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Modified Adsorbents Based on Glycidyl Methacrylate Copolymers for the Removal of Copper and Lead Ions from Wastewater

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Abstract

Pollution of water resources as a result of the discharge of industrial wastewater containing heavy metal ions is a serious problem in world practice. New ion exchange sorbents make it possible to solve two related problems at once: purification of industrial water from enterprises and regulation of the content of toxicants in the environment. This study is focused on the synthesis and use of modified glycidyl methacrylate copolymers as an adsorbent, providing the greatest selectivity among the heavy metal ions required for effective adsorption. A comprehensive characterization and analysis of ion exchanger glycidyl methacrylate-acrylonitrile-polyethylenimine (GMA-ACN-PEI) was carried out using Fourier transform infrared spectroscopy (FTIR), determination of chemical stability, thermogravimetric analysis (TGA). Efficiency of sorption-selective abilities towards Cu (II) and Pb (II) ions were assessed using atomic adsorption spectroscopy methods. Removal efficiency was obtained to be 85.6% and 77.8% for Pb (II) and Cu (II) ions, respectively. To assess the influence of various factors on the adsorption process, periodic experiments were carried out, varying parameters such as temperature and curing time. Langmuir adsorption isotherm was found to be the best model to describe the effectiveness of the synthesized copolymer.

Keywords: Adsorbents, Glycidyl methacrylate copolymers; Copper; Lead.
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1. Introduction

Water pollution due to the discharge of industrial wastewater containing heavy metal ions is a serious global problem arising from various industrial activities such as mining, metal processing and chemical manufacturing. These activities release heavy metal ions into water bodies, posing serious environmental and health risks. To solve this heavy metal ions problem, the development of efficient and economical sorbents for water purification is critical. The use of such sorbents will not only help in the purification of industrial waters but also helps in mitigating the impact of heavy metal pollution on the environment. One promising contribution involves the synthesis and use of modified glycidyl methacrylate copolymers as adsorbents that provide high selectivity towards heavy metal ions and enable efficient adsorption.[1,2] These copolymers serve as chelating agents, effectively binding heavy metal ions and facilitating their removal from aqueous solutions, thereby helping to regulate the level of toxic substances in the environment.[3-5] In addition to glycidyl methacrylate copolymers, other materials such as diethylenetriamine-functionalized resins have demonstrated the ability to selectively adsorb specific heavy metal ions such as As (V) and Cd (II), which form a critical aspect of environmental protection.[6] These resins exhibit high affinity for target contaminants while exhibiting minimal interference

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from common coexisting ions, highlighting their potential for selective removal of specific heavy metal pollutants from wastewater.[7] This selectivity is critical to ensure the effectiveness of adsorption processes in water treatment.

Immobilization of azo dyes on poly(glycidyl methacrylate-comethyl methacrylate) polymers is also being investigated as a new approach to the development of adsorbents adapted for water purification. These innovative adsorbents offer a versatile solution to combatting the diverse range of contaminants found in industrial wastewater,[8,9] and by exploiting the unique properties of these composites, researchers aim to increase the adsorption capacity of heavy metals and dyes in wastewater, contributing to an overall improvement in water quality.[10,11]

The use of crop waste as a biosorbent for the selective removal and recovery of lead(II) from multimetal solutions highlights the importance of considering interactive effects between different metal ions in wastewater. Competitive binding of multiple metals in solution can affect the overall efficiency of the adsorption process, requiring a comprehensive understanding of the factors influencing the removal of metal ions from complex industrial wastewaters. This highlights the need for specific sorbents that can address the problems associated with different metal mixtures in wastewater streams.[12] The application of technologies such as Pickering emulsion polymerization has opened new possibilities for the synthesis of nanostructured materials capable of extracting heavy metal ions from wastewater. This environmentally friendly, water-based technology produces micron-sized beads with ligands that exhibit high affinity for heavy metal ions, offering a sustainable solution for wastewater treatment.[13] Such advances in materials synthesis offer great promise for improving the efficiency of heavy metal ion removal processes in industrial settings.

However, the limited range of polymer matrices and carriers capable of a wide class of polymer-analogous transformations (PATs) and immobilization of various complexing agents is a complicated situation for researchers. Research into the reactivity of alternative polymer matrices and supports based on three-dimensional copolymers of glycidyl methacrylate becomes relevant. Undoubtedly, the kinetic assessment in a wide temperature range of the reactivity of the epoxy groups of such copolymers in PAT reactions is also important for achieving maximum degrees of conversion and concentration of active groups in modification reactions with amine containing sorbents. The development of fibrous ion-exchange sorbents is also promising for the treatment of wastewater contaminated with radionuclides, heavy metal ions and organic pollutants. These specialized sorbents provide a versatile solution for removing a wide range of contaminants from water sources, helping to protect both aquatic ecosystems and human health. The effectiveness of sorption-selective abilities in relation to Cu(II) and Pb(II) ions was assessed using atomic adsorption spectroscopy methods, which are necessary for quantitative determination of the amount of metal ions adsorbed onto ion exchangers.[14-17] These analyses provide valuable information on the ability of ion exchangers to remove heavy metal ions from solution, which is critical for their potential application in water treatment and recovery processes.[18,19] By varying parameters such as pH and contact time, researchers can optimize the adsorption process to achieve maximum removal efficiency of Cu(II) and Pb(II) ions, which is important for the practical application of these ion exchangers for environmental remediation. The synthesis and characterization of nanocomposite ion exchangers have been extensively explored in the literature, particularly in the context of heavy metal removal.[20] The physicochemical properties of ion exchangers play a crucial role in their efficiency in adsorbing heavy metal ions, such as Cu(II) and Pb(II). Studies have shown that the characterization of ion exchangers using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and Brunauer-Emmett-Teller (BET) methods provide valuable insights into their structure and properties.[21] Furthermore, the ion exchange mechanism plays a critical role in the adsorption process of heavy metal ions by ion exchangers. Studies have proposed ion exchange mechanisms for various materials, indicating a stoichiometric exchange between ions in the interlayer spaces of the exchangers and metal ions in solution.[22] Understanding the ion exchange mechanisms is essential for elucidating the sorption behavior and selectivity of ion exchangers towards specific metal ions. In this experiment, an anionic exchanger was synthesized from GMA-co-ACN copolymer and polyethylenimines (PEI) by radical polymerization. The effects of mass ratio, curing time and temperature was studied in determining the optimum conditions for the correct application of the anionic exchanger. Furthermore, characterization by Fourier transform infrared spectroscopy (FTIR), Energy Dispersive X-ray Spectroscopy (EDX) integrated with the SEM system and thermogravimetric analysis (TGA) of the exchanger was analyzed. The chemical stability as well as the Cu (II) and Pb(II) adsorption properties of the adsorbent were also studied using the Langmuir and Freundlich adsorption models to predict the extent and strength of the adsorption.

