at 2θ of 30.2°, 35.5°, 43.2°, 53.6°, 57.1°, and 62.7° could be indexed to the structure of Fe_3O_4 powder diffraction data [25,26].

TEM image and particle size distribution of the magnetic nanoparticles depict the physical appearance of a typical nanion oxide morphology with average diameter in the range between 5 and 15 nm (please see the Supplementary data). FTIR spectra of the nanoparticles were also recorded. The strong peak of Fe–O vibration appeared at 580 cm^{-1} . The adsorption bands of 1650 and 3450 cm^{-1} were assigned to the bending and stretching vibrations of hydroxyl group on the nanoparticle surface (please see the Supplementary data).

3.2. Characterization of the PVBC and M-PVBC

In this study, the PVBC microspheres were synthesized via a suspension polymerization between VBC, ST and DVB as shown in Scheme 1. These monomers were selected for specific reasons. ST is a commercially available monomer. It also provides strength and rigidity to the beads after crosslinking with DVB. VBC is a reactive monomer containing –Cl side group that can be readily converted to a chelating site. The magnetic composite beads, M-PVBC, were prepared by dispersion of magnetic nanoparticles, M, in the monomer mixture and polymerized by the same method as used for PVBC. Upon completion of polymerization, the magnetic composite microspheres were removed from the reaction with an external magnetic field. The average copolymerization yields of PVBC and M-PVBC were 96% and 93%, respectively.

For the application of waste water treatment, the beads should possess good dimensional stability and solvent resistivity. The swelling behavior in hexane and toluene was studied. It was found that the PVBC and M-PVBC beads exhibited swelling ratio less than 8% in both solvents indicating their potential as an adsorbent in terms of solvent resistivity.

The magnetization curve of M10-PVBC beads was recorded using VSM as shown in Fig. 2. The responding saturated magnetization value was 8.0 emu/g. When a magnet was put near a container of M-PVBC dispersed in aqueous medium, the composite beads were attracted towards the magnet within a few seconds. This phenomenon ensures the efficient and facile magnetic separation from suspension systems.

Fig. 3 shows the thermal decomposition of Fe_3O_4 nanoparticles and M-PVBC beads evaluated by TGA. The thermograms depict a variation of residual masses of the samples with temperature. The absolute weight loss of the Fe_3O_4 was less than 3.5% for the whole temperature range (up to 700 °C) indicating the high

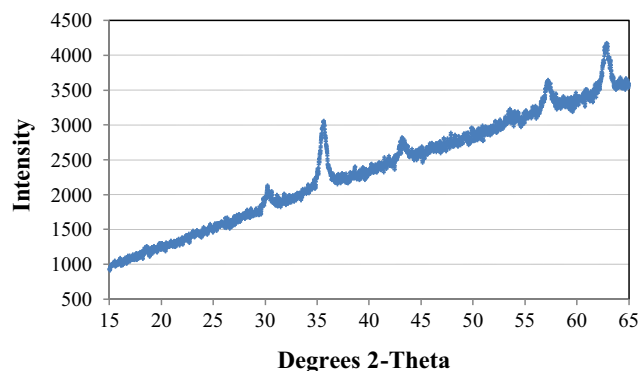
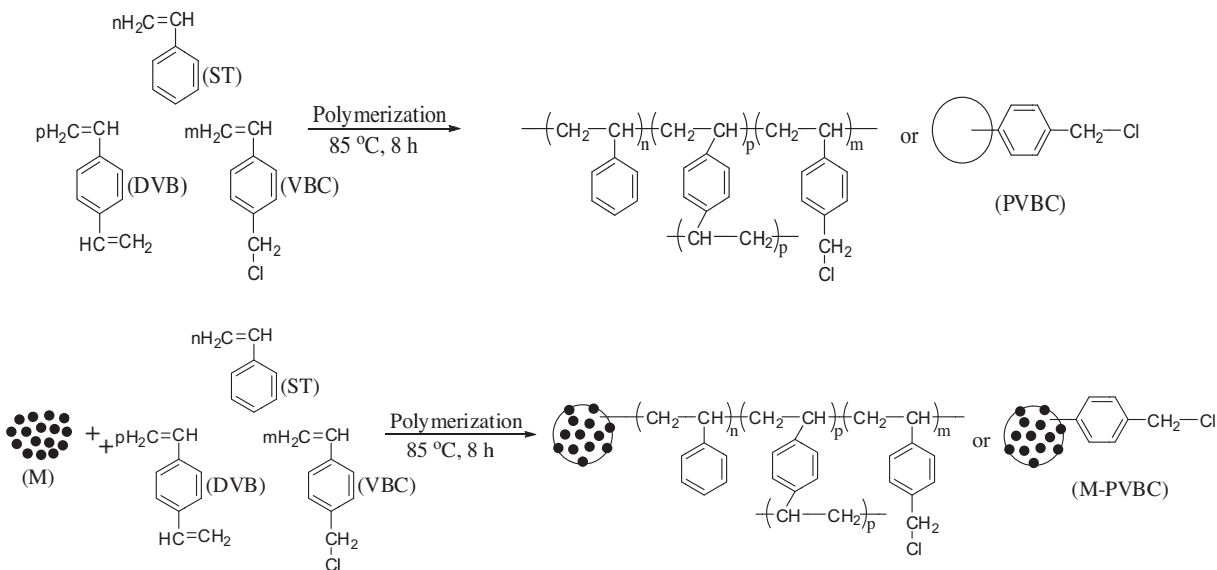


Fig. 1. XRD pattern of Fe_3O_4 nanoparticles.



Scheme 1. Preparation of PVBC and M-PVBC microspheres.

