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PolyHIPEs for Water Treatment

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Abstract PolyHIPEs (polymers synthesized within high internal phase emulsions) are porous materials with high specific surface area which suggests their use in ion exchange applications. We have successfully synthesized and functionalized such materials to make then hydrophilic by mixing an oil phase and an aqueous phase containing deionized water and sulphuric acid. The PolyHIPE samples were also subjected to a further microwave-assisted post-sulphonation process to increase hydrophilicity and water uptake. Post sulphonation results in a higher concentration of benzenesulphonic acid groups which are necessary for ion exchange. PolyHIPE beads processed in this manner were able to remove low concentrations (~20mg/l) of nickel and copper ions from solution with high removal efficiency (80-95%) depending on the initial pH of the water. However, recovery of the metal through regeneration at different pH levels was less successful.

Keywords: PolyHIPE, ion exchange, water treatment

1. Introduction

Wastewater treatment is used to remove heavy metals because they can have an adverse effect on human health (Molinari *et al*., 2008). Heavy metals such as nickel, cadmium and arsenic with different concentrations may be naturally available in water or they may originate from industrial processes.

Ion exchange, activated carbon, and nano-filtration are the three methods most widely used to remove heavy metals (Bowman *et al*., 2002; Verstraeten *et al*., 2003). Porous materials with high surface area that can be functionalized to bind to contaminant metal ions are expected to offer higher removal rates than other methods.

Due to their porous structure PolyHIPEs have high surface area which recommends their use in ion exchange applications (Hasan, 2013). Their use as ion exchange modules to remove metals from wastewater is most practical in a second filtration step after the removal of large diameter particulate contaminants otherwise, the PolyHIPE structure could be completely clogged by these large particles. The structure of PolyHIPEs consists of interconnected micro- and nano-pores which provide a very high surface area after the polymerization process. During the preparation, the material consists of an aqueous dispersed phase (internal phase) which creates the pores and a continuous oil phase (external phase) which creates the polymer walls between them. The ratio oil to aqueous phase should be at least 76% (Cameron, 2005; Boujelben *et al*., 2009). After polymerization this material can be treated

with sulphuric acid to functionalize the surface (post-sulphonation process). The surface converts from hydrophobic to hydrophilic, so the porous polymer can absorb water (Cameron, 2005). After sulphonation the PolyHIPE becomes acidic due to the formation of SO_3H groups in its structure (Yee *et al*., 2013). These groups are bonded to the PolyHIPE surface and their amount depends on the degree of sulphonation (Bhumgara, 1995).

The process of manufacture of polyHIPEs is based on creating a high internal phase emulsion (HIPE) by dosing controlled amounts of the aqueous phase into the oil phase with continuous mixing. During mixing a significant reduction in the aqueous droplet size occurs (Krajnc *et al*., 2005; Boujelben *et al*., 2009). The oil phase, which can be polymerized, provides the continuous phase which surrounds the aqueous droplets. The ratio between the two phases is a very important parameter in determining the structure of the resulting PolyHIPE (Jimat, 2011). The mixing processes puts the continuous phase in a low energy state creating a thin film between these droplets. Increased mixing times usually lead to a reduction in the pore size. During polymerization, the contraction that takes place in the oil phase leads to the formation of interconnecting pores as the pore walls are ruptured. New windows between the neighboring pores can be generated in the PolyHIPE by washing the samples in order to remove the aqueous phase, any surfactants and unreacted monomer.

In this study, sulphonated PolyHIPEs have been tested as ion exchangers for the removal of nickel (Ni^{2+}) from a standard solution. The PolyHIPEs were prepared from polystyrene because the phenyl groups act as active sites for sulphonation; the hydrophilic properties of PolyHIPEs can be controlled through the sulphonation process which takes place on these sites (Cameron, 2005). In situ sulphonation was achieved by the addition of sulphuric acid to the aqueous phase whilst post-sulphonation was also used to increase the concentration of Sulphur groups after polymerization.

