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Chemically modified cellulosic adsorbent for divalent cations removal from aqueous solutions

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ABSTRACT

Conversion of cellulosic wastes to valuable industrial product was achieved by one-step bleaching and grafting methacrylic acid onto cellulosic wastes using sodium chlorite/potassium permanganate redox system. The obtained polymethacrylic acid/cellulose graft copolymer (PMAAC) was used as an adsorbent for different divalent cations. The experimental activities include studying the factors affecting the adsorption process, like adsorption duration, pH of the adsorbate solution, material/liquor ratio, temperature of the adsorption medium and graft yield of the graft copolymer used as an adsorbent. The results obtained indicate that the optimum conditions for metal adsorption were, using PMAAC with graft yield of 100% in an M/L ratio 1:400, at initial pH 7 keeping the temperature constant at 50 °C for 60 minutes. At these optimum conditions, PMAAC could be used to remove divalent cations such as Cu^{2+}, Co^{2+}, and Ni^{2+} from wastewater with removal efficiency of about 250 mg per one gram PMAAC graft copolymer.

1. Introduction

Grafting of synthetic polymers onto biopolymers results in novel products having wide range of applications. This way of chemical modification yields new molecules with desirable properties of both biopolymer and synthetic polymer. Modern technologies require materials with precisely tuned properties by varying a set of parameters during synthesis, i.e. tailor-made materials (Abdel-Halim & Al-Deyab, 2011a, 2011b; Abdel-Halim, Fahmy, & Fouda, 2008; Abdel-Halim, El-Rafie, & Kohler, 2008; Abdel-Halim, Abdel-Mohdy, Al-Deyab, & El-Newehy, 2010; Abdel-Halim, Fouda, Hamdy, Abdel-Mohdy, & El-Sawy, 2010; Abdel-Halim, Abdel-Mohdy, et al., 2011; Abdel-Mohdy, Abdel-Halim, Abu-Ayana, & El-Sawy, 2009; Fahmy & Abdel-Halim, 2010; Hebeish, El-Rafie, Abdel-Mohdy, Abdel-Halim, & Emam, 2010). Grafted polymers fit well in this category of materials as their properties can be precisely controlled by controlling the percentage grafting. Chemical grafting is one of the most effective methods of modifying structure and properties of biopolymers. Graft copolymerization of natural polysaccharides is becoming an important resource for developing advanced materials as it can improve the functional properties of natural polysaccharides (Abdel-Halim, Emam, & El-Rafie, 2008; Abdel-Halim, El-Rafie, et al., 2011; Chen et al., 2005; Joshi & Sinha, 2007; Ly et al., 2010; Meshram, Patil, Mhaske, & Thorat, 2009; Rui-He et al., 2006; Szamel, Domjan, Klebert, & Pukanszky, 2008; Zhu, Dong, Wang, & Wang, 2010). The grafted polymers are usually synthesized by conventional redox grafting methods (da Silva, de Paula, & Feitosa, 2007; Hebeish, Abd El-Thalouth, El-Kashouti, & Abdel-Fattah, 2003; Kaith, Singha, & Kalia, 2007; Kang, Cai, & Liu, 2006; Singh, Tiwari, & Sanghi, 2005), by microwave irradiation (Kaith et al., 2007; Masuhiro, Shafiul, Takayuki, Alessandra, & Giuliano, 2005; Singh, Tiwari, Pandey, & Singh, 2007), by γ-ray irradiation (Geresh et al., 2004; Wang, Chen, Zhang, & Yu, 2008; Xu, Yang, Jiang, Sun, & Pang, 2008) or by using electron beam (Vahdat, Bahrami, Ansari, & Ziaie, 2007).

