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Egypt. J. Chem. **Vol. 64,** No. 6 pp. 3077 - 3085 (2021)

Egyptian Journal of Chemistry

Impact of Crosslinking Degree on Structure, Swelling Behaviour and Heavy Metals Uptake of Polyacrylate/Kaolin Hydrogel Composite

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Abstract

Polyacrylate/kaolin hydrogel composite was prepared via ultrasonic irradiation using various crosslinking agent contents (N, N'-Methylenebisacrylamide (MBA)) and characterized using X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and Brunauer Emmett and Teller (BET) method. Moreover, heavy metals adsorption was investigated using synthetic solutions and industrial wastewater (single and mixed elements) in both lab-scale batch and pilot-scale continuous modes. Results indicated that 0.3 wt% MBA is the optimum content regarding structure, swelling behavior and single element batch adsorption results. Batch tests revealed adsorption capacities of 75, 33, 38 and 96 mg/g for Cr, Co, Ni and Pb, respectively from mixed solutions. It is inferred that mixed synthetic solutions and industrial wastewater have lower adsorption capacities than single solutions, where Pb attained the highest performance. Pilot-scale continuous adsorption for mixed synthetic solutions in a fluidized bed column revealed that 24 h cycle time is appropriate for Cr and Pb removal while 48 h is optimum for Co and Ni. Sulphuric acid revealed the best desorption efficiencies which lie in the order of Co > Ni >Pb >>Cr. According to these results, the developed hydrogel composite is reliable for heavy metals uptake under different adsorption modes.

Keywords: polyacrylate composite; crosslinking degree; heavy metals; adsorption/desorption; industrial wastewater

1. Introduction

Heavy metal ions cause serious environmental and health problems, even at trace levels. Various conventional treatment approaches for heavy metals removal include chemical precipitation [1], ion exchange [2], adsorption [3], flocculation [4], electrolysis [5], electrocoagulation [6] and membrane filtration [7]. Adsorption technique is considered highly effective and widely used for heavy metals removal [8]. Natural and synthetic hydrogel adsorbents, especially acrylic based hydrogels [9], have recently attracted special attention for removing heavy metal ions due to the multiple functional groups, insignificant toxicity and hydrophilic nature. Hydrogels could be prepared using conventional heating, microwave, ultraviolet and ultrasonic irradiation techniques [10–12]. Ultrasonic technique is an effective method for the preparation of hydrogel due to the generation of free radicals and activation of free radical initiators [13]. Composite clay hydrogels have been successfully used as good adsorbents for heavy metal ions due to higher surface area, chemical and mechanical stability in addition to availability and relatively low cost [14,15]. For example, novel superabsorbent bentonite/acrylic acid composite was prepared and used for Pb, Ni, Cd and Cu adsorption [16–18]; montmorillonite/ polyacrylamide and poly acrylic acid composite hydrogel [19] in addition to poly acrylic acid bentonite composites [20] for Cu and Fe adsorption. Chemical crosslinking is a highly useful method to modify mechanical, thermal and chemical resistance of hydrogels [21,22]. Different crosslinking agents were used in hydrogel preparation including; N, N'-Methylenebisacrylamide (MBA) [23], formaldehyde, acetaldehyde and glutaraldehyde [24], kaolin [25], alumina nanoparticles [26], hallyosite [27] and allyl sorbitor, mannitor pentaerythritor [28]. MBA has been one of the most commonly efficient investigated crosslinking agents. Effect of its content, was

investigated regarding the hydrogel swelling behavior [29–32] and heavy metals removal [19,33].

In this study, polyacrylate/kaolin hydrogel composite (AKHg) samples were prepared using ultrasonic irradiation technique using different crosslinking agent (MBA) contents and thoroughly characterized. The adsorption performance of single and mixed Cr, Cd, Ni and Pb ions from synthetic solutions and industrial wastewater was also investigated using lab-scale batch and pilot-scale column modes, in addition to desorption experiments with different acids.