2. Experimental Method

2.1. *PolyHIPE Preparation*

PolyHIPEs were prepared using a previously described method (Akay *et al*., 2005). Here, the aqueous phase consists of 1% potassium persulphate as a free radical initiator and 5% sulphuric acid in distilled water. The oil phase contains 76w/w% styrene monomer, 14w/w% divinylbenzene (DVB) crosslinker, and 10w/w% Sorbian monolete (Span 80), non-ionic surfactant with low hydrophilic-lipophilic balance. Both phases were added to a stirred tank under a stirrer speed of 300 rpm. The oil phase was initially added to the tank and thee aqueous phase was slowly added to the oil phase by using a peristaltic pump with 20rpm flow rate under conditions of continuous stirring. After the addition of the aqueous phase was complete the stirring continued for another different times (between ten and thirty minutes) to generate a stable emulsion with different droplet size. The emulsion formed was transferred to a 50 mL container (a falcon tube) with a diameter of 2.6 cm. Subsequently, the container was placed inside an oven and the temperature was increased to 60 °C to enable polymerization in a 12h period. Disc samples of 5-7 mm thickness were cut from the monolithic PolyHIPE and then washed with isopropanol by using a soxhlet. Then, they were dried on a paper towel overnight in a fume cupboard. For in-situ sulphonation samples these discs were cut into 1 cm beads to use for the filtration process. For the post-sulphonation process the disc samples were soaked in concentrated sulphuric acid (98%) for three hours before being transferred to the plate of a microwave oven. Samples were microwaved at 650W for 60 seconds, 30 seconds on each face. Finally, the soxhlet washing and drying processes were applied again to remove any unreacted acid.

2.1. *1.PolyHIPE Characterization*

In situ and post-sulphonated samples, synthesized with different mixing times (10, 15, 20, 25 and 30 minutes) were used to measure the water uptake by immersing them in water for 48 hours and measuring their weight gain.

The structure of the PolyHIPEs was observed with a Philips Field Emission Gun (FEG) scanning electron microscope and, in order to investigate the influence of sulphonation on the micropore size and distribution. The specific surface area as well as the nanopore size distribution were determined using the Brunauer-Emmet-Teller (BET) method in a Thermo Scientific Surfer.

The functional groups present in the samples were determined using a Fourier transform infrared spectrometer (Varian 800 FT-IR)

2.1. 2.*Ion Exchange Experiments*

Nickel Nitrate $Ni(NO_3)_{2.9}H_2O$ (Merck) was used to prepare the standard solution to generate the nickel ions. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used to control the pH. Copper solution??? Starting solutions with a total metal ion concentration of 20mg/l were used throughout.

The ion exchange experiments were carried out by using a tube 7 cm in diameter and 70 cm height filled with polyHIPE beads. A plastic disc with an opening of 1 cm diameter was placed at the lower part of the tube to retain the beads. A fixed volume of deionized water containing nickel and/or copper ions was recirculated through the filter bed for 8 hours using a peristaltic pump. In order to increase the contact time between water and PolyHIPE the flow of water was kept low (drop by drop) at all times by adjusting the inlet and outlet valves.

After the experiments the solution was filtered using a 0.2 micrometers microfilter to remove any eventual particles that resulted from the experiment (chiefly polyHIPE debris). The concentration of nickel or copper in the solution after the ion exchange experiments was measured using inductively-coupled plasma optical emission spectrometry (PerkinElmer Optima™ 7300 DV ICP-OES instrument). The concentration of anions in the solution was measured with a Dionex ICS-1000 ion chromatograph.

