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Synthesis, characterization of polyvinyl chloride -graft-4-Amicacid phenol and application of adsorption for lead ions

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***Abstract*---**A new synthesis of polyvinyl chloride (PVC-grafted-4-amicacid phenol, which consist of a reaction between poly (vinyl chloride) and 4-amic acid phenol. Grafting structure has been checked by, FTIR, 1HNMR, 13C NMR, TG, DSC and X-RAY .The grafting of PVC work to changes the surface properties such as catalytic ability, adhesion and adsorption capacity. This paper describes grafting of polyvinyl chloride (PVC) as adsorbent for pb+2 ions removal. The adsorption process recorded comparatively rapid uptake of pb+2 by the new PVC-grafted-4-amicacid phenol which was mainly complexation controlled.

***Keywords*---**4-Amic acid phenol, PVC grafting, adsorption, thermal analysis, lead ions.

Introduction

Among the famous types of universal plastic materials it is polyvinyl chloride is the second to polyethylene. now adays , polyvinyl chloride has attracted a lot of researchers due to its unique properties and widely used in the industries involved electronic ,packaging, architecture and chemical engineering [1,2] . The researchers were able to grafting or modify PVC by prelude heterocyclic and aromatic moieties through halogen displacement reaction .The modification of poly (vinyl chloride) play great role in the development of new organic materials for huge new application [3,7]. Heavy metal ions are dominant pollution in water recycle out coming from industry and mining. They act a serious water contamination issue, threatening the human health and circumference. Some of heavy metals like mercury, lead, nickel and copper can cause earnest harm to the

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central nervous system, skin, kidneys, liver and lungs [8-15]. More recently, our research team reported the grafted sugar thiacrown ether polymer using an easy chemical rote for removal of heavy metal ions. The removal mechanism based on host-guest inclusion complex formation with ring of thiacrown ether canities [16]. Different methods can be used for the treatment of wastewater such as electrochemical treatment, ion exchange, chemical treatment, coagulation, membrane filtration and adsorption. This work currents as feature a high efficiency of removal of heavy metal ions at low concentrations. The aim of this work is to demonstrates the application of the based modified polyvinyl chloride and its graft polymerization of 4-amic acid phenol as potential adsorbent for the removal of the lead ions from aqueous solution. The chemical grafted of polyvinyl chloride was tested by fourier transform infrared (FTIR) and the measurement of percentage capacity was determined. The adsorbent was identified by x-ray diffraction, thermogravimetry and differential scanning calorimetry.

Experimental

General procedures

All solvents and chemicals were acquired commercially and were of the highest analytical grade from Sigma–Aldrich and Fluka. Infrared spectra were recorded using the Fourier transformation infrared Bruker ALPHA FT-IR, Faculty of Science, University of Kufa.^{1}H and ^{13}C NMR spectra in DMSO-d6 were acquired on the Bruker spectrometer (300MHz for ^{1}H NMR and 75MHz for ^{13}C NMR, respectively) at Shahid Beheshti University/Iran d6 with tetramethylsilane as an internal reference. The abbreviations for NMR multiplicities are as follows: s = singlet, d = doublet, t = triplet, and m = multiplet signal. XRD Rigaku(japan) and EDX BRUKER X FLASH6l 10 in Department of Chemistry, Faculty of Sciences, University of Tahran ,Iran . Flame Atomic Absorption Spectrophotometer, Shimadzu AA-6300, in Faculty of pharmacy, University of Kufa . Scanning Electron Microscope (SEM) Inspect S50 for Materials Science/EFI, Faculty of sceince, University of Kufa.The visualization was created using a UV Cabinet with Aluminum TLC Xtra SIL G/UV245 with silica 60, thickness 0.2, and a 10x20cm surface area in Germany (254 nm).

Synthesis of 4-amic acid phenol

(0.01mol) maleic anhydride was dissolved in absolute acetone (20 ml) and then (0.01mol) from 4-amino phenol was dissolved in 30ml of DMSO was added drop by drop and the mixture was stirred for 72 hours and follow the reaction by TLC . The mixture was wished extensively with water, and the product was dried to form yellow solid from 4-amic acid phenol solid (yield : 1.14 g).

Synthesis of PVC-g-4-amic acid phenol

4-amic acid phenol (0.5 g) was dissolved in (20 ml) of DMF and cool it to (0 ^{o}C) and stirred it and then added (0.3g) of NaH , after 30 min added (1 g) of PVC . The mixture was wished extensively with water, and the product was dried to form black solid compound.