2. Experimental

2.1. Materials

Acrylic acid (AA) with molecular weight 72.06 g/gmol was supplied from Research Lab-Egypt; potassium persulfate (KPS) initiator was supplied from Merck-Germany; N, N'-Methylenebisacrylamide (MBA) crosslinking agent was supplied from Fluka-Germany and Sodium dodecyl sulfate (SDS) anionic surfactant was supplied from Merck. Investigated heavy metal ions' salts used for the preparation of their synthetic solutions include $CoCl_2$ (Shantou Guanghua Chemical Factory Co., Ltd), $Cr(NO_3)_3.6H_2O$ (PRS Panareac Quimica Sa), $NiCl_2.6H_2O$ (S.d.fine-chem Ltd.) and Pb acetate were used. Other chemicals used include sodium hydroxide pellets, sodium carbonate, oxalic acid, hydrochloric acid 35% and sodium chloride (Modern Lab- Egypt) were also used. Raw kaolin was delivered from (Abu Zeneima- Egypt) [34]. Industrial wastewater samples were collected from Tenth of Ramadan disposal facility (Cairo, Egypt) after onsite treatment and preserved at pH 4.

2.2. Methods

2.2.1. Preparation of polyacrylate/ kaolin hydrogel composite using different crosslinking agent degrees/contents

The polyacrylate/kaolin hydrogel composite samples (AKHg) were prepared using ultrasonic irradiation technique as previously described by the authors [35]. Briefly, partially neutralized AA was mixed with 0.3 wt% MBA, KPS, SDS and acid washed kaolin at 40°C in distilled water under nitrogen atmosphere. The mixture was then heated to 70°C in an ultrasound water bath (Tru-sweep cleaner, Crest Ultasonics Cor, USA) until gelation occurs. The produced hydrogel was washed with acetic acid before drying at 60°C.

In this study, the effect of MBA content (wt%) on the preparation of AKHg was studied at various

MBA contents (0.1-0.7) wt%. Accordingly, four samples were prepared, namely; AKHg0.1, AKHg0.3, AKHg0.5 and AKHg0.7 where the number represents the MBA wt%.

2.2.2. Characterization

The structure of the prepared hydrogels was characterized via X-Ray Diffraction (XRD) technique using Philips X-Ray Diffraction equipment PW/1710 with Monochrom TOR, Cu-radiation at 40 K.V., 35 mA and scanning speed 0.02°/sec. In addition, Fourier transform infrared spectroscopy (FTIR) was performed using FT/IR-6100 type A Jasco Japan TGS detector with the absorbance ranging from 500 to 4000 cm^{-1} with scanning speed of 2 mm/s. The surface morphology of the prepared hydrogel samples was studied using a scanning electron microscope (SEM) model QUANTA FEG 250. BET surface area and mean pore size of the prepared hydrogels were evaluated using BelSorb Max apparatus (MicrotracBel. Corp.).

2.2.3. Swelling water ratio (SWR)

Dry hydrogel was soaked in distilled water (1g/L) for 24 h at pH values (5 and 7), approaching the adsorption pH range, then it was filtered using a plastic strainer to remove the excess water. The swollen hydrogel was weighed before and after swelling. SWR (g/g) has been calculated by the following equation [10]:

$$SWR = \frac{W_s - W_d}{W_d} \qquad (1)$$

Where, W_s and W_d are the weights of the swollen and dry samples, respectively. SWR was calculated as grams of absorbed water per grams of dry hydrogel.

2.2.4. Batch adsorption

Adsorption using batch mode was conducted by adding each of the prepared AKHg samples with particle size below 850 μm to the tested single element (non-competitive) or mixed elements (competitive) heavy metal containing solution in 250 ml flask. Adsorption was undertaken for 24 h at 25°C, pH 4-7 and initial concentrations 86-100 mg/L as previously depicted by the authors [35]. The flasks were sealed and constantly shaken using a water bath shaker (Julabo, SW-20C) with a constant agitation rate of 150 rpm. The supernatant was filtered using a Whatman filter paper no. 44 and then, analyzed to

determine the residual concentrations of Cr, Ni, Co and Pb using an atomic absorption flame spectrometer (GBC Avanta). pH and conductivity were measured using HANNA apparatus model-211. The adsorption capacity (q) was calculated using the following equation [36,37]:

$$q = \frac{Co - Ce}{m} \times V \qquad (2)$$

Where, q is the amount of metal ions adsorbed in (mg/g of dry adsorbent), Co and Ce are the initial and equilibrium ion concentrations (mg/L), respectively; V is the volume of metal ions solution used (L), and m is the weight of dry adsorbent (g).

Moreover, industrial wastewater was investigated for batch adsorption using AKHg prepared at the optimum MBA wt%, which was selected based on the characteristics and the performance of the prepared composites towards non-competitive batch adsorption experiments.