3. Results and Discussion

3.1 PolyHIPE characterization

3.1.1 SEM Analysis

The SEM images shown in Figure 1 confirm the existence of primary and secondary pores as well as their interconnectivity in the PolyHIPE structure. Smaller pores are observed in the walls of the larger pores. By comparing the two SEM images it can be concluded that post-sulphonation does not change the microstructure structure significantly. However, energy dispersive x-ray microanalysis in the SEM of similar areas shows that sulphur is present in both the in situ and post-sulphonated sampled but its concentration is greatly increased by the post sulphonation process. The original aim of the in situ sulphonation process was to reduce the number of process steps and hence the cost of the material and the question remains if this can be done without sacrificing performance.
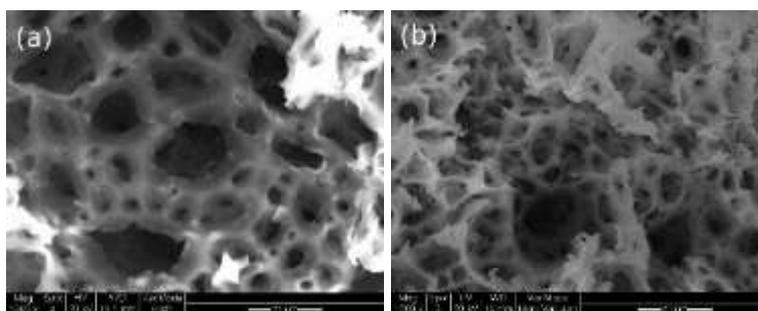
Figure 1. SEM images showing the pore structure of PolyHIPEs
(a) In situ sulphonated, (b) Post-sulphonated.

3.1.2 BET Measurements

Figure 2 show that the adsorption isotherm for in situ sulphonated polyHIPE after ten minutes mixing time is rapidly increasing which is related to macropores of large size, and there is no hysteresis in any isotherm due to the macropores being more significant than mesopores (Sing, 1985) in dictating behaviour. This agrees with the microstructure in SEM images as shown in Figure 1. The Surface area was measured from these curves and it was 9.96 m^2/g while pore size was 0.005 μm and Pore volume was 0.01 cm^2/g.
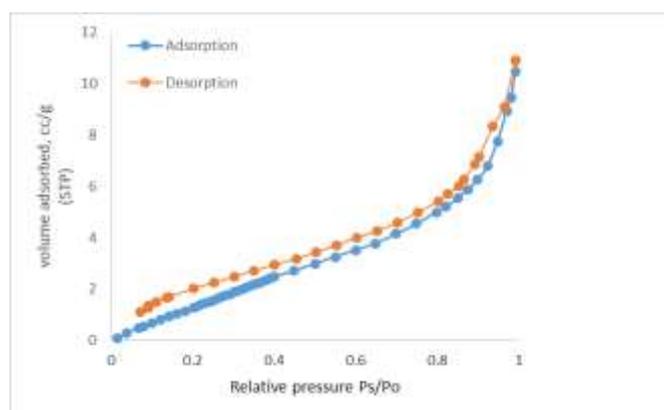

Figure 2. Isotherm plot for surface area and pore size analysis for PHP
sample produced with 10 (min) mixing time after in situ sulphonation.

The specific surface area increased from 9.96 m²/g for the in situ-sulphonated samples to 11.9 m²/g for the post-sulphonated ones while the average pore volume did not vary significantly: from 0.013 cm³/g for in situ-sulphonated to 0.015 cm³/g for post-sulphonated samples. These nanopores are in the surface of the micropore walls in Figure 1. There was no significant variation in the nanopore size with mixing time.

3.1.3 FTIR Analysis

The FTIR analysis shows that the sulphonation processes have been able to introduce Sulphur functionality into the polyHIPE (Figures 3 and 4). The groups that appear around 1150cm^{-1} are due (S=O) stretching. The (S=O) stretching peaks for post sulphonated PolyHIPE are much higher intensity than the samples with in situ sulphonation. There are also aromatic groups arising from the styrene monomer in the structure which provide the attachment points for the active SO$_3$H ion

exchange sites. Thus the benzesulphonic acid groups which are important for ion exchange are present in this material.
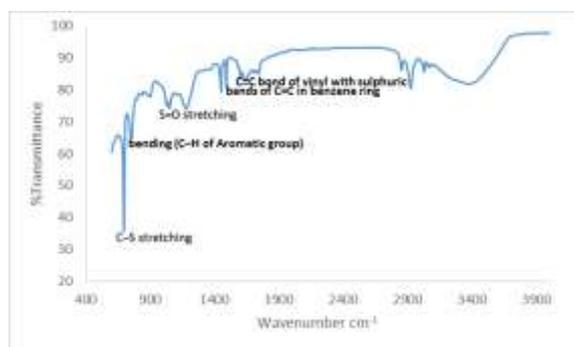