2. Materials and methods

2.1 Materials and reagents

Dimethylformamide (DMF), glycidyl methacrylate (GMA), acrylonitrile (ACN), polyethylenimines (PEI), peroxybenzoyl, ethyl alcohol, sodium hydroxide (NaOH), hydrochloric acid (HCl), sulfuric acid (H_2SO_4), nitric acid (HNO_3), hydrogen peroxide (H_2O_2), potassium nitrate (KNO_3) and sulfate were all purchased from Sigma-Aldrich (Germany) and used without further purification.

2.2 Synthesis of double copolymers based on GMA and ACN

Copolymerization of GMA and ACN was carried out by the free radical method using a DMF as solvent and peroxybenzoyl as the initiator. The resulting double copolymer, a white gel-like mass, was repeatedly washed with DMF solvents and precipitated in ethyl alcohol, after which it was vacuum dried to a constant weight. The content of epoxy groups (EC, %) was determined using known methods as presented in Eq. 1 below:

$$EC = \frac{(V_1 - V_2)\times 0.0043\times K\times 100}{g} \quad (1)$$

where V_1 denotes the volume (mL) of 0.1 N NaOH solution used for titration of the blank sample; V_2 is the volume (mL) of 0.1 N NaOH solution used for titration of the as-prepared material; K represents the correction factor to the titer of 0.1 N NaOH solution while g denotes the weight (g) of the substance. The epoxy number (EN) of double copolymers GMA-ACN is = 23%

2.3 Synthesis of anion exchangers based on double copolymers GMA-ACN and PEI

Amination of cross-linked double copolymers of GMA with PEI was carried out in organic solvents. A sample of the amine was loaded into a three-neck flask equipped with a mechanical stirrer, a thermometer, and a dropping funnel. A solution of the copolymer in an organic solvent was gradually added in dropwise. The mixture was heated to 80 °C while under intensive stirring and a gel formation was carefully monitored. After gel formation, the polymerized material was unloaded into a porcelain cup, cured for 24 hours at 80-90 °C, crushed, sieved, and a fraction with a granule size of 0.25-1.00 mm was selected. The anion exchangers were repeatedly washed with water and extracted using a Soxhlet apparatus and ethanol to remove any unreacted substances, dried to constant weight under vacuum at 25-30 °C. The dried substance was then treated with 5% solutions of HCl and NaOH to neutralize its acidic and basic nature using DI water. The anion exchanger was labelled as GMA-ACN:PEI and the yield was calculated using Eq. 2. The static exchange capacity (SEC) is 0.1 N each and HCl solution 6.22 meq/g.

$$SEC = \frac{Total\ equivalent\ of\ ions\ exchaged}{mass\ of\ the\ material} \quad (2)$$

The schematic representation of the general synthesis procedure is presented in Fig. 1.

2.4 Characteristics of the adsorbent

2.4.1 Determination of mass ratio, temperature and curing duration of ion exchangers

To establish optimal conditions for the synthesis of cross-linked polyelectrolytes, the influence of the nature concentration of the reacting components, temperature and duration of curing on the ionic exchange properties of anion-exchange polymers was studied. To determine the optimum SEC of the resulting ion exchanger, various ratio of the copolymer: aminating agent was performed and the results analyzed. This was achieved by keeping a constant amount of the copolymer, and varying the amount of the aminating agent (PEI). The optimum ratio of the reacting components was determined by that which gave the highest SEC, and the influence of temperature and duration of curing on the properties of cross-linked polyelectrolytes was studied using the optimum ratio obtained.

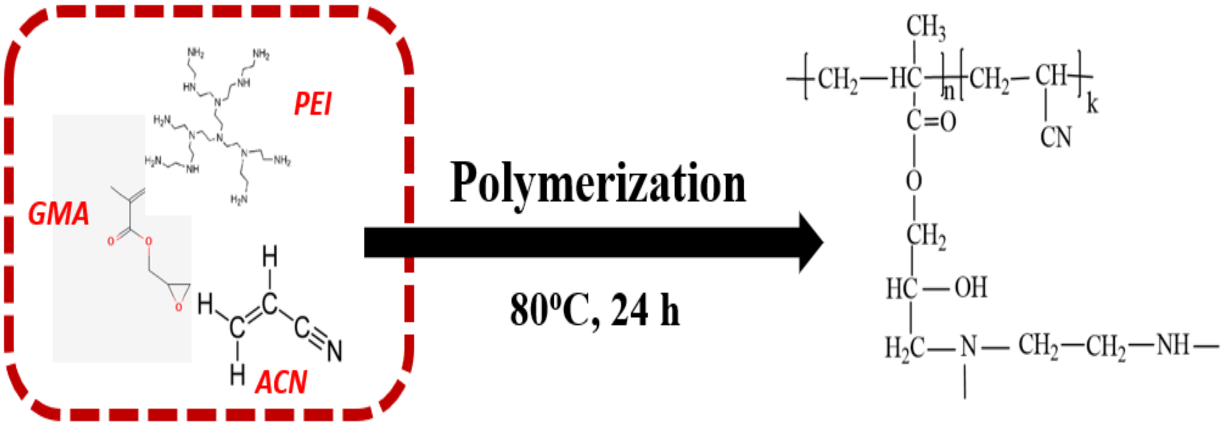

Fig. 1 Synthesis process scheme of GMA-ACN:PEI copolymer.