2.2.5. Column adsorption studies (pilot-scale)

Continuous adsorption experiments using hydrogel composites were rarely discussed in literature and was only investigated in small scale columns with 30 cm length and 2-12 mm width and solution flowrates 2-20 ml/min [33,38].

In this study, Continuous adsorption experiments for mixed elements (competitive) synthetic solutions containing Cr, Co, Ni and Pb were tested with initial concentrations of 86-100 mg/L using a pilot-scale adsorption system which was previously described by the authors [39], as shown in Figure 1. The system mainly consists of a perspex fluidized bed adsorption column with 15 cm diameter and 55 cm height, 25-50 L tanks and feed & wash pumps. It is equipped with piping, valves, cartridge filter, pressure gauges, frequency converters, pH sensors and flow meters. Experiments were undertaken using 150 g of the optimum AKHg sample, contained in a net, at pH 5, 25°C and at flowrate of 1 L/min with cycle time of 6 days. Samples were taken periodically for heavy metals analysis.

Fig. 1. Photo of pilot-scale adsorption system using the fluidized bed column

2.2.6. Desorption studies

The reuse of adsorbents helps to minimize the cost of the adsorption process. After adsorption, the adsorbent was filtered, washed, dried and experiments for heavy metals elution from the hydrogel were undertaken using different acids: H_2SO_4, H_3PO_4, HNO_3 and HCl. Desorption experiments were performed at pH 4-4.5 for 3 days duration at 40°C in triplicates and the mean values are presented.

3. Results and Discussion

3.1. Characteristics of the prepared polyacrylate hydrogel composites: AKHg

3.1.1. XRD Patterns

XRD patterns for the prepared AKHg at different MBA wt% are shown in Figure 2. It is clear that the kaolin original structure is retained in the hydrogel, where its main characteristic peak (at 2 theta of 27°) is obvious in all the composite samples with lower intensities due to the composite formation. It is clear that increasing the crosslinking agent content has increased the intensity of this peak. It is also noticed that a broad peak at 2 theta of 18°-25° is present in all types which may be attributed to the amorphous nature of the acrylic acid which is considered the main component of this hydrogel.
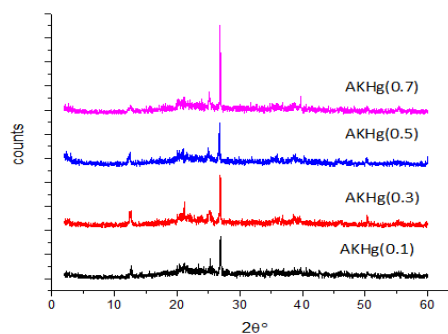

Fig.2. XRD patterns of AKHg at different MBA wt%

3.1.2. FTIR spectra

The FTIR spectra of AKHg at different MBA wt% are depicted in Figure 3. The absorption peak at 3419 cm^{-1} is corresponding to –OH stretching. The absorbance at 2927 cm^{-1} is assigned to C-H stretching of the acrylate group. The peak within 1722-1625 cm^{-1} are assigned to C=O stretching of the acrylate groups [40]. The absorption peak at 1722 cm^{-1} could be attributed to the ester groups formed during graft polymerization. The carboxylic groups of the grafted

poly(acrylic acid) can react with the –OH groups on the kaolin surface [41]. The replacement of the –OH groups on the surface of kaolin by carboxylic ones results in ester formation [30,32]. The change of MBA content has no effect on FTIR analysis of the kaolin composite hydrogels where the main bands of AA and kaolin exist at different intensities in the formed composites. The absence of some peaks and appearance of others in the FTIR spectrum of grafted hydrogel samples were attributed to the formation of crosslinking at these bands region.