Batch adsorption experiments

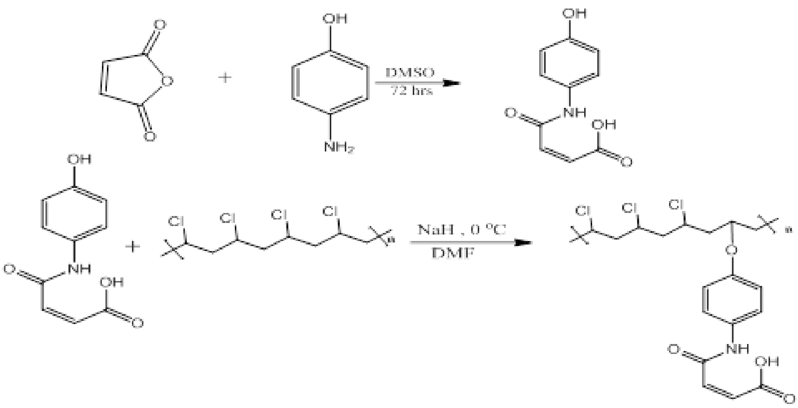
Measurements of metal ions uptake using a batch method were conducted by placing) 0.05, 0.1 and 0.15) g of PVC-g-4-amicacid phenol in a conical flask containing mL (100 mg/L) metal ion solution (Pb^{2+}) at pH 7.0. The mixture were shaken at 180 rpm at 25 °C. Samples were taken at time intervals of (0.25, 0.5, 1, 2, 4, 5 and 4 hrs.) in order to assess the remaining metal ion concentration. The effect of the initial concentration of the lead ions solution (Pb^{2+}) on the metal ion using polymer PVC-g-4-amicacid phenol was performed by adding 0.1g of dried PVC-g-4-amicacid phenol in a series of flasks containing 10 mL of metal ions at certain concentrations (100 mg/L) and pH 7.0 .The flasks were placed on a shaker at 180 rpm and 25 °C for 4 hrs. to achieve the equilibrium. The concentration of remaining metal ions in solutions was measured after filtration of the solid. In addition, metal ions uptake experiments were conducted at controlled pH and 25 °C by shaking 0.05 g of dry PVC-g-4-amicacid phenol with 10 mL (100 mg/L) metal ion solution (Pb^{2+}) for 4h at 180 rpm. Three different pH values 3, 5 and 7 were adjusted in suspensions of the PVC-g-4-amicacid phenol followed by adding the metal solutions.absorption spectrophotometer (Shimadzu Spectra Instrument Model AA-6300) .Adsorption efficiency of PVC-g-4-amicacid phenol is calculated according to the equation 1 .

$$\textbf{\%adsorption} = \frac{C_i - C_f}{C_i} * \textbf{100} \qquad \text{.........equation (1)}$$

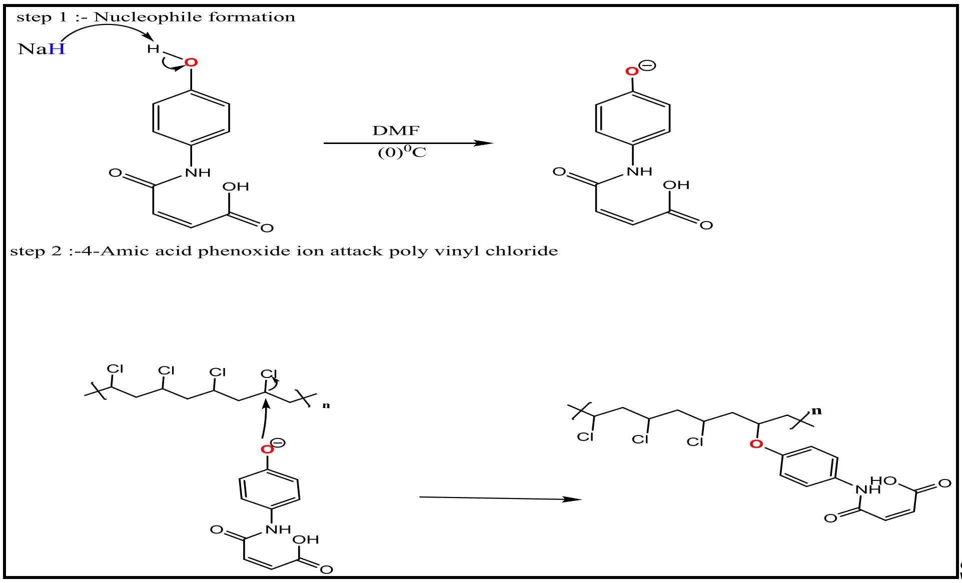
C_i (mg/L): initial concentration of metal ion before adsorption.
C_f (mg/L): final concentration of metal ion in solution after adsorption.