2.4.2 Determination of the chemical stability of ion exchangers

In relation to acids and alkalis solution, the chemical stability of ion exchangers was determined. Two weighed portions of the dry polymer material (0.1 g each) were placed in 250 mL round-bottomed flasks. One filled with 100 ml of a 5 N H_2SO_4 solution while the other with a 5 N NaOH solution. The contents of the flasks were kept for half an hour in a boiling water bath. The mixture was then cooled in air to room temperature, filtered and the filtrate separated from the ion exchanger, which was converted into OH^- form and the SEC was determined. The chemical resistance (Y, %) was calculated using Eq. 3 as presented below:

$$Y = \frac{E_1}{E_0} \times 100 \tag{3}$$

where E_0 and E_1 are SEC (meq/g) before and after contact with acid or alkali, respectively.

2.4.3 Determination of the chemical stability of polyelectrolytes in relation to oxidizing solutions

Regarding oxidizing solutions, the chemical stability of polyetrolytes was determined. In the determination process, 0.8 g of of the ion exchanger was mixed with 100 mL of 1 N solution of HNO_3 and H_2O_2 and kept at room temperature for two days with periodic stirring. The chemical stability was characterized by the ratio of SEC before and after treatment with an oxidizing solution.

2.4.4 Determination of swelling of ion exchangers

To measure the swelling capacity of the ion exchangers, a 3-5 g sample of the sorbent was placed in a measuring cylinder with a ground stopper and filled with the appropriate solvent. The cylinder was kept in a horizontal position for (2-3) days, then transferred to a vertical position and the level of the polymer in it was noted. The volume of the swollen sample was measured. The swelling capacity of the dry ion exchanger (Q, mL/g) was determined from the ratio of the volume of the swollen sample (V, mL/g) to the mass of the dry polymer (g, grams) as presented in the Eq. 4 below:

$$Q = \frac{V}{g} \tag{4}$$

2.4.5 Study of the sorption capacity of ion exchangers by ions metals

The complexing properties of ion exchangers were studied in relation to ions of Cu and Pb from solutions of the corresponding reagent grades, nitrate and sulfate salts. Before each series of experiment, polymer samples were dried in a vacuum oven to a constant weight. To determine the sorption capacity of ion exchangers, 0.1 g of the prepared polymer was weighed to the nearest 0.0002 g, placed in an Erlenmeyer flask with addition of 20 mL of a salt solution of the corresponding metal. The ionic strength of the solution was created by adding the calculated amount of dry sulfate and KNO_3. To determine the concentration of metal cations, the method of atomic adsorption capacity was used. The sorption capacity (SC, meq/g) of polymers was determined by Eq. 5:

$$SC = \frac{C_i - C_o}{W} \times V \tag{5}$$

where C_i represents the initial concentration (mg/L) of metal ions in solution; C_o denotes the final concentration (mg/L) of metal ions in solution; V is the total volume (mL) of solution and W represents the mass (g) of the synthesized polymer.

2.4.6 Characterization methods

The physical and chemical composition of the synthesized material was characterized by FTIR where infrared spectra were measured in the range 400-400 cm^{-1} at a scanning speed of 1 $cm^{-1}s^{-1}$ and a resolution of 4 cm^{-1} using Cary 600 FT-IR Spectrophotometer series (Agilent, Germany) coupled with an attenuated total reflection module. The porosity of the ion exchanger was analyzed using Scanning Electron Microscopy (SEM) with a SEM, ZEISS Crossbeam 540 instrument, allowing for high-resolution imaging of the surface morphology and microstructure. The SEM technique provided detailed insights into the pore distribution, shape, and size within the material, crucial for understanding the ion exchanger's functionality and its potential for applications. Additionally, elemental composition analysis was performed through Energy Dispersive X-ray Spectroscopy (EDX) integrated with the SEM system. The combined SEM-EDX analysis offered a comprehensive characterization of the material both before and after the sorption of metal ions, including elemental distribution, to better understand its performance in ion exchange processes. The compositions of the ion exchanger materials were determined by using both thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) technique. Thermal analysis carried out with a Thermal Analyzer (STA) 6000 in Nitrogen environment, heated from 30.00 °C to 800.00 °C at 10.00 °C/min.

3. Result and discussion

3.1 Study of the influence of various factors (mass ratio, temperature and duration) on the modification of the copolymer

The data on the effect of the ratio of the GMA-ACN copolymer: aminating agent (PEI) (mass parts) shows that the SEC of the resulting polymers increases in proportion to the increase in the content of PEI in the initial mixture until a plateau, where there is saturation. This results in a proportional increase in nitrogen content of the resulting polymer. From Fig. 2, the highest exchange capacity values are observed at a copolymer: PEI mass ratio of 1.0:6.0 parts. The output of ion exchanger was calculated to be 85% and the static exchange capacity by HCl solution (0.1 N) was 6.13 mEq/g at 100 °C with 12 hours curing time. This ratio proved to be the optimum and was selected for the rest of the experiment.

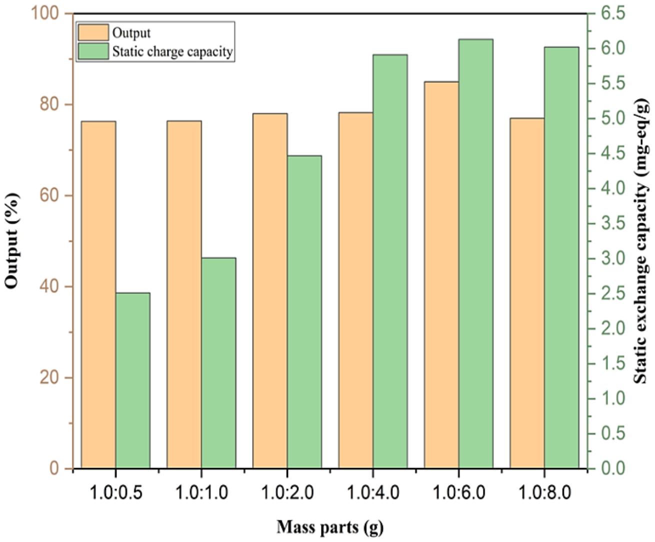

Fig. 2 Influence of the ratio of the initial components on the static exchange capacity of the anion exchanger.