The use of low-cost adsorbents has been investigated as a replacement for costly current methods. Natural materials or vast products from certain industries with a high capacity for heavy metals can be obtained, employed, and disposed of with little cost. Heavy metals are often discharged by a number of industries, such as metal plating facilities, mining operations and tanneries; this can lead to the contamination of freshwater and marine environment (Abdel-Halim & Al-Deyab, 2011c; Aguado, Arsuaga, Arencibia, Lindo, & Gascón, 2009). Heavy metals are not biodegradable and can lead to accumulation in living organisms, causing various diseases and disorders (Ju et al., 2009). It is well known that some metals are harmful to life, such as antimony, chromium, copper, lead, manganese, mercury, cadmium, etc., they are significantly toxic to human being and ecological environments (Mohan & Sreelakshmi, 2008). Numerous techniques are available for water purification and metal recovery operations from wastewaters. Many of these

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are established methods, while others are still in the experimental stage. Generally, the techniques employed for heavy metal removal include precipitation, ion exchange, adsorption, filtration, electrodeposition and reverse osmosis (Miretzky, Saralegui, & Cirelli, 2006). Precipitation methods are particularly reliable but require large settling tanks. The precipitation of voluminous alkaline sludge and a subsequent treatment is needed. Ion exchange has the advantage of allowing the recovery of metallic ions, but it is expensive and sophisticated. Adsorption on solid–solution interface is an important means for controlling the extent of pollution due to heavy metal ions. The above mentioned techniques are used to concentrate waste streams and remove the heavy metals. Activated carbon is effective in reducing hexavalent chromium, mercury and many metals complexed by organic legends. Similarly, various ion-exchange resins have been found to be effective in removing metal ions from solution. Interest has arisen recently in removing heavy metals from solution by binding with agricultural cellulosic wastes such as, nut wastes, tree barks, modified cotton and sawdust. Many agricultural and industrial byproducts have little or no economic value, and some, such as short fibers from jute waste processing, and sawdust, which are produced in large quantities, are often present a disposal problem. If these byproducts could be used as adsorbents, contaminated water streams would be cleaned, and a new market would be opened for these byproducts (Vinodh, Padmavathi, & Sangeetha, 2011). The use of activated carbon and ion exchange resins is not suitable for developing countries due to their high capital and operational costs (Cao, Tan, Che, & Xin, 2010). This has encouraged researchers into discovering materials that are both efficient and cheap. Interest has recently arisen in the investigation of some unconventional methods and low cost materials for scavenging heavy metal ions from industrial wastewaters (Abdel-Halim & Al-Deyab, 2011d; Abdel-Halim, Abou-Okeil, & Hashem, 2006; Hashem, Abdel-Halim, & Hebeish, 2005; Hashem, Sokkar, Abdel-Halim, Gamal, 2005; Hashem, Abdel-Halim, & Sokker, 2007; Hashem et al., 2007b; Sokkar, Abdel-Halim, Aly, & Hashem, 2004). In general, an adsorbent can be assumed as "low cost" if it requires little processing, is abundant in nature, or is a by-product or waste material from industry (Demirbas, 2008; Liang, Guo, Feng, & Tian, 2010). Some of the reported low-cost adsorbents include bark, tannin-rich materials, lignin, chitin, chitosan, peat moss, modified wool and cotton. Insoluble starch xanthates have been found to be very useful to remove heavy metal ions from solutions (Aziz, Adlan, & Ariffin, 2008; Xia et al., 2010). Agricultural waste materials such as spent grain (Argun, Dursun, Ozdemir, & Karatas, 2007), polymerized onion skin (Coşkun, Soykan, & Saçakj, 2006), rice husks (Duran, Soylak, & Tuncel, 2008), bark and sawdust (Afkhami, Saber-Tehrani, & Bagheri, 2010; Bhattacharyya & Gupta, 2008; Jang, Seo, & Bishop, 2005; Ngah & Hanafiah, 2008;Yu, Zhang, Shukla, Shukla, & Dorris, 2001), maize cobs (Tofighy & Mohammadi, 2011) and wheat bran (Song, Oh, Kong, & Jang, 2011) have been studied to investigate their affectivities in binding heavy metal ions. The adsorption of heavy metals by these materials might be attributed to their proteins, carbohydrates or phenolic compounds which have carboxyl, hydroxyl, sulfate, phosphate and amino groups that can bind metal ions.