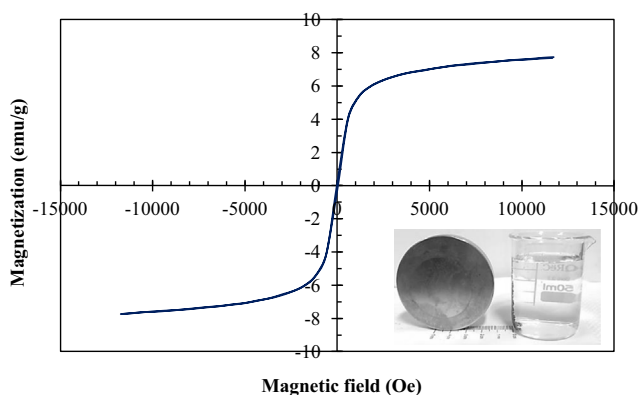


Fig. 2. Magnetization curve of M10-PVBC beads. The inset displays dispersion of the composite beads in aqueous medium under an external magnetic field.

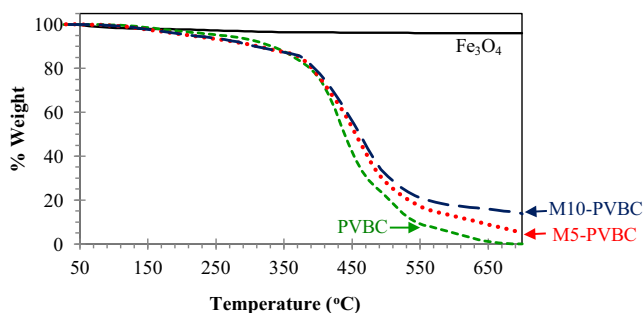


Fig. 3. Thermogravimetric analysis of the Fe₃O₄ and M-PVBC beads.

thermal stability of these magnetic nanoparticles. For the M-PVBC samples, the first stage of small weight loss (below 200 °C) can be attributed to the evaporation of moisture and volatile molecules, while the later stage of weight loss was due to the breakdown of crosslinked structure and decomposition of copolymer matrix. The values of %residual for M5-PVBC and M10-PVBC at the end of the test were in good agreement with the contents of Fe₃O₄ nanoparticles incorporated into the copolymerization mixtures.

3.2.1. Particle size distribution of the copolymers

Particle size and size distribution of the composite beads were analyzed by the use of sieves and the results are shown in Fig. 4. It was observed that the average size of copolymer beads gradually increased with increasing the content of magnetic nanoparticles.

3.2.2. SEM–EDX analysis

Surface morphology and EDX analysis of the PVBC and magnetic beads were investigated and the results are shown in Fig. 5. The PVBC was sphere with smooth surface. On the other hand, the rough and rugged surfaces were obviously seen from the M1-PVBC, M5-PVBC and M10-PVBC microspheres, as a result of nano-Fe₃O₄ agglomeration. EDX analysis confirmed the presence of magnetic nanoparticles in the microspheres with the Fe signal. The intensity of this signal became stronger with increasing the content of nanoparticles.

3.3. Characterization of the chelating beads prepared by click reaction

In this study, the azide–alkyne click chemistry was chosen to functionalize copolymer beads because of its selectivity, high yield and fast reaction time under a facile and mild condition. The –Cl end group of copolymer was transformed to azide functionality by a nucleophilic substitution with sodium azide in DMF, see Scheme 2. %Azide grafting was calculated using Eq. (3):

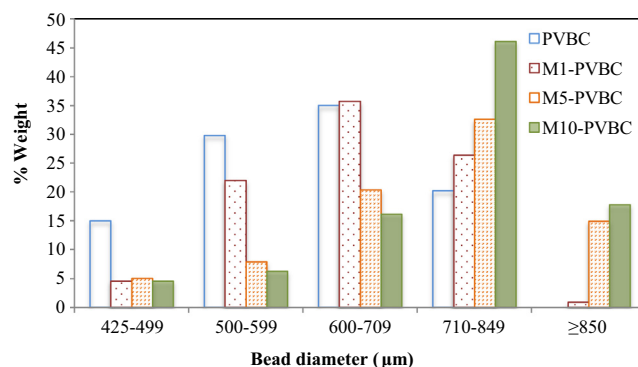


Fig. 4. Particle size distribution of PVBC and M-PVBC beads.