Figure 3 shows the effect of modification duration on the output and SEC of the double copolymer GMA:ACN:PEI at a ratio (1:6) anion exchanger at 80 °C. This was achieved by setting different curing times. It was observed that the highest ionic exchange was achieved when the curing time was set at 24 hours, recording 6.22 mEq/g with 85% output.

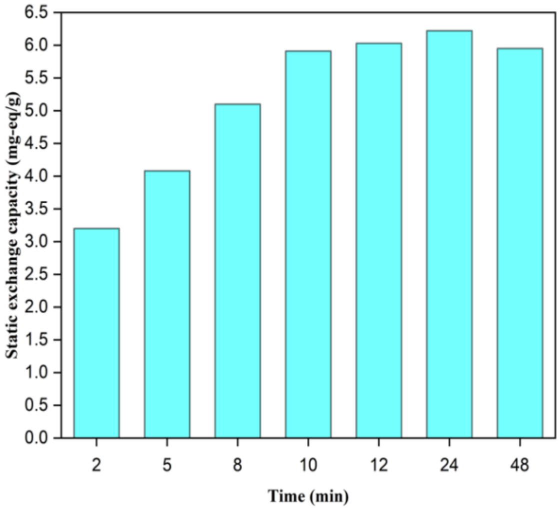

Fig. 3 Effect of temperature on the static exchange capacity of anion exchangers.

The effect of different temperature on SEC was analyzed, and it could be seen from Fig. 4 that with an increase in the temperature above 80 °C, the exchange capacity of the anion exchanger starts to decrease steadily. This is probably due to additional structure formation of the polymers, leading to compaction of the ion exchanger matrix and, consequently, a decrease in the availability of ionogenic groups to low-molecular-weight electrolyte molecules during ion exchange. The most optimal temperature regime to produce anion exchangers based on the double copolymer GMA:ACN:PEI at a ratio (1:6) was found to be 80 °C.

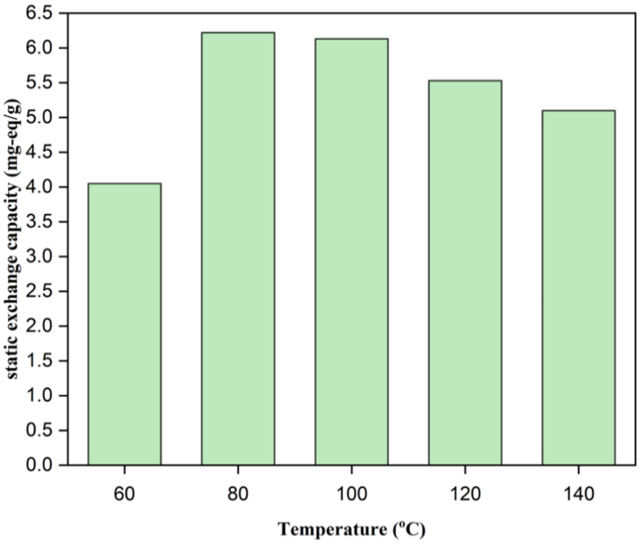

Fig. 4 Effect of polymer curing time on the static exchange capacity of anion exchange resins.

Based on the results of a series of studies to establish optimal conditions for the synthesis of complexing ion exchangers based on double copolymers of GMA with PEI, the influence of the ratio of the initial reacting components, temperature and duration of the process on the static exchange capacity of the ion exchangers (Table 1). It was found that in all cases, with an increase in the concentration of PEI in the initial mixture, the exchange capacity and nitrogen content in the structure of the ion exchangers increase.

The output of ion exchanger is 85% and the static exchange capacity by HCl solution (0.1 N) is 6.22 mEq/g.

3.2 Fourier transform infrared spectroscopy (FTIR) of synthesized adsorbent

The physicochemical properties of the as-prepared polymeric material were analyzed with an FTIR spectroscopy. A good correlation between the synthesized material and data reported in literature.[23] is presented in Fig. 5. As a result of amination of the GMA-ACN copolymer with PEI, good absorption bands

Table 1. Optimal conditions for the synthesis of nitrogen-containing ion exchangers based on double and ternary copolymers.

Polymer	Mass parts, (Copolymer: PEI)	t°C	τ, hour	Output η, %	Static exchange capacity (SEC) by 0.1 N HCl solution (mg-eq/g)
(GMA-ACN): PEI	1.0:6.0	80	24	85	6.22

were obtained. The analysis was carried out for the synthesized material before and after target metals adsorption from water solution. The broad stretching vibration peak observed at 3354 cm^{-1} is ascribed to the O-H band possibly obtained from the PEI units and it is in correlation with the work published in literature.[24] The sharp peak observed at 2843 cm^{-1} is attributed to the C-H stretching band in the synthesized material before adsorption of the target heavy metals while its intensity weakens after adsorption experiment. Peaks at 1715 cm^{-1} and 1100 cm^{-1} are respectively attributed to C=O and C-O stretching vibrations while characteristic of epoxy groups disappear in the spectra of anion exchangers and new ones were observed.[25] The data from the IR spectra of the anion exchangers confirmed the presence of an intramolecular hydrogen bond between the O-H group and the nitrogen atoms of the tertiary amino group. The spectrum contains absorption bands at (1040-1060) cm^{-1} which corresponds to the bending vibrations of O-H groups associated with the carbon skeleton and tertiary amino groups of the polymer. Planar deformation vibrations of the secondary O-H group formed during the opening of the epoxy ring by amines are observed at 1310-1330 and 1410-1420 cm^{-1}.