The aim of this work is to report the efficiency of modified cellulosic wastes in removal of toxic heavy metal ions, like Zn(II), Co(II) and Ni(II) from their aqueous solutions.

2. Experimental

2.1. Materials and chemicals

Cotton fabric wastes were collected from tailoring workshops and subjected to cutting and shredding processes. Sodium chlorite, copper sulfate, nickel nitrate, cobalt nitrate, sodium hydroxide, sodium carbonate, sodium bicarbonate, sodium thiosulfate, potassium permanganate, potassium iodide, methacrylic acid and sulfuric acid were all laboratory grade reagents. Non-ionic wetting agent, Nonidet LE was supplied by Shell Textile Chemicals, Cairo, Egypt.

2.2. Bleaching and grafting methacrylic acid onto cotton fabric wastes

Polymethacrylic acid/cellulosic waste (PMAAC) graft copolymer was prepared according to reported methods (Abdel-Halim, Emam, & El-Rafie, 2008; Abdel-Halim, Konczewicz, Zimniewska, Al-Deyab, El-Newehy). Unless otherwise indicated, treatment of the cellulosic wastes with $KMnO_4$ and grafting of the so treated wastes with methacrylic acid (MAA) were carried out as described below.

2.2.1. Treatment with $KMnO_4$

The cellulosic wastes were impregnated in an aqueous solution containing a specific concentration of $KMnO_4$ and 2 g/l nonionic wetting agent. The treatment was carried out at 50 °C for 15 min using a material to liquor ratio of 1:50 with continuous shaking to avoid the heterogeneity of MnO_2 deposition on the fiber surface. After treatment the cellulosic waste was thoroughly washed with water squeezed before immersing in the polymerization solution.

2.2.2. Polymerization

The so obtained $KMnO_4$-treated cellulosic waste was introduced in a l00 ml-stoppered conical flask containing an aqueous solution of methacrylic acid and sodium chlorite. Material to liquor ratio of 1:50 was used. The grafting reaction was carried out at different temperatures for different time intervals and at the end of the polymerization reaction, the grafted cellulosic waste sample was removed, thoroughly washed with boiling water followed by cold water, and finally dried at 105 °C for 3 h. The total conversion percentage (T.C.) of methacrylic acid to polymethacrylic acid (grafted and homopolymer) was determined via estimation of residual double bonds. Percentage graft yield (G.Y.) was calculated as follows:

$$\%\text{G.Y.} = \frac{W_2 - W_1}{W_1} \times 100$$

where W_1 is the dry weight of original sample and W_2 is the dry weight of the grafted sample. The homopolymer percent ($H\%$) and graft efficiency (%G.E.) were determined by mathematical calculations based on the total conversion and the graft yield percent.

2.3. Adsorption experiments

For metal adsorption experiments, copper sulfate, nickel nitrate and cobalt nitrate were used. The metal ion solutions were prepared by dissolving 1 g of each salt in 1 l of distilled water. (PMAAC) samples (1 g each) were introduced into stoppard Erlenmeyer flasks together with the metal salt solutions at different material to liquor ratios. The flasks were fixed in a temperature-controlled shaking water bath and the adsorption experiments were carried out at different temperatures for different time intervals. At the end of experiment, the (PMAAC) was removed by filtration. The extent of heavy metal adsorption was estimated by measuring the metal concentration in the filtrate by atomic absorption.