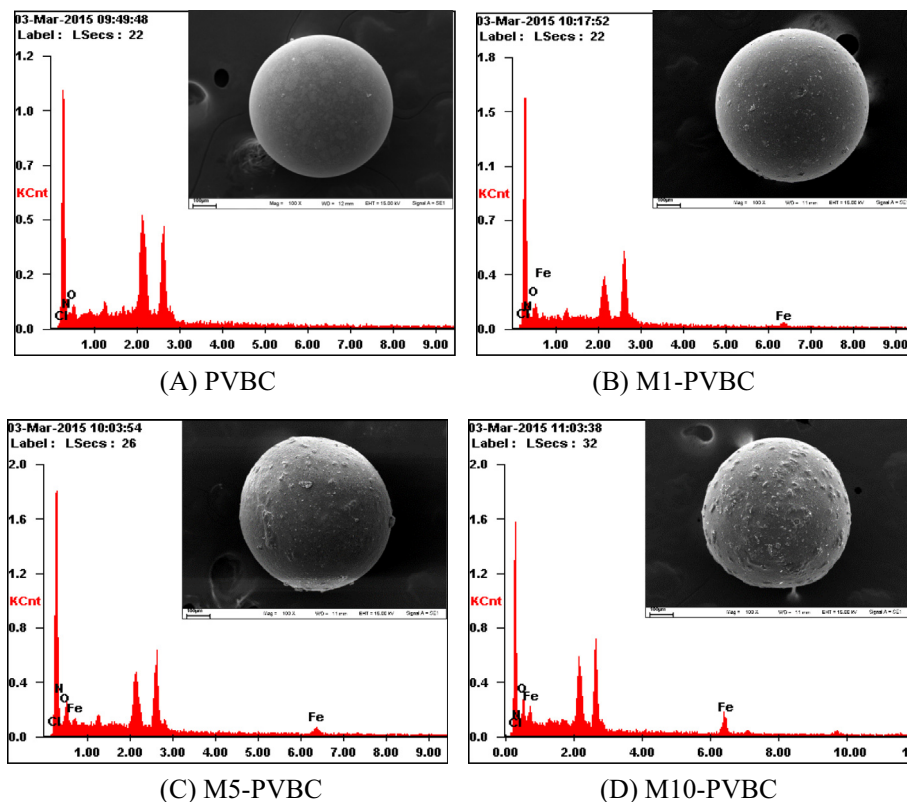
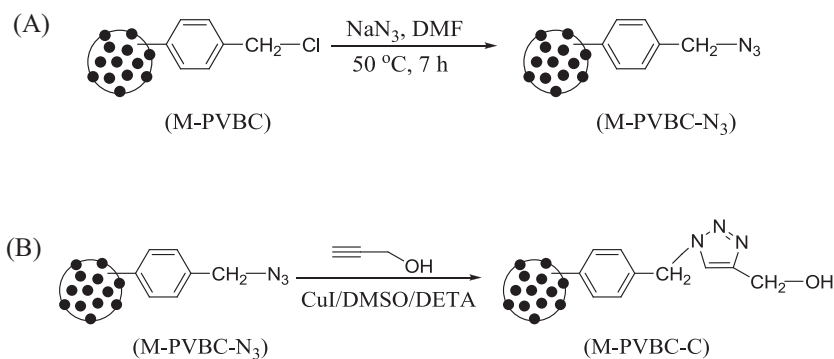


Fig. 5. SEM-EDX micrographs of PVBC, M1-PVBC, M5-PVBC and, M10-PVBC.



Scheme 2. Reactions of (A) the grafting of azide onto the beads, and (B) the azide-alkyne cycloaddition with propargyl alcohol.

$$\% \text{Azide grafting} = [(W_1 - W_0)/W_0] \times 100 \quad (3)$$

where W_0 and W_1 are the weights (g) of the initial beads and N_3 -grafted beads after drying. The value was approximately 6.5% for all samples.

3.3.1. FTIR analysis

FTIR spectra were recorded to identify the formation of chelating microspheres at different modification steps. In the spectrum of M10-PVBC (Fig. 6A), the absorption peaks of $=C-H$ (aromatic) stretching above 3000 cm^{-1} and the strong bands of $C-H$ (CH_2) stretching around $3000-2800$ were seen. The peaks around $1680-1560$, 1470 and 707 cm^{-1} were $C=C$ ring stretching, CH_2 bending and aromatic $C-H$ deformation vibration, respectively. The identification of $C-Cl$ frequency was rather difficult, since mixing of bands was possible in this region. The characteristic peak of $C-Cl$ could be seen as a shoulder of $C-H$ deformation vibration at 670 cm^{-1} . Grafting of azide on M10-PVBC was confirmed by the

presence of a new intensive band at 2100 cm^{-1} assigned to the asymmetric stretching of $-N_3$ group and the lower of $C-Cl$ characteristic peak, see Fig. 6B, [24,27]. The click-cycloaddition between azide and propargyl alcohol was also monitored. A broad $O-H$ stretching band around 3450 cm^{-1} of M-10PVBC-C was observed in Fig. 6C. The disappearance of characteristic azide band at 2100 cm^{-1} indicated that the azide groups were consumed during the click reaction [28].

3.3.2. SEM analysis

The shape and surface of the M10-PVBC beads before and after chemical modification were investigated by SEM and the micrographs are displayed in Fig. 7. At $100\times$ magnification, it was observed that surface morphology of M10-PVBC- N_3 and M10-PVBC-C differed from the unmodified M10-PVBC. The irregularity of the surface with micron-sized voids could be due to the azide grafting and cycloaddition of propargyl alcohol onto the beads.

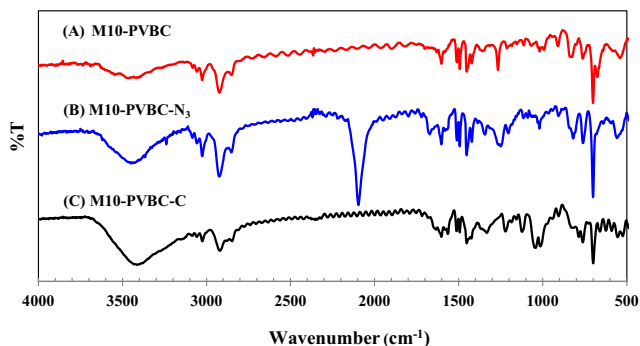


Fig. 6. FTIR spectra of (A) M10-PVBC, (B) M10-PVBC-N₃ and (C) M10-PVBC-C.

3.4. Adsorption study

In this study, Cu(II) ion was selected as a model ion for the optimization of adsorption capacity. The proposed mechanism for adsorption is shown in Scheme 3. The advantage of these magnetic copolymer beads is the ease and simplicity in recovering from the liquid phase. After ion adsorption, the beads can be easily separated using an external magnetic field.

3.4.1. SEM-EDX analysis

SEM images of the M10-PVBC-C after Cu(II) ion uptake were taken to visualize its surface morphology (Fig. 8). At high magnification, the solid crystals randomly dispersed over the bead were clearly observed. Elemental composition at the bead surface was analyzed by EDX and the result confirmed an uptake of Cu(II) with a strong characteristic of Cu signals.