3.3 Thermogravimetric analysis (TGA) of synthesized ion exchangers

Thermogravimetric analyses of the synthesized GMA-ACN double copolymer with and without adsorbed Cu and Pb were performed with Netzsch DSc-TGA (Germany) within the temperature range of 0 - 900 °C with a heating and cooling rates of 0.001 - 50 °C/min under an inert atmosphere of N_2. Thermogravimetric analysis of GMA-ACN copolymer before Cu and Pb sorption (Fig. 6a) showed a gradual weight loss of about 18% between ~ 50 - 220 °C and a sharp weight loss of about 80% at ~ 450 °C, probably due to the decomposition of excess ethyl alcohol and moisture and glycosidic bonds (C-O-C) of the cellulosic backbone respectively.[26] Final decomposition temperature (FDT) was observed at 750 °C with only about 1% residue left. This relatively high FDT could be as a result of oxygen impurities arising from reactant materials, or other impurities such as double bonds, aromatic groups, bulky or large side groups present in the copolymer. Two exothermic peaks at around 350 and 400 °C can be seen in DTG thermogram of the copolymer. These peaks can be associated with the degradation of carbon chains between the copolymers. The second peak around 400 °C is related to the degradation of the crosslinks between the copolymers.[27] However, the DTG thermogram for the copolymer-metal chelate shows only one prominent exothermic peak at 350 °C with a more diminished peak for crosslinks, indicating more chelation with metals and even less crosslinking.

Thermogravimetric analysis was also conducted for the copolymer-metal chelate (Fig. 6b) and it was observed that the

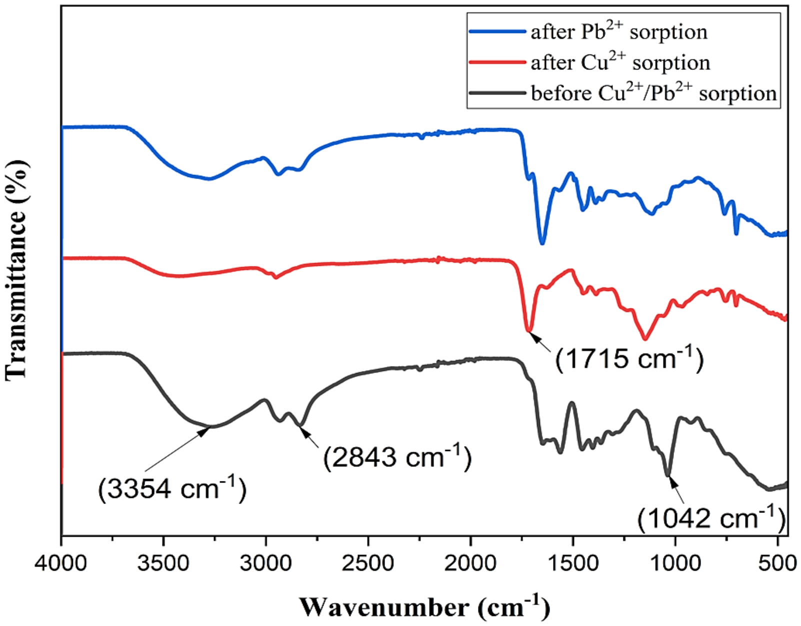

Fig. 5 IR spectrum of anion exchanger (GMA-ACN: PEI.

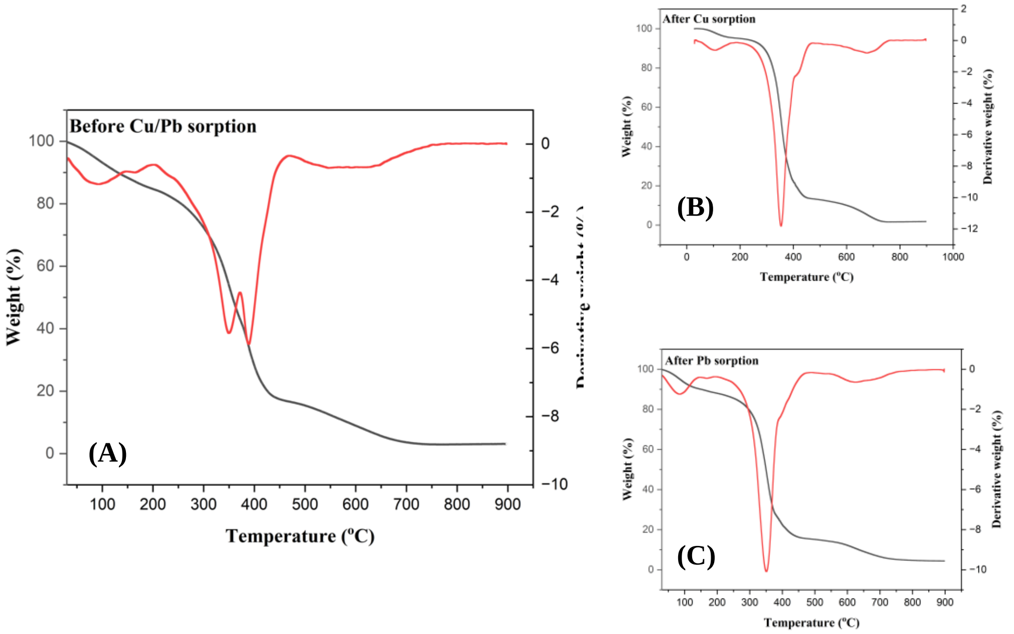

Fig. 6 TGA of synthesized GMA-ACN: PEI copolymer (A) before metals (Cu, Pb) adsorption and (B, C) after Cu and Pb adsorption from wastewater.

copolymer-Cu chelate had a very intense decomposition peak around 350 °C. Comparing this peak with that of the copolymer peak shows that, the copper decomposition, which decomposes around 200 - 315 °C in the form of acetate,[28,29] actually enhanced the decomposition peak around that region, by appearing to join the two peaks associated with the degradation of carbon chains. A copper residue mass of about 1% remain at the FDT of copolymer-Cu chelate. This shows that the relative amount of cupper present in the sample is very small. The same can be said for the TGA of the copolymer-Pb chelate in Fig. 6c.