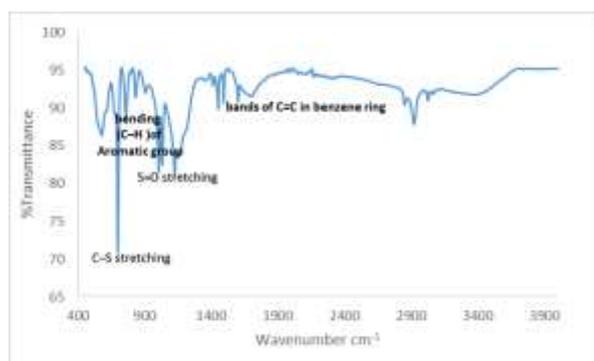**Figure 3.** FTIR spectrum for the PolyHIPE with 10 minutes mixing time with in situ sulphonation.

Figure 4. FTIR spectrum for the PolyHIPE with 10 minutes mixing time after post sulphonation.

3.1.4 Water uptake

Given the higher degree of sulphonation, the water uptake was higher for the post-sulphonated samples as shown in Figure 5. The in situ sulphonated material is not completely hydrophobic so will absorb water but the water penetration is slower and more unreliable than the post-sulphonated material.
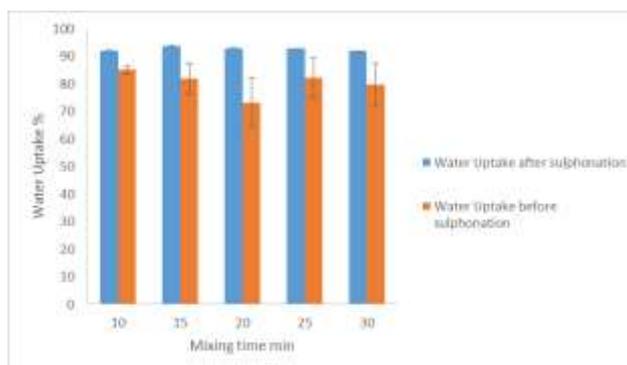

Figure 5. Water uptake measurements.

3.2 Filtration studies

Since there was little difference in structure with mixing time for any samples filtration studies were undertaken with 10min stirring time samples Only post-sulphonated samples were used due to the increased Sulphur uptake and the higher number of potential ion exchange sites for filtration.

Samples were exposed to a solution containing 20mg/l metal ions for 8 hours and the change in metal ion concentration in the solution was determined by ICP and the metal accumulated in the solid determined was determined by XRF.

Two different trial solutions were initially analysed:
1. 20mg/l nickel solution
2. 20mg/l copper solution

3.2.1 Metal take-up Analysis
3.2.1.1. Nickel
ICP studies indicate that most of the nickel was removed from solution – solution concentration reduced to 1 or 2mg/l from the 20mg/l standard. X-ray fluorescence measurement was done to determine the concentration of nickel in the solid beads from a trial experiment. Standard samples with known concentration were used calibrate concentration – the reliability of these standards is a significant source of error which is about 25%. In one sample there was 0.26±0.06 mg of nickel in the PolyHIPE sample demonstrating that the material has acted as an absorber. However, there was 1mg nickel in the starting solution so the measurement does not represent the complete loss of metal from the solution. This could be due to variations in nickel concentration in the analysis volume as well as experimental error. Using the solid accumulation measured in the beads is not sufficiently accurate to judge the performance of the polyHIPE.