2.4. Testing and analysis

2.4.1. Carboxyl content

Carboxyl contents of bleached cellulosic waste and polymethacrylic acid/cellulosic waste (PMAAC) graft copolymer were

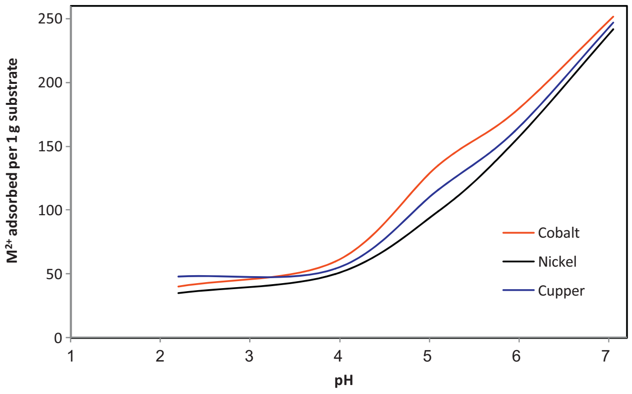


Fig. 1. Effect of initial pH on the extent of metal ion adsorption onto PMAAC.

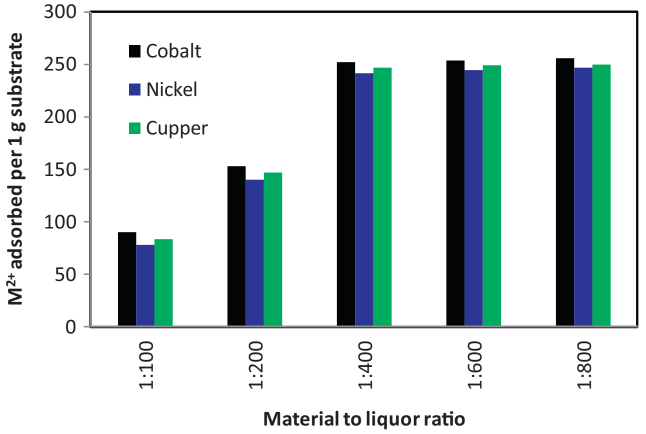


Fig. 2. Effect of material to liquor ratio on the extent of metal ion adsorption onto PMAAC.

measured according to the following reported method (Mattisson & Legendre, 1952).

2.4.2. *Determination of residual metal cations*

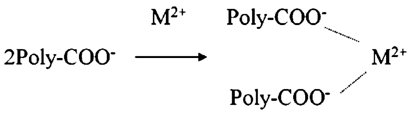
Estimation of residual metal cations after adsorption experiments was carried out using a high-resolution continuum source atomic absorption spectrometer (HR-CSAAS), ContrAA700, Analytik Jena AG (Jena, Germany).

3. Results and discussion

3.1. *Effect of initial pH*

Initial pH is one of the most important factors that affect the adsorption process. It affects not only the surface charge of the adsorbent, but also the ionization degree of the adsorbate. Fig. 1 shows the effect of pH of aqueous copper sulfate, cobalt nitrate and nickel nitrate on the extent of Cu^{2+}, Co^{2+} and Ni^{2+} ions removal, expressed in mg M^{2+}/1 g PMAAC (100% grafted cellulosic waste). As is evident the pH determines the magnitude of the adsorption capacity. The adsorption capacity increases by raising the pH of the adsorption medium and the uptake reaches maximum values 247 mg Cu^{2+}, 252 mg Co^{2+}, and 242 mg Ni^{2+} per 1 g PMAAC at pH 7. pH values in the alkaline range were of course not suitable for the adsorption processes, this is because the metal hydroxide is precipitated in the alkaline range. At pH values less than 7 the percent removal decreases continuously until it reaches almost 50 mg M^{2+}/1 g PMAAC at pH 2. The first stage of ion exchange is deprotonation of the carboxylic group of the graft copolymer which is represented by Eq. (1), while Eq. (2) represents the attachment of the metal cation to the reactive carboxylate anion. The low percent removal at pH 2 can be attributed to the fact that at pH $\leq$ 2, the high concentration of H^+ in the adsorption medium shifts the equilibrium in Eq. (1) to the left direction. This means that the carboxyl groups do not ionize and the ion exchange sites on the surface of PMAAC are still protonated. Under such conditions the metal ions do not exchange and remain in the solution. As the pH value increases from 2 to 7, the deprotonation equilibrium in Eq. (1) is shifted to right and as a result, the adsorption capacity increases according to Eq. (2) until it reaches its maximum value at pH 7.