3.4 Testing the chemical resistance of ion exchangers to concentrated acids and alkalis

The harsh nature of industrial effluents in terms of their chemical compositions warrants that, any material that will be subjected to such wastewaters should be able to withstand harsh chemical environments without any significant deterioration, at least until the intended purpose of it being subjected to is achieved. In view of that, it necessary to examine the stability of the ion exchanger in various chemical surroundings. The results of testing the chemical stability of anion exchangers showed (Table 2) that the resulting ion exchangers are quite inert to chemical reagents. The degree of loss of capacity of ion exchangers synthesized on the basis of ternary copolymers of GMA when treated with solutions of oxidizing, acidic and alkaline solutions does not exceed 5%. It could also be seen that, the anion exchanger was destroyed most, although not substantial enough, in the diprotic H_2SO_4 solution. The diprotic nature makes it a stronger solution. Thus, the anion exchanger will still be able to actively adsorb heavy metal ions even after it has been subjected to some harsh solutions for almost up to 48 hours in some instances.

Table 2. Chemical stability of anion exchangers.

Solutions	(GMA-AKN): PEI		
	SEC by 0.1 N NaOH solution (mg-eq/g)		Chemical stability, %
	Before	After	
5N solution of NaOH	6.22	6.07	96.58 %
5N solution of H_2S0_4,	6.22	5.91	95.11 %
1N solution of $HN0_3$	6.22	6.00	96.47 %
10% solution of H_20_2	6.22	5.92	95.32 %

Estimated structural formula of the anion exchanger GMA-ACN: PEI based on a double copolymer modified with polyethyleneimines.

3.5 Adsorption study

To evaluate the efficiency of the synthesized material, sorption experiment was conducted towards Cu and Pb removal from wastewater. The results obtained are presented in Fig. 7 where the percentage of metals adsorbed by the synthesized material show acceptable range compared with literature results. By

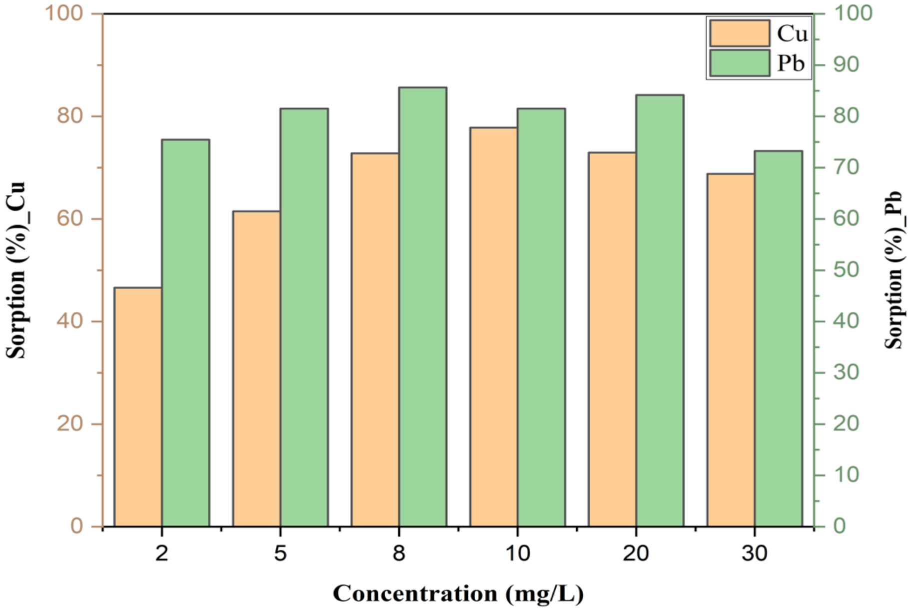

Fig. 7 Sorption efficiency of Cu^{2+} and Pb^{2+} from wastewater.

comparing the sorption efficiency of Cu and Pb at different concentration using GMA-ACN: PEI, Pb shows the highest sorption amount.

Experiments conducted in different concentrations of Cu^{2+} and Pb^{2+} strongly affects the adsorption efficiency of the metal ions in solution. For instance, for a 2ppm Cu^{2+} solution, removal efficiency was 46.6% as depicted in Fig. 7 while as the concentration increases, removal efficiency increases but in contrast decreases as a result of further increment of concentration. A Cu^{2+} concentration of 5ppm, 8ppm, 10ppm, 20ppm and 30ppm respectively provides removal efficiency of 61.5%, 72.8%, 77.8%, 73.0%, and 68.8% using GMA-ACN: PEI adsorbent. A clear indication to prove the efficiency of the synthesized material. The use of GMA-ACN: PEI towards Pb^{2+} removal from wastewater also shows similar trend as compared with what was observed for Cu^{2+} removal. Initial concentration at 2ppm, 5ppm, 8ppm, 10pp, 20ppm, and 30ppm shows removal efficiency of 75.5%, 81.5%, 85.6%, 81.5%, 84.2% and 73.3% respectively. Meanwhile the removal efficiency was higher in Pb^{2+} solution compared with Cu^{2+} solution. This could be as a result of several properties such as the ionic radius and charge density of the metals since Pb^{2+} has a lower charge density and higher ionic radius compared to Cu^{2+} which helps in better interaction with the synthesised GMA-ACN: PEI polymer.[30-35]

3.6 Adsorption isotherm

The primary methods in describing adsorption processes are via the use of adsorption models of isotherms such as Langmuir and Freundlich. These isotherms describe how metal ions interact with their adsorbates in solution when in equilibrium and can be applied to effectively predict the best choice of model based on the results obtained after applying the models. In our work, we applied the models to calculate the sorption isotherms based on Langmuir and Freundlich theories and results are presented in Fig. 8 after the experimental data was fitted.