3.2.1.2 Copper
In the filtration process 50ml of copper solution with 20mg/l was used. The ICP test shows that the majority of copper is bound with the PolyHIPE beads after the sulphonation process with little or no copper remaining in solution. X-ray fluorescence analysis was done to measure the concentration of copper in the solid beads. The results indicate there is 1.44 mg of copper in the PolyHIPE sample, this supports the ICP results which show that most of the copper is bound with the beads. The amount of copper in the sample is greater than the total amount in the solution (1mg) probably due to a combination of experimental error and other sources of copper contamination

Given the errors in analysis of the solid samples the change in solution ion concentration measured by ICP has been used to judge the efficiency of the filtration process.

3.2.2 Removal Efficiency
The removal efficiency was calculated after filtration by using PolyHIPE beads after post-sulphonation with three solutions containing (Ni^{+2} (20mg/l), Cu^{+2} (20 mg/l) and (Ni^{+2} (10mg/l) + Cu^{+2} (10 mg/l)) respectively. Each system will be discussed in individual sections where the removal efficiency was calculated according to equation 1 below.

$$\text{Removal efficiency } RI(\%) = \frac{c_i - c_f}{c_i} x 100\% \qquad (1)$$

c_i: - Initial concentration of metal (mg/l)

c_f: - Final concentration of metal (mg/l).

Three experiments were done for each concentration.

3.2.2 Nickel Removal Efficiency

The nickel removal efficiency increases with the pH of the solution as shown in Figure 6. This may be due to a reduced competition between H^+ and the active sites (SO_3H) groups which are available in the PolyHIPE structure.   Changing the pH of the solution can also lead to the formation of new compounds such as nickel hydroxide which is generated at pH 8.2 (Gupta et al., 2003). Therefore, a small removal efficiency increase after pH 8 is observed.

The interaction mechanism between Benzenesulfonic acid groups and nickel follows equation 2 and 3 (Cheremisinoff, 2001). The best removal efficiency was at pH 8 (0.83) but this was still above the acceptable limit specified by the world Health Organization which is about 0.07 mg/l (Edition, 2011).
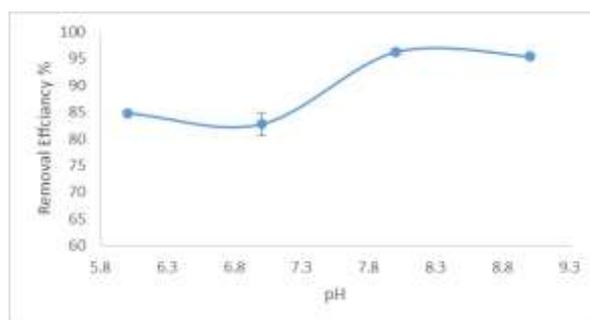
$$2(R - SO_3H) + NiSO_4 \rightarrow (R - SO_3)2Ni + H_2SO_4$$

(2)

$$NR - SO_3H + M^{n+} \rightarrow (R - SO_3)n\, M^{n+} + nH^+$$
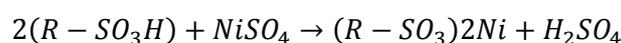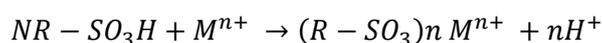
(3)

Figure 6. Nickel removal efficiency function of the pH of the solution.
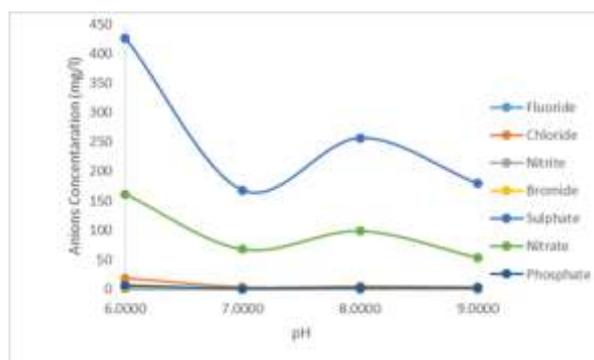

Figure 7. The concentration of anions in the solution after ion exchange.