3.1.3. SEM images

The SEM images of AKHg at different MBA wt% are shown in Figure 4. It is obvious that increasing the MBA degree causes morphological changes where the composite becomes less smooth and less dense.
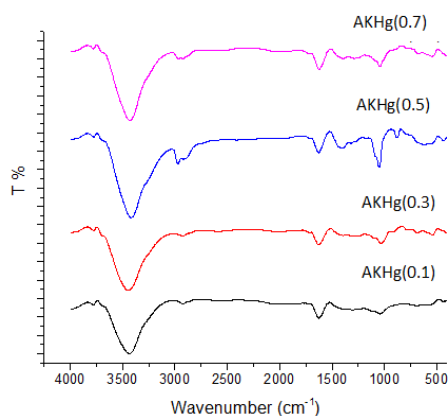
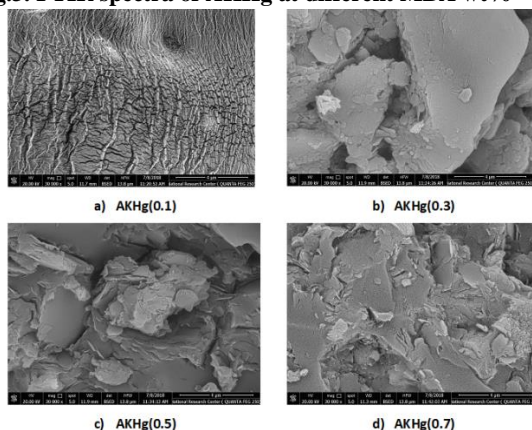

Fig.3. FTIR spectra of AKHg at different MBA wt%

Fig. 4. SEM images of AKHg at different MBA wt%

3.1.4. Porosity measurements

N$_2$ adsorption/desorption isotherms for AKHg are presented in Figure 5. Adsorptive nitrogen was used at 25°C, vacuum degree before measurement

was 7.55E^{-4} Pa and standard vapor pressure was 108 kPa. The isotherm obtained for all samples exhibited, according to the IUPAC classification, hysteresis loops which are the characteristic feature of the mesoporous materials (type IV isotherm), which agree with He et al. [18]. The desorption cycle of the isotherm showed a hysteresis loop which is attributed to the capillary condensation occurring in the mesopores for type IV isotherm. The shape of hysteresis loops is identified with the specific pore shape. All samples exhibited H2 type of hysteresis loop and corresponds to the pores with ink bottle shape [42].
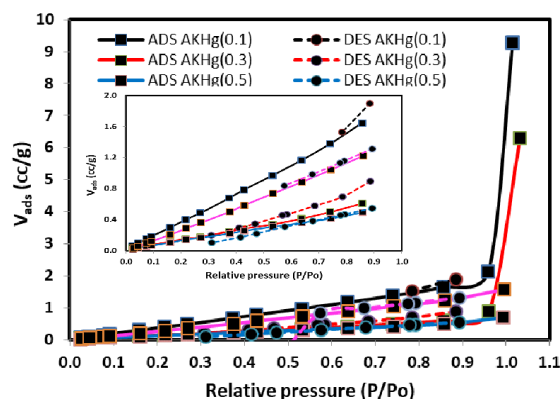

Fig.5. N$_2$ adsorption/desorption curves for AKHg at different MBA wt%

The textural properties of the synthesized AKHg samples have been summarized in Table 1. The results indicated that increasing the crosslinking agent content leads to decreasing the mean pore diameter (MPD) from 14 to 4.4 nm, BET surface area (SA) from 2.7 to 0.5 m^2/g and total pore volume (TPV) from 9.4E^{-03} to 2.4e^{-03} cm^3/g. The BET surface area results agree with He et al. [33] who recorded a surface area of 2 m^2/g for sodium acrylate acrylamide copolymer hydrogel and higher values were obtained (5.9 to 16.3 m^2/g) for polyacrylate bentonite[18].

Empirical correlations representing the relationship between mean pore diameter (MPD), BET surface area (SA) and total Pore volume (TPV) with MBA wt % were formulated with R^2= 98-99%. These equations are listed as follows:

$$MPD = 3.4 \ MBA^{0.6} \quad\quad\quad (3)$$

$$SA = 0.4 \ MBA^{0.83} \quad\quad\quad (4)$$

$$TPV = 0.013 - 0.04 \ MBA + 0.037 \ MBA^2 \quad (5)$$

Table 1.
Textural properties of AKHg at different MBA wt%

Adsorbent	Textural properties		
	MPD (nm)	BET (m^2/g)	TPV (cm^3/g)
AKHg (0.1)	14.04	2.68	9.4E^{-03}
AKHg (0.3)	6.5	1.08	4.84E^{-03}
AKHg (0.5)	5.2	0.81	1.06E^{-03}
AKHg (0.7)	4.4	0.49	2.41E^{-03}