3.4.2. Effects of time and Fe₃O₄ content on adsorption capacity

The effect of time on Cu(II) adsorption of M5-PVBC-C and M10-PVBC-C was investigated using 500 ppm solution without adjusting pH (natural pH). The adsorption capacities at different time intervals are shown in Fig. 9. Both chelating beads showed a rapid increase of binding between metal ions and the beads at the initial state of adsorption. The equilibrium was attained within 120 min, after which the change in adsorption capacity was insignificant. Results show that an increase in magnetic nanoparticle showed no marked difference in the adsorption capacity. The PVBC beads also showed approximately the same metal uptake and adsorption kinetics curve as those measured from the magnetic composite beads indicating that the metal chelation occurred via the reactive sites chemically modified by click reaction.

3.4.3. Effect of pH on adsorption capacity

The efficiency of adsorption is significantly dependent on solution pH because the process is primarily influenced by the surface charge of the beads and the degree of ionization. Fig. 10 shows the

adsorption behavior of M10-PVBC-C over a range of pH. The comparative experiment was only carried out in acidic solutions to avoid the precipitation of metal hydroxide by OH⁻ ions. It was clearly seen that the adsorption capacity decreased continuously with decreasing pH. The observed pH-dependent adsorption could be attributed to the change in surface of chelating beads. With decreasing pH, the electron-rich functional groups were electrostatically attracted by protons resulting in a poor interaction between the metal ions and the beads. Under this condition, the adsorption was unfavorable and Cu(II) ions remained in the solution [29].

3.4.4. Effect of solution concentration on adsorption capacity

The effect of ion concentration on adsorption behavior of M10-PVBC-C was examined at a fixed adsorbent dose and the results are shown in Fig. 11. As expected, an increase in solution concentration enhanced the ion uptake. The adsorption profile is a single curve leading to a saturation point in 1500 ppm of Cu(II) ions.

3.4.5. Adsorption isotherm

The study of adsorption isotherms is a useful tool for the application of adsorbents. In this study, the adsorption capacities of the beads are mathematically expressed in terms of the Langmuir and Freundlich isotherm models. The equations are given below in order:

$$q_e = K_L C_e / (1 + b_L C_e) \quad (4)$$

and

$$q_e = K_F C_e^n \quad (5)$$

The two isotherms are only applicable to a batch adsorption system where sufficient time is provided to allow equilibrium between the pollutant in medium solution and the pollutant adsorbed on the adsorbent. The Langmuir isotherm model assumes monolayer adsorption with equal energy and enthalpy for all adsorption sites. This model can be linearized to give

$$1/q_e = 1/K_L C_e + b_L/K_L \quad (6)$$

where C_e (mmol/L) and q_e (mmol/g) show the equilibrium metal ion concentration in solution and the amount of metal ions adsorbed on the adsorbent at adsorption equilibrium, respectively. K_L (L/g) and b_L (L/mmol) are the Langmuir isotherm constants of the system. The ratio of K_L/b_L is the maximum adsorption capacity. A plot of $1/q_e$ versus $1/C_e$ would result in a straight line with a slope of $1/K_L$ and intercept of b_L/K_L [30,31]. The calculated data are given in Table 2.

The Freundlich isotherm model assumes that the adsorption energy of a metal binding to an adsorption site depends on whether or not the adjacent sites are already occupied. The adsorption occurs on heterogeneous surfaces and possibly in multilayer adsorption. The linearized isotherm equation is as follows:

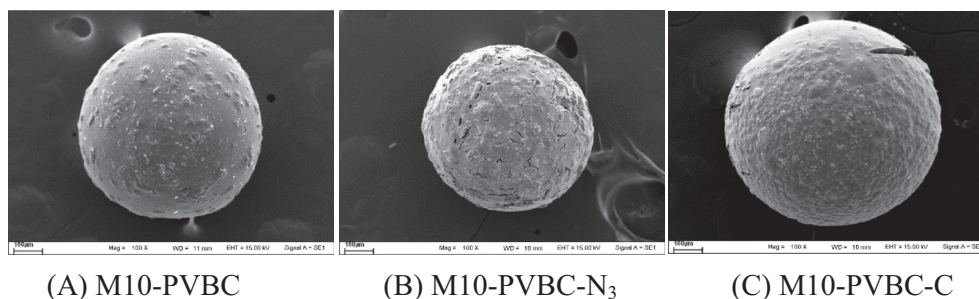
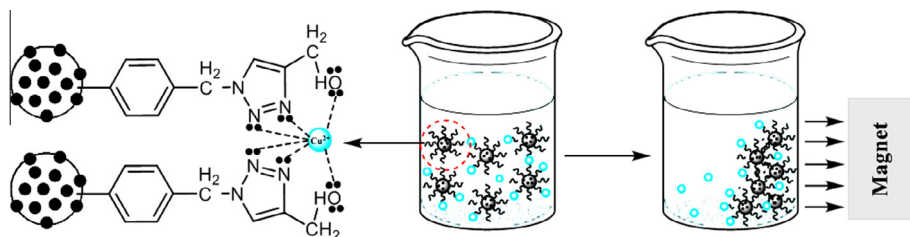


Fig. 7. SEM micrographs of the magnetic beads before and after chemical modification by click reaction.



Scheme 3. Metal ion adsorption by the chelating sites of M-PVBC-C beads and the separation of beads under an external magnetic field.