The concentration of anions in the filtered solution was measured using ion chromatography as a function of the pH of the solution is shown in Figure 7. Sulphate ions are released from the sulphonated polyHIPE at low pH. The concentration of nitrate ions from the standard nickel solution does not vary very much with pH and other ion concentrations are minimal.

3.2.3 Copper Removal Efficiency

The removal of copper by post-sulphonated polyHIPE follows the mechanism shown in equations 2 and 3, in that Benzenesulfonic acid replaces two hydrogen ions (H^+) with copper ions. However, from Figure it can be seen that, the removal efficiency increases with increasing pH and the maximum value was at pH 9 where it reaches values specified by the World Health Organization acceptable concentration Guideline value which is (2mg/l) (Edition, 2011). In the pH range 6.2 to 6.8 copper hydroxide (Cu (OH)$_2$) starts to form (Vengris et al., 2001). Therefore, the removal efficiency decreases above pH 7. The high removal efficiency at pH 9 might be due an insufficient amount of copper in solution for precipitation processes (Arai, 2008, Eick and Fendorf, 1998, Rajapaksha et al., 2012). However, there are enough free ions in the solution to participate in the ion exchange process.
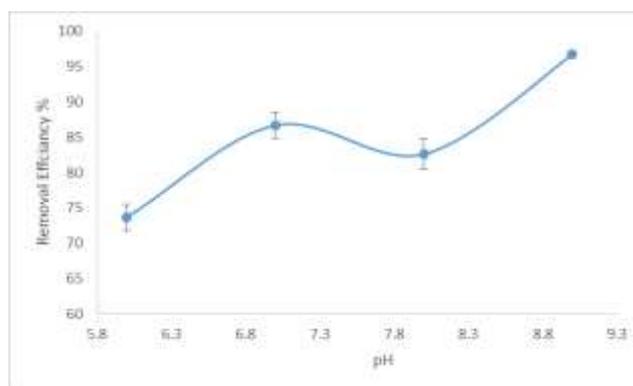

Figure 8. Removal efficiency of copper with pH

3.2.4. Binary System Removal Efficiency

In this experiment both nickel and copper ions were in the solution before filtration and the ratio was 50/50 for each one (10mg/l Ni $^{2+}$ and 10 mg/l Cu^{2+}). The removal efficiency behaviour of the two metals is shown in figure 9 and follows approximately the behaviours as the same single metal ion system when the concentrations of these metals was 20 mg/l as shown in figure 6 and figure 8, except at pH 8 when the removal efficiency for nickel is at minimum value instead of constant in the single system which may be attributed to the formation of cooper hydroxide at pH between 6.2 and 6.8, which is less than the pH required to form nickel hydroxide (pH=8.2) (Vengris et al., 2001, Gupta et al., 2003). This copper hydroxide may act as barrier between nickel and the active sites. At pH higher than 8 and close to 9.5 the amount of nickel and copper in solution may not be enough for the precipitation processes, because the precipitation process required a certain minimum concentration of metal in the water to occur (Arai, 2008, Eick and Fendorf, 1998, Rajapaksha et al., 2012, Gupta et al., 2003, Ismail et al., 2012). Thus there were more free ions in the solution which participate in the ion exchange process leading to an increase of the removal efficiency.
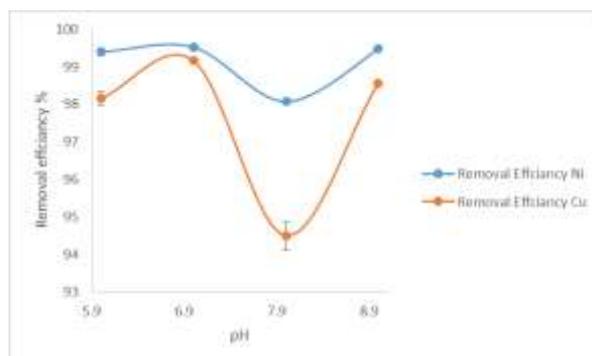
Figure 9. Removal efficiency of copper and nickel in a binary system with pH.

3.3. Regeneration

The regeneration process was done for the three systems nickel, copper and the binary system investigate the ability to recover the metals from the absorber by using solutions with different pH values.