3.2. Swelling behaviour

Swelling water ratio (SWR) for the prepared AKHg at different MBA degrees investigated at two different pH values are shown in Figure 6. It is clear that by increasing the MBA wt%, SWR values decreases and this may be attributed to the generation of more crosslinkage points causing the formation of additional network and decreasing the available free volume in the formed hydrogel composite [25]. SWR values at pH 5 were higher than those at pH 7 only at 0.1% and highly comparable for 0.3%-0.7%. Where at 0.1% MBA and pH 5 SWR approached 85 g/g while, it was 58 at pH 7. Atia et al. achieved comparable SWR of 95 for kaolinite polyacrylic acid-co-acrylamide hydrogels[43].
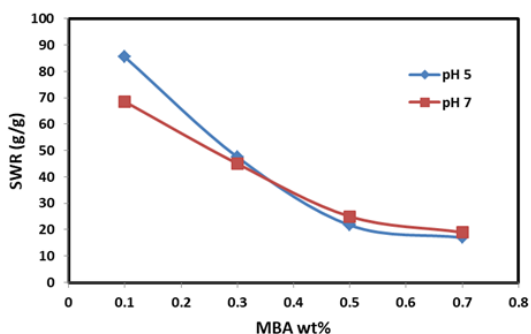

Fig. 6. Effect of MBA wt% content on SWR for AKHg

3.3. Batch adsorption studies

3.3.1. Effect of MBA on heavy metals adsorption

The effect of MBA content on the adsorption capacity of Cr, Co, Ni and Pb from their single (non-competitive) synthetic solutions is shown in Figure 7. It is clear that increasing the MBA content leads to slight increase in adsorption capacities of Co (from 75.4 mg/g to 86 mg/g) and Ni (from 73 mg/g to 79 mg/g). A higher increase is noticed for Pb adsorption

capacity at MBA content from 0.1 to 0.3% (from 69.6 mg/g to 99.9 mg/g) reaching a plateau afterwards. On the contrary, increasing MBA from 0.1 to 0.3% leads to decrease in Cr adsorption capacity (from 91 mg/g to 60 mg/g). These results partially agree with Natkanski et al. who revealed the decrease of the adsorption capacity of Cu and Fe onto polyacrylamide polyacrylic acid montmorillonite composite due to the increase of MBA content from 1% to 5% [19] and He et al 2016 who showed the increase of Pb and cd adsorption capacity by increasing MBA wt% from 0.2% to 0.8% then it decreased after that [33].

Results indicated that 0.3% MBA could be selected as the optimum wt% for further investigations in the following sections.
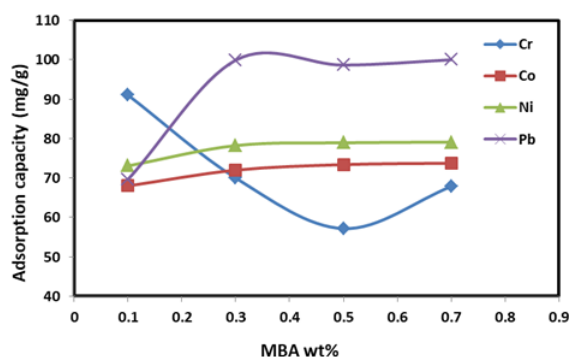

Fig. 7. Effect of MBA wt% on the adsorption capacity of heavy metals onto AKHg

3.3.2. Adsorption of synthetic solutions and industrial wastewater

Analysis of industrial wastewater sample is presented in Table 2. The composition of industrial wastewater was considered not representative due to fluctuating along the day and some adsorption occurred by the sludge after treatment at the disposal facility. Accordingly, it was enriched with the investigated heavy metals, up to their equivalent concentrations in synthetic solutions, to imitate the actual industrial wastes.

Table 2.
Analysis of industrial wastewater

	Concentration (mg/L)
Cr	-
Co	-
Ni	0.56
Pb	1.6
Ca	97.1
Mg	32.8
COD	420
BOD	165

Accordingly, batch adsorption experiments were conducted using the optimum conditions on synthetic solutions and industrial wastewater as follows:

- Single element synthetic solutions
- Plain industrial wastewater
- Single element enriched industrial wastewater
- Mixed elements synthetic solutions
- Mixed elements enriched industrial wastewater.