According to the results obtained, Langmuir isotherm shows a better agreement towards Cu^{2+} and Pb^{2+} removal from wastewater using GMA-ACN: PEI Polymer. In contrast to Freundlich isotherm, fitting result was inefficient making it to conclude that Langmuir isotherm is the best model to describe the effectiveness of the synthesized polymer. All parameters obtained after fitting experimental results of Langmuir and Freundlich isotherms are presented in Table 3.

As depicted in Table 3, Langmuir isotherm is the best

Table 3. Parameters of Langmuir and Freundlich isotherm after fitting experimental data.

	Theory	intercept	slope	q_{max} (mg/g)	K_L	R_L	R^2
Pb	Langmuir	0.0656±0.031	1.5972±0.033	15.253	0.041	0.708	0.9979
Cu	Langmuir	0.4089±0.099	5.2943±0.285	2.446	0.077	0.564	0.9857
Pb	Freundlich	0.066±0.069	0.9406±0.151	15.11	0.0704	0.587	0.8830
Cu	Freundlich	0.5156±0.172	1.2784±0.309	1.94	0.4032	0.199	0.7623

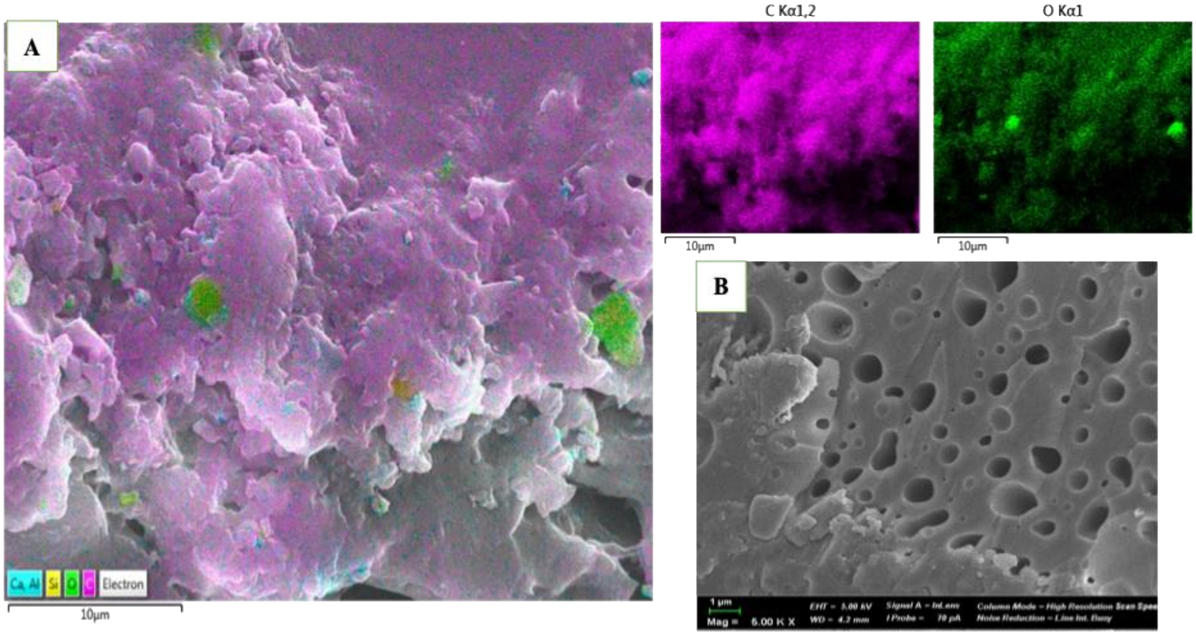

Fig. 9 EDX analyses (A) and cross section SEM image (B) of GMA-ACN-PEI terpolymer before metal adsorption.

isotherm of choice in describing the sorption efficiency of Pb and Cu ions in wastewater solution by the synthesized polymer. This is due to the higher correlation coefficient (R^2) of 0.9979 and 0.9857 for Pb and Cu respectively compared to the R^2 values of 0.8830 and 0.7623 respectively for Pb and Cu from Freundlich results. According to the work published,[36] the separation factor (K_R) could be calculated from the isotherms to determine whether the separation is favorable or not. The separation equation used for batch systems is reported in Eq. 6 below:

$$K_R = \frac{1}{1+K_L C_O} \tag{6}$$

where K_L denotes Langmuir constant, L/mg, C_O represents initial concentration of metal ions, mg/L. The adsorption is classified as not favorable if $K_R > 1$ while it is considered as linear if $K_R = 1$ but favourable if $0 < K_R < 1$ and irreversible if $K_R = 0$. The separation factors for both ions are within $0 < K_R < 1$ proving that the adsorption method chosen is favourable. Since the values obtained from Pb sorption is higher than that of Cu, it can be concluded that the synthesized material is more favourable towards Pb adsorption from wastewater.

Figures 9-11 present the results from SEM (Scanning Electron Microscopy) and EDX (Energy-Dispersive X-ray Spectroscopy) analyses. Fig. 9 shows the SEM and EDX Spectroscopy of the GMA-ACN-PEI (glycidyl methacrylate-acrylonitrile-polyethylenimine) polymer before the adsorption of heavy metal ions. From the image, only carbon and oxygen elements are visible, aside from negligible amounts of other trace elements. The SEM image shows a rough and porous surface. In Fig. 9B, a highly porous structure is observed in the