$$\text{Polymer-COOH} \longrightarrow \text{Polymer-COO}^- \qquad (1)$$



$$2\text{Poly-COO}^- \xrightarrow{M^{2+}} \begin{matrix}\text{Poly-COO}^- \\ \text{Poly-COO}^-\end{matrix}\!\!>\! M^{2+} \qquad (2)$$

3.2. *Effect of M/L ratio*

Fig. 2 shows the effect of adding different volumes of Cu^{2+}, Co^{2+}, and Ni^{2+} solutions at pH 7 to 1 g PMAAC. M/L ratios used were varied from 1:100 to 1:800 and the effect of varying material to liquor ratio on the adsorption capacity of PMAAC was evaluated. Treatment was carried out at 50 °C for 1 h using PMAAC with graft yield 100%. The data indicates that the maximum adsorption of metal ions is obtained on using material to liquor ratio of 1:400. Further increase in the M/L ratio above 1:400 is accompanied by marginal increase in the amount of adsorbed metal ions. This behavior could be attributed to the available carboxyl groups in 1 g of 100% grafted PMAAC. This amount of carboxyl groups is just enough to bind to certain amount of metal ions. After these carboxyl groups are fully reacted with metal ions any excess metal ions due to the increased liquor will not be adsorbed since the adsorbent has the same carboxyl content.

3.3. *Effect of adsorption medium temperature*

Figs. 3–5 show the effect of temperature on the adsorption capacity of PMAAC for Ni^{2+}, Cu^{2+} and Co^{2+} ions, respectively, from their solutions. It is clear that, regardless of the temperature and the metal ion solution used, increasing the duration up to 20 min is accompanied by significant enhancement in the amount of M^{2+} ions removed from their aqueous solutions and then prolonging the duration is accompanied by little increments in the metal ion removal. It is also seen that raising the temperature from 30 °C

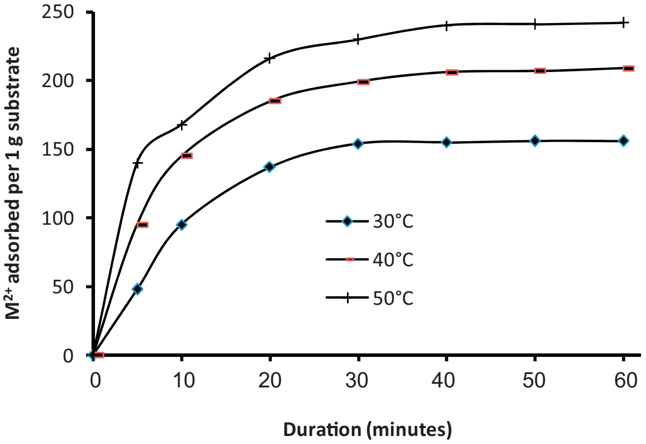


Fig. 3. Effect of temperature on the extent of nickel ion adsorption onto PMAAC.

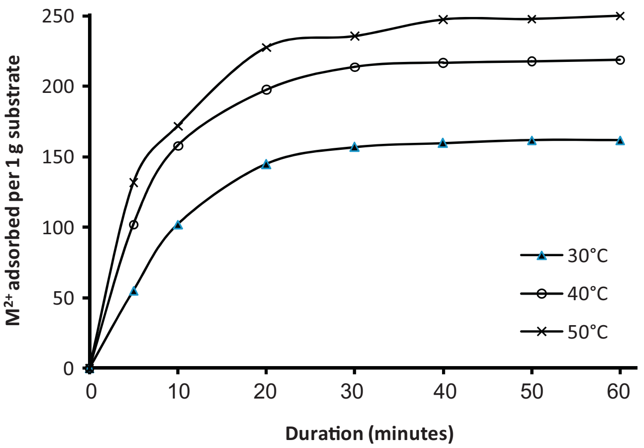


Fig. 4. Effect of temperature on the extent of cupper ion adsorption onto PMAAC.