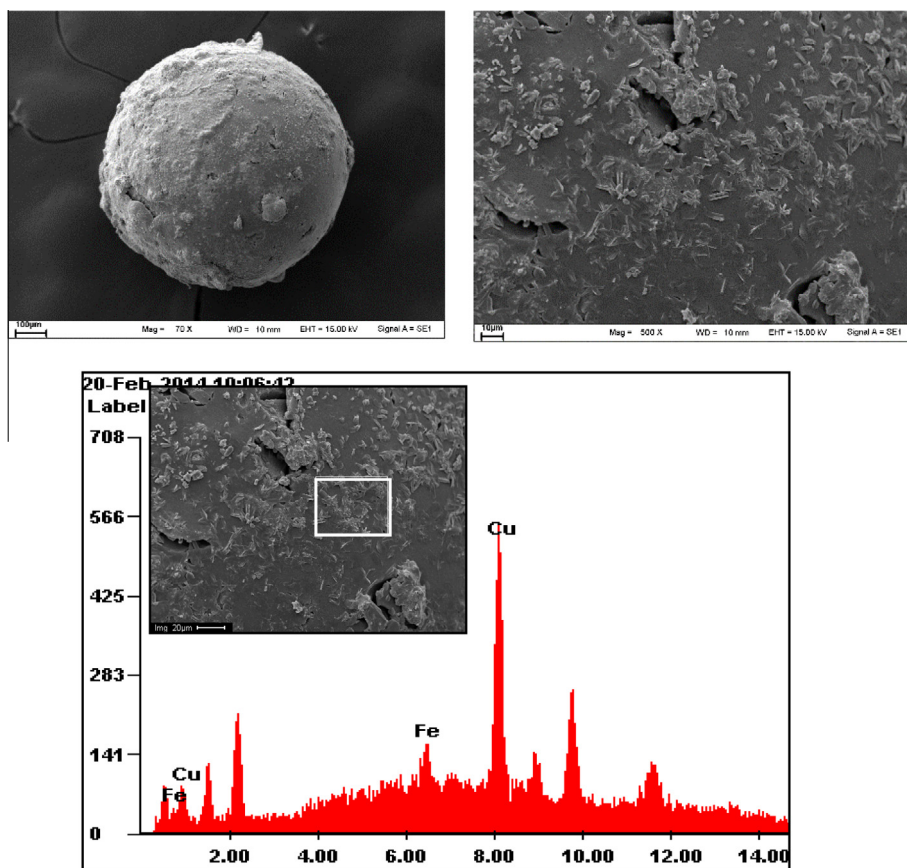


Fig. 8. SEM-EDX analysis of the M10-PVBC-C after Cu(II) adsorption.

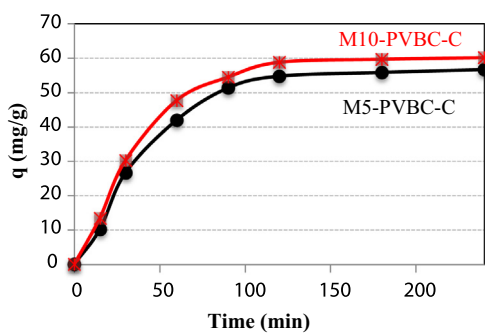


Fig. 9. The adsorption capacity of M5-PVBC-C and M10-PVBC-C beads in 500 ppm Cu(II) solution (natural pH).

$$\ln q_e = n \ln C_e + \ln K_F \quad (7)$$

where K_F ($\text{mmol}^{1-n} \cdot \text{L}^n/\text{g}$) is the Freundlich constant depicting adsorption capacity, n is a constant indicating adsorption intensity,

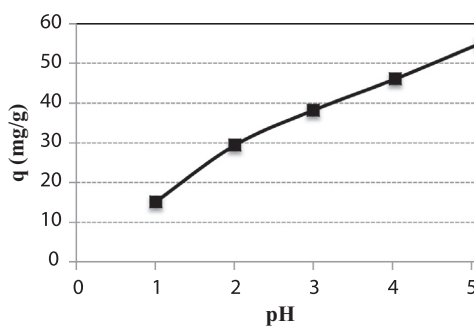


Fig. 10. The adsorption capacity of M10-PVBC-C beads in 500 ppm of Cu(II) solution at 120 min adsorption time.

and C_e (mmol/L) and q_e (mmol/g) have the same definitions as before. Therefore, a plot of $\ln q_e$ versus $\ln C_e$ would result in a straight line and enable the constants n and K_F to be determined [32].

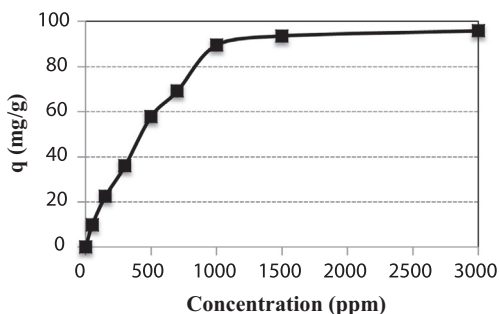


Fig. 11. The adsorption capacity of M10-PVBC-C beads in different concentrations of Cu(II) ion (natural pH), 120 min adsorption time.

Table 2

Langmuir and Freundlich constants for Cu(II) adsorption of the M10-PVBC-C beads.

Langmuir			Freundlich		
K_L (L/g)	b_L (L/mmol)	R^2	K_F (mmol ¹⁻ⁿ ·L ⁿ /g)	n	R^2
0.2131	0.1206	0.9937	0.2149	2.0706	0.9179

In this study, the two models were tested for Cu(II) adsorption using M10-PVBC-C beads. The best-fitted model was determined depending on the linear correlation coefficient, R^2 . The parameters obtained by applying both models to the experimental data are given in Table 2. The Langmuir isotherm correlated with our experimental data better than the Freundlich isotherm, indicating that adsorption occurs uniformly on the active sites of the adsorbent, and stops at one monolayer with specific and strong adsorption onto the binding sites [33].