Results and Discussion

The initial portion of this research focused on Synthesis of 4-amic acid phenol equation, which was made by malic anhydride with 4-amino phenol (1:1) and react with polyvinyl chloride will get the product PVC-g-4-amicacid phenol as showing in scheme equation reaction scheme 1 . And scheme 2 showing the mechanism of synthesis PVC-g-4-amicacid phenol



Scheme 1. Equation reaction of 4-amicacid phenol and PVC-g-4-amicacid phenol as polymer



Scheme 2. Mechanism of synthesis PVC-g-4-amic acid phenol

FTIR data

FTIR spectrum of 4-amicacid phenol showed two clear characteristic absorption bands at 3297.92 cm^{-1}and3135.57 cm^{-1}which are due to ν(OH) carboxylic and ν(NH) amide. Absorption bands due to ν(C=O) carboxyl and ν(C=O) amide appeared at 1695.17 $cm^{-1}$and 1610.97 cm^{-1} while absorption bands belong to ν(C=C) aromatic and ν(C=O) ketone appeared at 1382.34 cm^{-1}and1447.45 cm^{-1}respectively ,The PVC-g-4-amic acid phenol 1591.53 cm^{-1} [17]

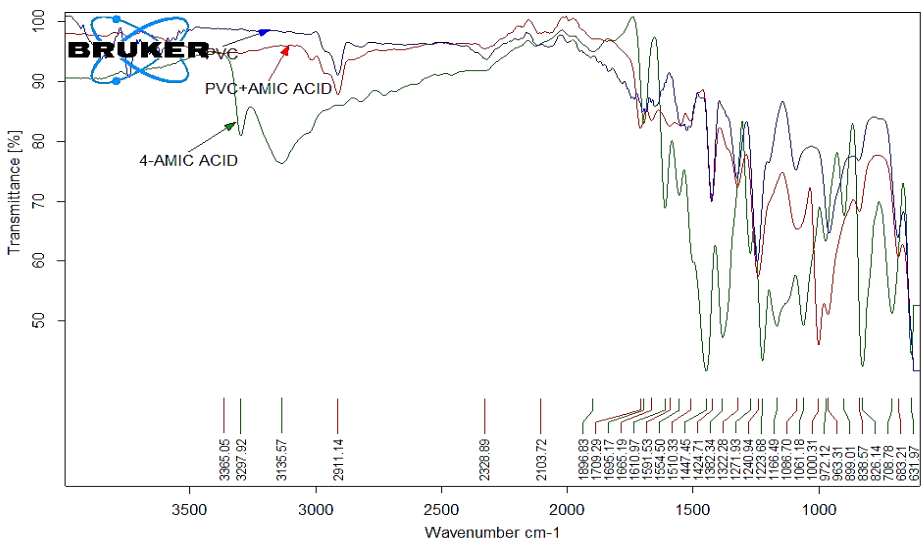


Figure 1. IR spectra for 4-amicacid phenol, PVC and PVC-g-4-amic acid phenol

NMR data

^{1}H NMR (300 MHz, DMSO) δ 13.72 (s, 1H) OH carboxylic acid , 10.37 (s, 1H) NH amide , 9.36 (s, 1H) OH alcohol , 7.42 (d, 1H) 6.73 (d, 1H) aromatic reign , 6.57 – 5.87 (m, 2H) CH of ethylene , 3.38 water solvent, 2.50 DMSO solvent figure 2 [18].