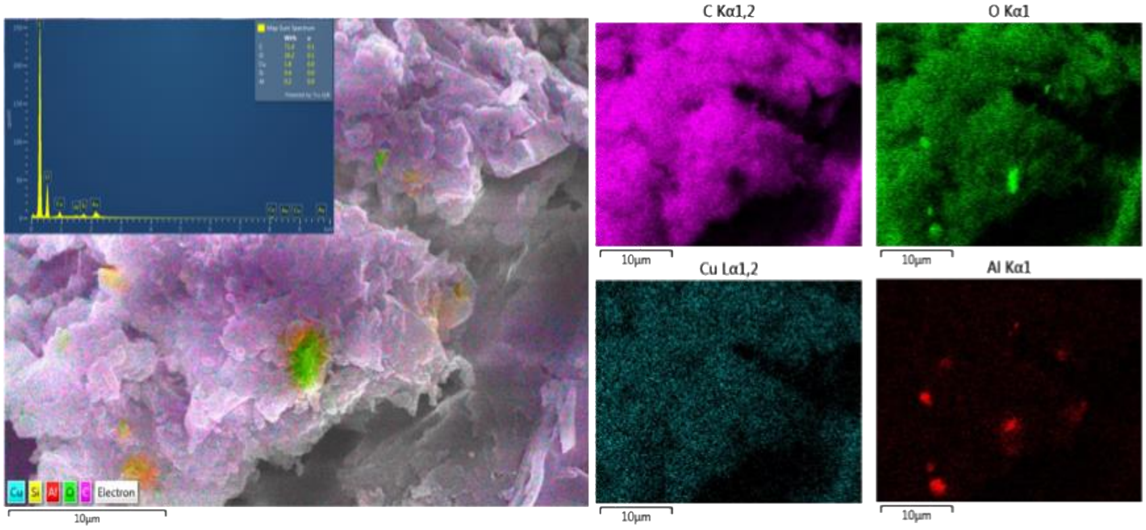

Fig. 10 SEM and EDX analyses of GMA-ACN-PEI terpolymer after copper adsorption.

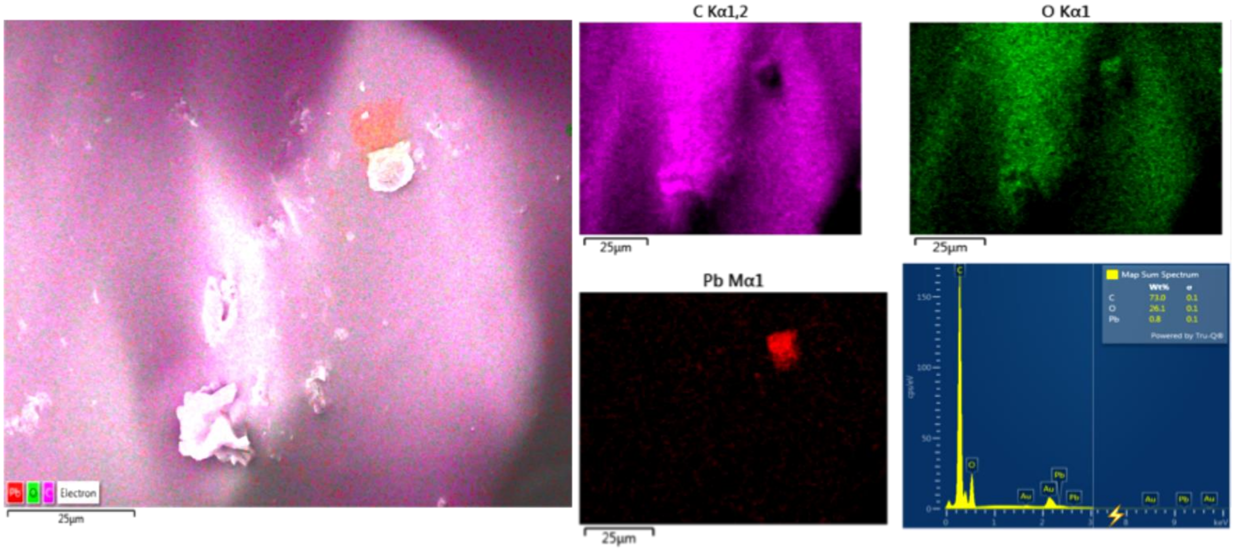

Fig. 11 SEM and EDX analyses of GMA-ACN-PEI terpolymer after lead adsorption.

cross-section of the polymer, which likely contributes to its high adsorption capacity. This porous structure offers more surface area for interaction between both copper and lead ions and the polymer matrix, facilitating higher adsorption efficiency.

The EDX spectrum in the top left corner (Fig. 10) and the bottom right corner (Fig. 11) shows prominent peaks, indicating the presence of copper (Cu) and lead (Pb) elements. The strong copper and lead peaks suggest successful absorption of these ions into the polymer matrix. The distribution of copper ions across the polymer surface is indicated by the dark blue areas in the EDX map, while lead ions are observed in dark red regions within the polymer matrix. This confirms that the GMA-ACN-PEI polymer matrix effectively adsorbed both copper and lead ions from the solutions. The presence of yellow, red, and light blue maps indicates other elements, such as silicon, sodium, and magnesium, but these are less prominent compared to copper and lead. The evidence provided by SEM and EDX Spectroscopy suggests that the GMA-ACN-PEI polymer has a high affinity for copper and lead ions, making it a promising material for applications in water treatment and purification systems. These findings underline its potential effectiveness in industrial settings for heavy metal removal, thus contributing to environmental protection and sustainability efforts. Further studies could focus on optimizing the polymer's adsorption capacity, improving its regeneration capabilities, and assessing its performance with other heavy metals or contaminants.

4. Conclusion

In summary, the adsorption efficiency of synthesized GMA-ACN: PEI polymer was investigated towards Cu and Pb ions removal from wastewater. The maximum removal efficiency was 85.6% and it was obtained from Pb^{2+} removal from wastewater while for Cu^{2+}, the maximum removal efficiency was 77.8%. To prove the sorption efficiencies and describe the adsorption mechanism, two isotherm models, viz, Langmuir and Freundlich isotherms were used. According to results obtained after fitting the experimental data, Langmuir isotherm best describes Cu and Pb adsorption from wastewater due to the higher results obtained from correlation coefficients for both metals when GMA-ACN: PEI polymer was used. From the Langmuir isotherms, the separation factors and other parameters were calculated to prove the favourable nature of the sorption method chosen. In conclusion, low-cost adsorbent, GMA-ACN: PEI polymer, could be employed as a good adsorbent in wastewater treatment from Cu^{2+} and Pb^{2+} ions.

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Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable.

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