3.4.6. Adsorption capacity in a single and mixed metal ion solutions

The M10-PVBC-C was also tested for the uptake of Zn(II) and Ni(II) ions in 500 ppm single ion solutions at 120 min adsorption time. The chelating beads provided satisfactory results for the removal of metal ions in a mass basis order of Zn(II) > Cu(II) > Ni(II) (Fig. 12). The maximum loading capacities of Zn(II), Cu(II) and Ni(II) were determined to be 67.29, 61.20 and 57.18 mg/g. The greater affinity for Zn(II) could be due to its smaller ion radius that facilitated the binding between ion and the chelating site.

A competitive adsorption test was attempted using a solution prepared by mixing 500 ppm solutions of Ni(II), Cu(II) and Zn(II) ions. It was found that adsorption was not selective and the ion uptake followed the order Zn(II) > Cu(II) > Ni(II), see Fig. 13. The adsorption capacity for each metal decreased in the presence of competitor metal ions. The results indicated that these metal ions

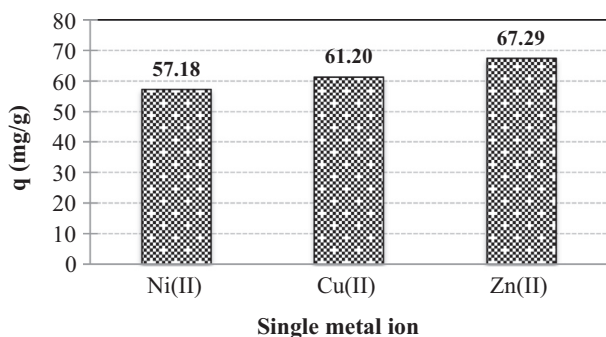


Fig. 12. Adsorption capacity of M10-PVBC-C in single ion solutions at 500 ppm (natural pH) and 120 min adsorption time.

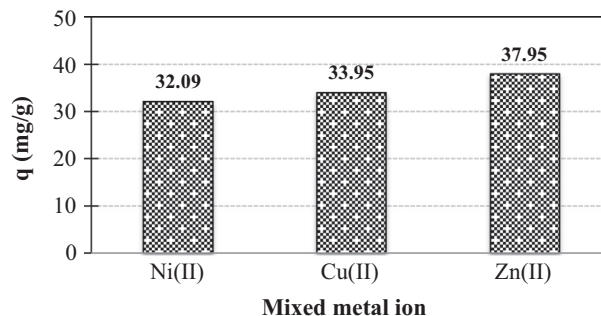


Fig. 13. Adsorption capacity of M10-PVBC-C in a mixed ion solution at 500 ppm (natural pH) and 120 min adsorption time.

competed for the same adsorption site and the number of available chelating sites decreased for one ion in a mixed solution.

3.4.7. Desorption and reusability

From the practical point of view, reusability is a key factor of an adsorbent. In this work, the regeneration was performed by immersion the M10-PVBC-C beads in 500 ppm solution. After reaching the maximum ion uptake, the beads were then subjected to desorption by 1 M HNO₃ solution. The adsorption–desorption cycles were repeated using the same beads and the results are shown in Fig. 14. After five cycles of regeneration, the re-adsorption amount of ions remained almost constant suggesting that the chelating sites on the beads were reversible. The M10-PVBC-C could be repeatedly used without significantly loss in the binding affinity. The excellent reusability made it economically possible for the application of heavy metal removal from wastewater.

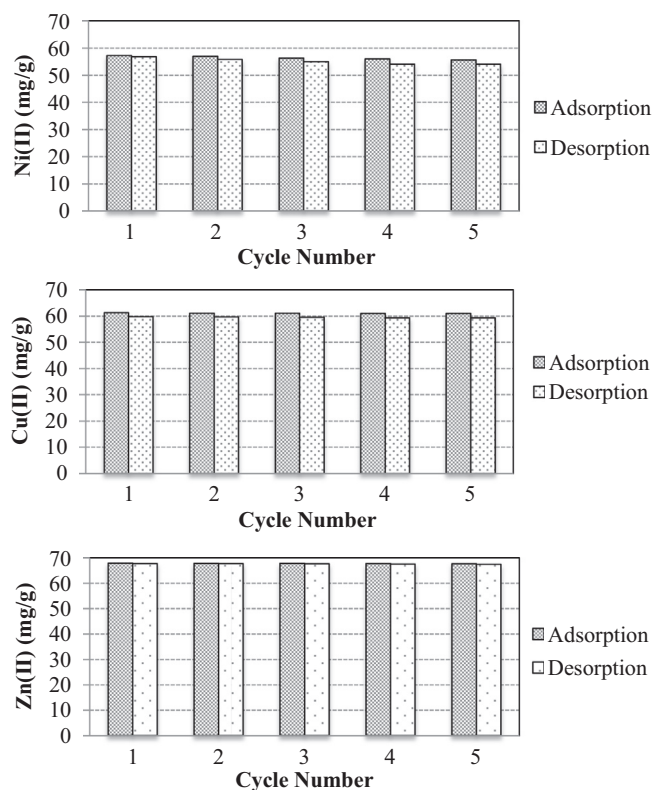


Fig. 14. The adsorption–desorption of Ni(II), Cu(II) and Zn(II) ions on the M10-PVBC-C beads.

Table 3
Comparison of adsorption behavior of the M10-PVBC-C with different adsorbents reported in the literature.