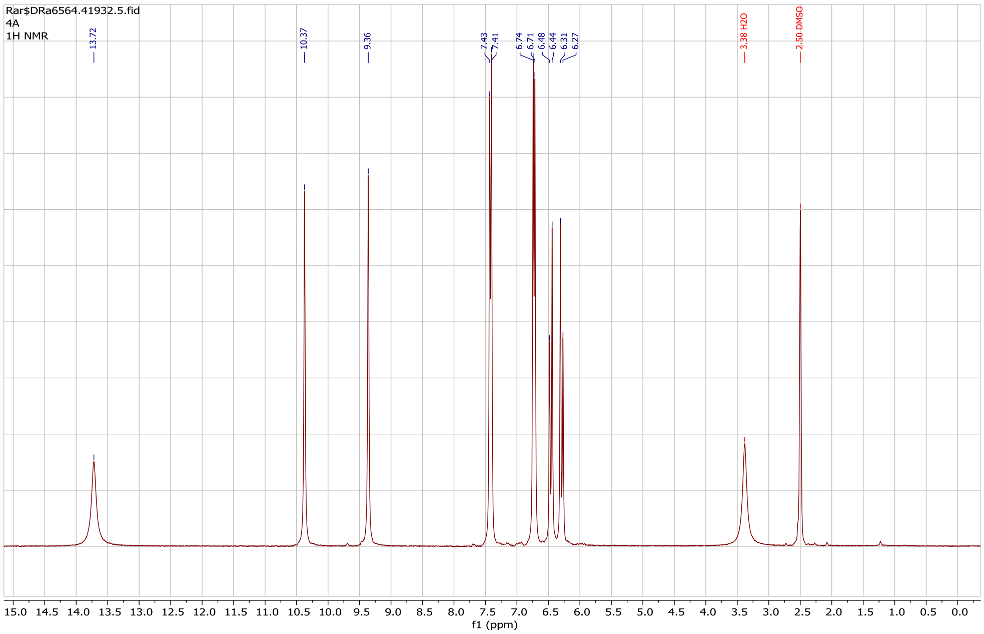


Figure 2. ^{1}HNMR spectrum for PVC-g-4-amic acid phenol

The ^{13}CNMR spectrum offered a signal at the downfield zone of the spectrum, δ=166.98 ppm corresponding to the presence of the (C=O) of carboxylic acid . A peak at δ=163.16ppm is attributed to the carbon related with OH group . The lasting (C=N) carbon was observed at δ=154.60 ppm . Aromatic carbons appeared at δ=132.17,131.68,130.23,121.93 and 115.68ppm figure (3) [19] .

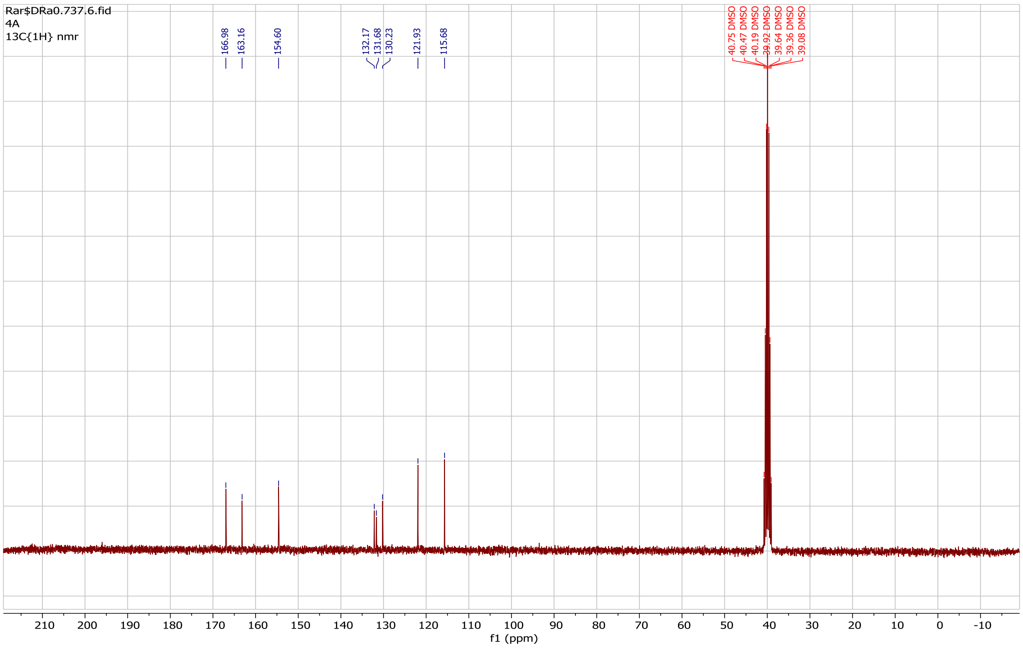


Figure 3. ^{13}CNMR spectrum for PVC-g-4-amic acid phenol

Thermo Gravimetric (TGA) AND (DSC)