to 50 °C is accompanied by significant increase in the amount of M^{2+} ions adsorption. It is understandable that the increment in the metal ion adsorption is attributed to the favorable effect of the temperature on the swellability of the grafted cellulosic waste and accordingly there will be increase in the diffusion and penetration of M^{2+} ions from the aqueous phase to the PMAAC phase. Also as the temperature increases, the metal ions acquire more kinetic energy and there will be chance for more diffusion into the fiber phase and reaction with the exchangeable sites in the grafted cellulosic waste fiber.

3.4. *Effect of agitation time*

Fig. 6 shows the effect of agitation time on the adsorption capacity of M^{2+} by PMMAC at fixed pH 7, temperature 50 °C and at metal ion concentrations of 1000 mg/l, using a material to liquor ratio of 1:400. Time taken for the adsorption process to attain thermodynamic equilibrium is very important in characterization and prediction of both the efficiency and the feasibility of an adsorbent for its use in water pollution control. The effect of agitation time was studied for only one adsorbate concentrations 1000 mg/l. Fig. 6 shows that irrespective of the type of metal ion to be adsorbed, the percent M^{2+} removal increases sharply with increasing agitation time up to 20 min, and then it increases very slowly and becomes almost constant after 50 min. The almost constant percent removal after 50 min means that monolayer of the adsorbate was formed on the surface of adsorbent and thermodynamic equilibrium is attained at that extent.

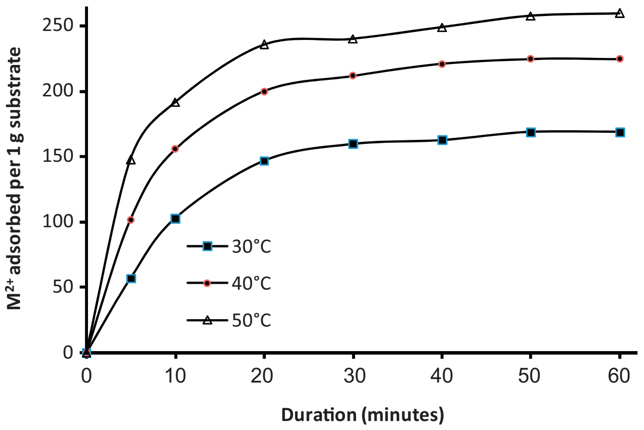


Fig. 5. Effect of temperature on the extent of cobalt ion adsorption onto PMAAC.

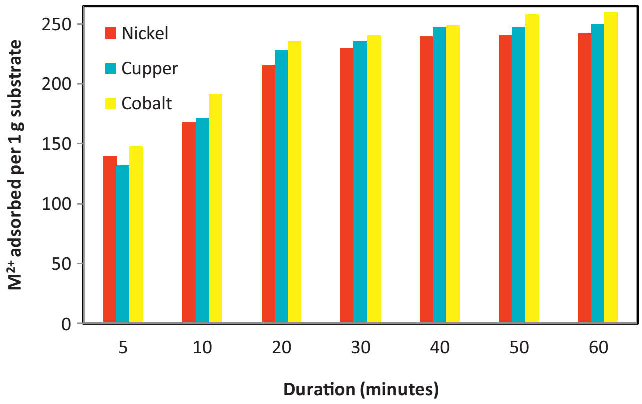


Fig. 6. Effect of agitation time on the extent of metal ion adsorption onto PMAAC.