Type of adsorbent	Targets	Adsorption capacity (mg/g)	pH	Reusability (%adsorption efficiency)	Refs.
Amino-functionalized polyacrylic acid coated Fe ₃ O ₄ nanoparticles	Cu(II)	12.43	5	–	[9]
	Cr(VI)	11.24	2		
Fe ₃ O ₄ nanoparticles modified with amino-propyltriethoxysilane and copolymers of acrylic acid and crotonic acid	Methylene blue	142.9	7.5	94 after 4 cycles	[10]
Chitosan/clay/magnetite composite	Cu(II)	17.2	7	99	[11]
	As(V)	5.9	3	20	
Magnetic polymer beads (PMMA-DVB) modified with ethylene diamine	Cu(II)	51.7	3–5	98 after 5 cycles	[12]
	Ni(II)	49.6			
	Co(II)	50.3			
Resin loaded magnetic β -cyclodextrin beads and graphene oxide sheet	Hg(II)	88.43	7.1	76 after 4 cycles	[16]
Cross-linked chitosan/magnetite/heulandite composite	Methylene blue	45.1	5.5	–	[17]
Carboxymethyl- β -cyclodextrin modified Fe ₃ O ₄ nanoparticles	Pb(II)	64.50	5.5	96% for Pb(II) after 4 cycles	[18]
	Cd(II)	27.70			
	Ni(II)	13.20			
Hyaluronic acid immobilized magnetic/silica microspheres	Cu(II)	13.0	7.0	–	[25]
Magnetic copolymer bead (PVBC) modified by click reaction	Zn(II)	67.29	5.5	99.7	This work
	Cu(II)	61.20		99.2	
	Ni(II)	57.18		95.1 after 5 cycles	

3.4.8. Comparison of the adsorption behavior with other adsorbents

A list of the maximum adsorption capacities of some recent results obtained using different types of magnetic adsorbent, is presented in Table 3. A direct comparison between the M10-PVBC-C and other adsorbents was not straightforward, because there many parameters that can have significant impacts on the adsorption process.

The listed results were gained from materials of distinct structures and different experimental conditions, such as solution concentration, pH, time and adsorbent dose. In terms of adsorption capacity and reusability, it can be observed that the M10-PVBC-C is a good candidate as an adsorbent in the removal of metal from aqueous solutions. The simple and fast synthesis method and efficient removal efficiency will benefit the M10-PVBC-C to a broad application prospects.

4. Conclusions

In this work, the efficient removal of heavy metal ions from aqueous solution using a newly synthesized magnetic copolymer was investigated. The Fe₃O₄-PVBC microspheres were successfully synthesized from VBC, ST and DVB via suspension polymerization in the presence of Fe₃O₄ nanoparticles. The obtained magnetic beads, M-PVBC, were chemically modified by click reaction to produce a chelating composite. FTIR, SEM and EDX techniques proved the presence of chelating sites for heavy metals on the composite surface. The study of adsorption characteristic indicated that various parameters such as adsorption time, solution concentration and pH played important roles in the adsorption behavior. The Langmuir isotherm was demonstrated to provide the best correlation for adsorption of Cu(II) ion. In addition, regeneration study showed that the chelating magnetic beads were stable after repeated uses and the percentage of desorption was high without significant decrease in adsorption capacity. According to the obtained results, the novel chelating magnetic beads could be a promising adsorbent for the removal of heavy metals, with the advantages of high adsorption capacity and a convenient recovery from waste water by applying a magnetic field.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2015.12.073>.

References

- [1] A. Demirbas, Heavy metal adsorption onto agro-based waste materials, review article, *J. Hazard. Mater.* 157 (2008) 220–229.
- [2] P.V. Nidheesh, R. Gandhimathi, Trends in electro-Fenton process for water and wastewater treatment: an overview, review article, *Desalination* 299 (2012) 1–15.
- [3] Z. Hasan, S.H. Jung, Removal of hazardous organics from water using metal-organic frameworks (MOFs): plausible mechanisms for selective adsorptions, review article, *J. Hazard. Mater.* 283 (2015) 329–339.
- [4] M. Rossier, A. Schaez, E.K. Athanassiou, R.N. Grass, W.J. Stark, Reversible As(V) adsorption on magnetic nanoparticles and pH dependent desorption concentrates dilute solutions and realizes true moving bed reactor systems, *Chem. Eng. J.* 175 (2011) 244–250.
- [5] D. Mohan, C.U. Jr, Pittman, Arsenic removal from water/wastewater using adsorbents – a critical review, review article, *J. Hazard. Mater.* 142 (2007) 1–53.
- [6] T. Trakulsujaritchook, N. Noiphom, N. Tangtreamjitmun, R. Saeng, Adsorptive features of poly(glycidyl methacrylate-co-hydroxyethyl methacrylate): effect of porogen formulation on heavy metal ion adsorption, *J. Mater. Sci.* 46 (2011) 5350–5362.
- [7] G. Dodi, D. Hritcu, Core-shell magnetic chitosan particles functionalized by grafting: synthesis and characterization, *Chem. Eng. J.* 203 (2012) 130–141.
- [8] B.L. Rivas, E.D. Pereira, M. Palencia, J. Sánchez, Water-soluble functional polymers in conjunction with membranes to remove pollutant ions from aqueous solutions, review article, *Prog. Polym. Sci.* 36 (2011) 294–322.
- [9] S.H. Huang, D.H. Chen, Rapid removal of heavy metal cations and anions from aqueous solutions by an amino-functionalized magnetic nano-adsorbent, *J. Hazard. Mater.* 163 (2009) 174–179.
- [10] F. Ge, H. Ye, M.M. Li, B.X. Zhao, Efficient removal of cationic dyes from aqueous solution by polymer-modified magnetic nanoparticles, *Chem. Eng. J.* 198–199 (2012) 11–17.
- [11] D.W. Cho, B.H. Jeon, C.M. Chon, Y. Kim, F.W. Schwartz, E.S. Lee, H. Song, A novel chitosan/clay/magnetite composite for adsorption of Cu(II) and As(V), *Chem. Eng. J.* 200–202 (2012) 654–692.
- [12] Z.Y. Lin, Y.X. Zhang, Y.L. Chen, H. Qian, Extraction and recycling utilization of metal ions (Cu²⁺, Co²⁺ and Ni²⁺) with magnetic polymer beads, *Chem. Eng. J.* 200–202 (2012) 104–112.
- [13] K. Pyrzynska, M. Bystrzejewski, Comparative study of heavy metal ions sorption onto activated carbon, carbon nanotubes, and carbon-encapsulated magnetic nanoparticles, *Colloids Surf. A: Physicochem. Eng. Aspects* 362 (2010) 102–109.
- [14] A.E. Chávez-Guajardo, J.C. Medina-Llamas, L. Maqueira, C.A.S. Andrade, K.G.B. Alves, C.P. de Melo, Efficient removal of Cr (VI) and Cu(II) ions from aqueous