3.3.1. Nickel Regeneration

Three different aqueous solutions with different pH (1, 5, and 11) were used to regenerate the PolyHIPE beads after the nickel filtration process. Cation concentrations were measured by ICP whilst anion concentrations were measured by the ICS-1000 (Ion Chromatography System) in the solution after regeneration. The results show that the anion concentration is below the assessable limit specified by the world health organization guideline. The sulphate which came from unreacted sulphuric acid during the sulphonation process and nitrate that came from nickel nitrate which was used to prepare nickel standard solution remain at the same concentration after regeneration. However, only a small amount of nickel was recovered during regeneration. Figure shows that, with solution pH 5 the highest amount of nickel was recovered from the PolyHIPE which was about 0.5 mg/l but it is still a low value compare with the estimated value if all nickel in the bead is removed which is approximately 16.5 mg/l.
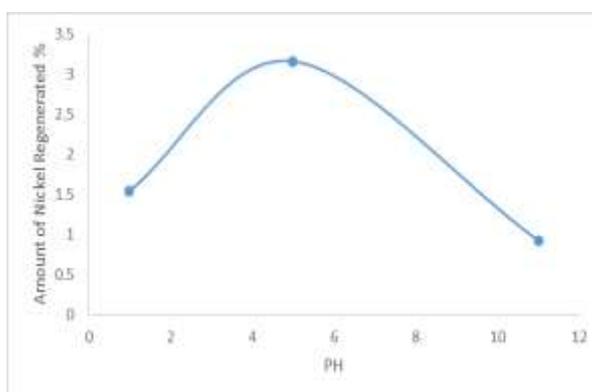

Figure 10. The ratio of nickel which is removed during regeneration compared to the initial nickel concentration for PolyHIPE beads at different pH

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3.3.2. Copper Regeneration

Regeneration experiments for copper were done using solutions with different pH values (3 and 11) than was used to recover the nickel from PolyHIPE beads after filtration. The amount of copper in solution regenerated at high pH is higher than at low pH (Table 1) but it is still very low compared with the amount copper inside PolyHIPE beads which if it were all to be removed would be about 16.50 mg/l when the initial concentration for the copper before filtration was 20 mg/l.

Table 1. The concentrations of copper in (mg/l) after regeneration
with high and low pH solution.

Sample pH	C.Cu before filtration	C.Cu after regeneration
3	20	1.069+_1.07
11	20	0.288-+0.24

As with Nickel there is not much copper removal from the PolyHIPE during regeneration so this would suggest it is only suitable for a single use filter. An alternative method to extract copper from the PolyHIPE needs to be developed.

3.3.3. Binary System (Nickel and Copper) Regeneration

The regeneration process for the PolyHIPE beads after filtration was done by using solutions with different pH values (11 and 3), and because the initial concentration for both metals was less than single system which is (10 mg/l) the amount of nickel and copper which is recovered from the beads was less as well as shown in table 2, and is still a low value compared with the initial concentration of the metals.

Table 2. The concentrations of nickel and copper in (mg/l) after regeneration with high and low pH solution for the binary system.

Sample pH	C. before filtration	C.After regeneration for nickel	C.After regeneration for copper
3	20	0.1575-$^+$0.05	0.011 +-0.006
11	20	0.165+- 0.06	0.022+- 0.01

Although nickel is preferentially removed from the PolyHIPE the amount removed is small so this method of recovery is not suitable to extract the metal from the PolyHIPE and the filter would be single use as stated previously.

4. Conclusions

The polyHIPEs produced at low stirring times have larger interconnected pores and as a result they have higher water uptake capability.

Sulphonated polyHIPEs show good removal efficiency for Nickel and copper from a standard solution. The removal efficiency increases with the pH up to a value of pH=8 then it sharply increased due to the formation of metal hydroxides. At lower pH there is greater release of sulphate from the sulphonated polyHIPE. Thus these materials are most suitable for ion exchange filtration if the pH can be controlled at 8.

Acknowledgment

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