3.5. *Effect of graft yield*

Fig. 7 shows the effect of graft yield percent, i.e. the available carboxyl groups in PMAAC graft copolymer, on the adsorption capacity of the metal ions. The data indicates that ungrafted cellulosic waste fiber adsorbs about 30 mg M^{2+} per 1 g bleached cellulosic waste (0% graft yield). This significant amount of adsorbed metal ions on the surface of cellulosic waste fiber without any graft yield reflects the effect of the carboxyl content of the bleached cellulosic waste (100 m equiv. carboxyl/100 g cellulosic waste) on its affinity to metal ion adsorption, whatever the carboxyl groups come from the grafted methacrylic acid or come from the oxidation of cellulosic component of cellulosic waste during the bleaching process. The amount of the adsorbed metal ions increases by increasing the graft yield percent until it reaches its maximum amount at graft yield of 100% then, at graft yield higher than 100%, namely, 120% and 140%, the amount of adsorbed metal ion decreases by increasing the % graft yield. The increase in adsorption capacity of the graft copolymer by increasing the graft yield up to 100% is understood because increasing the polymethacrylic acid component in PMAAC will increase the carboxyl content of the modified fiber and this means increase in the active sites available for ion-exchange or adsorption. The unexpected decrease in adsorption capacity upon increasing the graft yield above 100% could be explained in terms of the very compact structure of graft copolymer having graft yield higher than 100% which makes the copolymer less swollen and accordingly decreases the diffusion of the metal ion from the solution phase into the fiber phase.

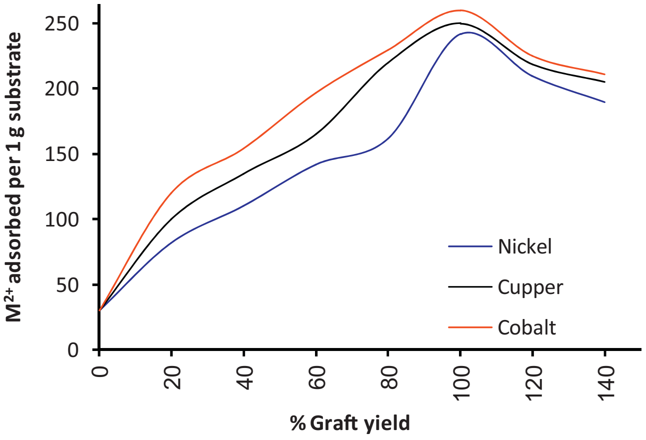


Fig. 7. Effect of material to liquor ratio on the extent of metal ion adsorption onto PMAAC.

4. Conclusion

Cellulosic fabric waste was subjected to one-step bleaching and grafting copolymerization with methacrylic acid. Sodium chlorite/potassium permanganate redox system was used to simultaneously bleach the cellulosic waste fiber, and initiate graft copolymerization of methacrylic acid onto the fiber. This economical one-step treatment has converted low-value cellulosic fabric processing wastes to valuable industrial product. The polymerization reaction was monitored by following the percent total monomer conversion during the reaction course and then, at the end of polymerization, the graft yield was calculated on dry bases. The so-obtained graft copolymer was used as adsorbent for different divalent heavy metal. The experimental activities include studying the factors affecting the adsorption process, adsorption duration, pH of the adsorbate solution, material to liquor ratio, temperature of the adsorption medium, agitation time and graft yield of the graft copolymer used as an adsorbent. The adsorption efficiency of the graft copolymer was evaluated by measuring the concentration of the adsorbate solution before and after the adsorption process via atomic absorption. The results obtained indicate that the optimum conditions for metal adsorption were, using methacrylic acid grafted cellulosic waste with graft yield of 100% in a material to liquor ratio 1:400, at initial pH 7 keeping the temperature constant at 50 °C for 60 min. At these optimum conditions, PMAAC could be used to remove divalent cations such as Cu^{2+}, Co^{2+}, and Ni^{2+} from wastewater with removal efficiency of about 250 mg per 1 g PMAAC graft copolymer.

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