- media by use of polypyrrole/maghemite and polyaniline/maghemite magnetic nanocomposites, *Chem. Eng. J.* 281 (2015) 826–836.
- [15] J. Gómez-Pastora, E. Bringas, I. Ortiz, Recent progress and future challenges on the use of high performance magnetic nano-adsorbents in environmental applications, *Chem. Eng. J.* 256 (2014) 187–204.
- [16] L. Cui, Y. Wang, L. Gao, L. Hu, Q. Wei, B. Du, Removal of Hg(II) from aqueous solution by resin loaded magnetic β -cyclodextrin bead and graphene oxide sheet: synthesis, adsorption mechanism and separation properties, *J. Colloid Interface Sci.* 456 (2015) 42–49.
- [17] D.W. Cho, B.H. Jeon, C.M. Chon, F.W. Schwartz, Y. Jeong, H. Song, Magnetic chitosan composite for adsorption of cationic and anionic dyes in aqueous solution, *J. Ind. Eng. Chem.* 28 (2015) 60–66.
- [18] A.Z.M. Badruddoza, Z.B.Z. Shawon, W.J.D. Tay, K. Hidajat, M.S. Uddin, Fe₃O₄/cyclodextrin polymer nanocomposites for selective heavy metals removal from industrial wastewater, *Carbohydr. Polym.* 91 (2013) 322–332.
- [19] H.C. Kolb, M.G. Finn, H.B. Sharpless, Click chemistry: diverse chemical function from a few good reactions, *Angew. Chem. Int. Ed.* 40 (2001) 2004–2021.
- [20] C. Speyerer, K. Borchers, T. Hirth, G.E.M. Tovar, A. Weber, Surface etching of methacrylic microparticles via basic hydrolysis and introduction of functional group for click chemistry, *J. Colloid Interface Sci.* 397 (2013) 185–191.
- [21] B. Jang, S.Y. Kim, J.Y. Do, Dye-incorporated water-soluble polymer via click triazole formation, *Dyes Pigments* 94 (2012) 217–223.
- [22] A. Koschella, M. Hartlieb, T. Heinze, A “click-chemistry” approach to cellulose-based hydrogels, *Carbohydr. Polym.* 86 (2011) 154–161.
- [23] W.H. Binder, Click-chemistry in polymer and material science: the updated, *Macromol. Rapid Commun.* 12–13 (2008) 943–1185.
- [24] J. Amici, M.U. Kahveci, P. Allia, P. Tiberto, Y. Yagci, M. Sangermano, Polymer grafting onto magnetite nanoparticles by “click” reaction, *J. Mater. Sci.* 47 (2012) 412–419.
- [25] S. Lan, X. Wu, L. Li, M. Li, F. Guo, S. Gan, Synthesis and characterization of hyaluronic acid-supported magnetic microspheres for copper ions removal, *Colloids Surf. A* 425 (2013) 42–50.
- [26] X. Zeng, Y. Zhou, W. Ma, S. Wang, K. Xie, J. Wu, K. Wei, Selective Zn(II) chemosensor based on di(2-pocoly)amine functionalized inorganic/organic hybrid magnetic network, *Chem. Eng. J.* 244 (2014) 75–81.
- [27] X. Liu, H.N. Zheng, Y.Z. Ma, Q. Yan, S.J. Xiao, Microwave irradiated click reactions on silicon surfaces via derivitization of covalently grafted poly (PEGMA) brushes, *J. Colloid Interface Sci.* 358 (2011) 116–122.
- [28] H.B. Bu, G. Götz, E. Reinold, A. Vogt, S. Schmid, J.L. Segura, R. Blanco, R. Gómez, P. Bäuerle, Efficient post-polymerization functionalization of conducting poly (3,4-ethylenedioxythiophene) (PEDOT) via ‘click’-reaction, *Tetrahedron* 67 (2011) 1114–1125.
- [29] G.Z. Kyzas, M. Kostoglou, N.K. Lazaridis, Copper and chromium(VI) removal by chitosan derivatives – equilibrium and kinetic studies, *Chem. Eng. J.* 152 (2009) 440–448.
- [30] L. Zhou, J. Jin, Z. Liu, X. Liang, C. Shang, Adsorption of acid dyes from aqueous solutions by the ethylenediamine-modified magnetic chitosan nanoparticles, *J. Hazard. Mater.* 185 (2011) 1045–1052.
- [31] H.M.F. Freundlich, Over the adsorption in solution, *J. Phys. Chem. A* 57 (1906) 358–471.
- [32] K.Y. Foo, B.H. Hameed, Insights into the modeling of adsorption isotherm systems, review article, *Chem. Eng. J.* 156 (2010) 2–10.
- [33] W. Guoa, W. Hua, J. Pan, H. Zhou, W. Guan, X. Wang, J. Dai, L. Xu, Selective adsorption and separation of BPA from aqueous solution using novel molecularly imprinted polymers based on kaolinite/Fe₃O₄ composites, *Chem. Eng. J.* 171 (2011) 603–611.