Adsorption experiments conducted on plain industrial waste water resulted in 100% removal of Ni and Pb with adsorption capacities oh 0.56 mg/g and 1.6 mg/g, respectively. Adsorption capacity of heavy metals from single and mixed synthetic and enriched industrial wastewaters onto the optimum selected composite is presented in Figure 8. Adsorption capacity in single enriched industrial wastewater is considered higher in case of Cr by 50% to reach 91 mg/g (99.3%removal), comparable in case of Pb >99 mg/g and >99% removal. It was lower in case of Co by 31% to reach 58 mg/g (63% removal) and Ni by 40% to reach 46 mg/g (54% removal).

Regarding mixed heavy metals solution, adsorption capacities for mixed solutions are comparable (±4-8%) with average values for Ni (36 mg/g, 42% removal) and Pb (98 mg/g, 98% removal). On the other hand, Cr removal from enriched industrial wastewater showed 10% increase than synthetic wastewater to reach 83 mg/g (91% removal) while, Co showed decrease by 17% to reach 28 mg/g (30% removal). These values are higher than those obtained by Sezgin et al. for the removal of Cu, Ni, Zn and Cr from galvanotechnic wastewater using polyacrylic acid hydrogel and lower than those reported by Zhou et al for Pb and Cd adsorption from smelting plants [38,44].

It is obvious that mixed element synthetic solutions and industrial wastewater have lower adsorption capacities than single element solutions. Also, the composition of the industrial wastewater hindered the heavy metals adsorption, except for Cr. It is worth mention that adsorption capacities of Pb in all tested solutions attained high comparable values.
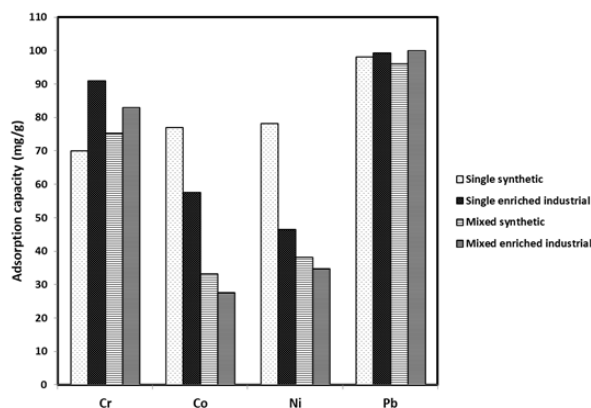

Fig. 8. Adsorption capacity of heavy metals from synthetic solutions and enriched industrial wastewater onto the optimum AKHg

3.4. Continuous adsorption on pilot-scale set-up

3.4.1. Column performance

Results of pilot-scale adsorption experiments using AKHg are presented in Figure 9 where the initial concentrations of Cr, Co, Ni and Pb in the mixed element solution (pH 5) were 86-100 mg/L. Results depict time dependence of effluent concentrations where a sharp decrease in the concentrations was observed in the first 10 h (45, 22, 24 and 69% removal for Cr, Co, Ni and Pb, respectively). The corresponding values after 24 h were 84, 38, 41 and 99%. The concentrations decline decreased to a large extent after 24 hours where it reached after 48 h 95, 49, 53 and 97% removal and after 6 days 98, 55, 60 and 100% removal for Cr, Co, Ni and Pb, respectively. Accordingly, 24 h could be a proper time for sufficient Cr and Pb removal in continuous adsorption, while 48 h could be more appropriate for Co and Ni removal. These results are comparable with those reported by Zhou et al for Pb and Cd adsorption from smelting plants using polyampholytic hydrogel [38].

3.4.2. Desorption

Desorption efficiencies of heavy metals adsorbed on the composite in column operation were evaluated using different acids and presented in Figure 10. It is clear that H_2SO_4 was the most efficient acid for desorption at after 3 days at 40°C. The highest obtained desorption efficiency was obtained for Co (11.5%). Desorption efficiencies are in the order Co > Ni >Pb >>Cr.

Different acids were investigated for heavy metals desorption from polyacrylate hydrogels with

high efficiency [16,18,33,45]. Further experiments are still needed to improve the current desorption efficiencies.
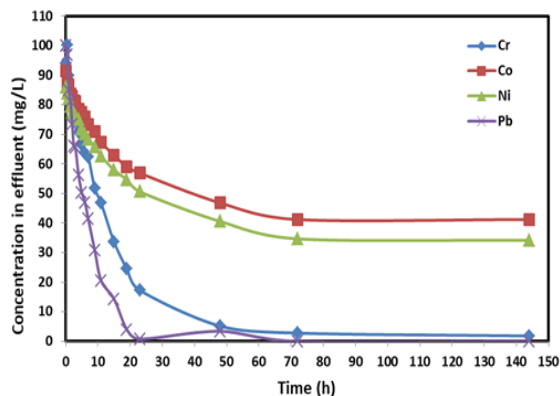

Fig. 9. Variation of heavy metals concentrations in effluent during column operation
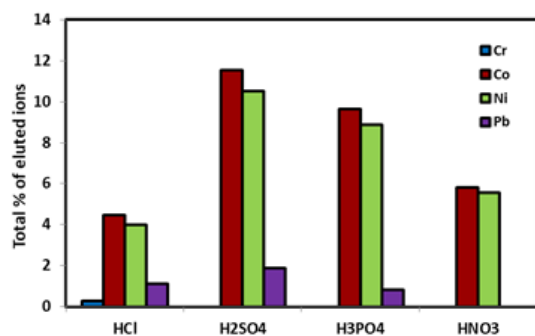

Fig. 10. Desorption efficiency of heavy metals adsorbed on the optimum AKHg

4. Conclusion

Polyacrylate/kaolin hydrogel composite was prepared with different MBA wt%. Increasing the MBA above 0.3% had no significant effect on the product specifications or performance. Accordingly, 0.3% was selected as the optimum crosslinking wt % for preparation of AKHg.

Adsorption capacity in single enriched industrial wastewater is considered higher than synthetic solutions in case of Cr, comparable in case of Pb and lower in case of Co and Ni. It is concluded that mixed synthetic element solutions and industrial wastewater have lower adsorption capacity than single element solutions. Results of pilot-scale column adsorption experiments explored under continuous operation for 6 days revealed that 24 h could be a proper time for sufficient Cr and Pb removal (84% and 99%, respectively), while 48 h could be more appropriate for Co and Ni (49, 53 removal%). Desorption studies were undertaken

using different acids reaching 11.5% Co desorption using H_2SO_4. Acids could be arranged in the order of their desorption efficiency as follows: $H_2SO_4 > H_3PO_4 > HNO_3 > HCl$.

5. Conflicts of interest

"There are no conflicts to declare".

6. Acknowledgments

7. References

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تأثير درجة التشابك على التركيب والانتفاخ وادمصاص المعادن الثقيلة لمتراكب بولي أكريلات / الكاولين هيدروجيل

تم تحضير متراكب بولي أكريلات / الكاولين هيدروجيل عن طريق التشعيع بالموجات فوق الصوتية باستخدام عامل التشابك (MBA) بكميات مختلفه وتم تحديد الخصائص باستخدام حيود الأشعة السينية ، والتحليل الطيفي للأشعة تحت الحمراء ، والمسح المجهري الإلكتروني ، وطريقة Brunauer Emmett and Teller (BET). علاوة على ذلك ، تم فحص ادمصاص المعادن الثقيلة باستخدام المحاليل الاصطناعية ومياه الصرف الصناعي (عناصر مفردة ومختلطة) في كل من نظام الدُفعات على نطاق المختبر والأنماط المستمرة على نطاق تجريبي. أشارت النتائج إلى أن 0.3٪ MBA هي المحتوى الأمثل فيما يتعلق بالتركيب والانتفاخ ونتائج الادمصاص بنظام الدفعة للعناصر منفرده. أظهرت التجارب بنظام الدفعة قدرات امتصاص 75 ، 33 ، 38 ، 96 ملجم / جم لكل من Cr، Co، Ni، Pb ، على التوالي من المحاليل المختلطة. يُستنتج أن المحاليل التركيبية المختلطة ومياه الصرف الصناعي تتمتع بقدرات ادمصاص أقل من المحاليل الفردية ، حيث حقق الرصاص أعلى أداء. أظهر الادمصاص المستمر على نطاق نصف صناعي للمحاليل الاصطناعية المختلطة أن وقت الدورة 24 ساعة مناسب لإزالة Cr و Pb بينما 48 ساعة هو الأمثل لـ Co و Ni. كشف حمض الكبريتيك عن أفضل كفاءات استرجاع والتي تقع في ترتيب Co> Ni> Pb << Cr. وفقًا لهذه النتائج ، فإن مركب الهيدروجيل المطور يمكن الاعتماد عليه في ادمصاص المعادن الثقيلة في ظل أوضاع ادمصاص مختلفة.