Thermal stability of PVC-g-4-amic acid phenol estimated through thermo gravimetric curve as given figure (4) . the PVC appears three thermal steps the sample starts to loss mass at temperature between (240-350)℃ attributed to the thermal dehydrochlorination , with a reduction of about 50% in mass . the second step started at 420 ℃ is regarding to chain rearrangement reactions . the third weight loss begin at temperature of above 480 ℃ assigned to decomposition of carbonaceous residues . The TGA of PVC-g-4-amic acid phenol is shown in figure .most chlorine in the structure was stripped by dehydrochlorination ,the percentage weight loss are related to the removal of residual chlorine and other like to decarboxylation , which commands to decrease in the thermal stability of the grafted polymer since materials with carboxylic groups display decomposition between 200℃ and 300℃ . The other thermal steps are noticed at temperatures up 300℃ may be concerning to the decomposition of grafted PVC due to the remains of the main chain.

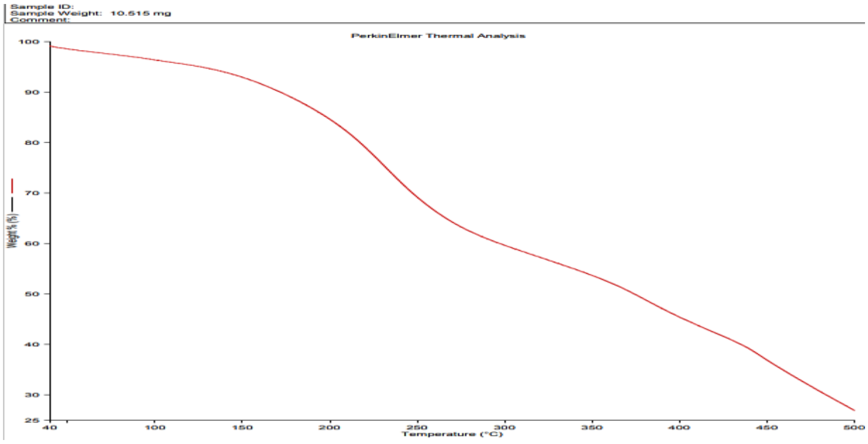


Figure 4. Thermo gravimetric for PVC-g-4-amic acid phenol

The DSC thermogram of PVC-grafted-4-amic acid phenol exhibited a broad endothermic peak 116℃ corresponding to the loss of glass transition and at about 280℃ the hydration temperature is appeared in a medium exothermic peak [20] . the third endothermic at about 340℃ corresponded to the chemical bond decomposition of PVC chains figure (5) .

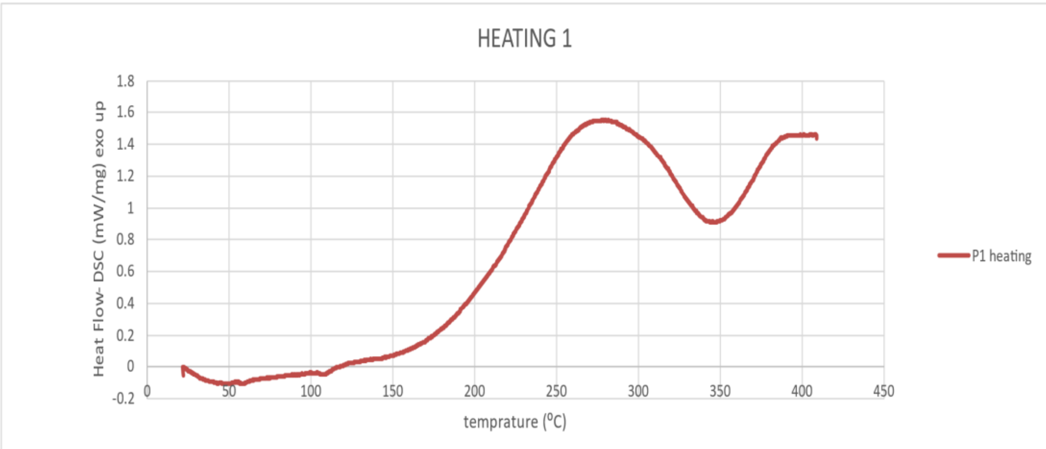


Figure 5. DSC for PVC-g-4-amic acid phenol

X-ray diffraction and SEM

The X-ray method allows the measurements of the nature of crystalline and amorphous in a polymer . the diffraction pattern for PVC is partially crystalline with peaks of 12° and 17° at 2θ angles . Figure(6) for PVC and pvc-grafted-4-amic acid phenol . the grafting of PVC changes the diffraction pattern of the grafted produce PVC-grafted-4-amic acid phenol , increasing the amorphous character with increasing the distance or broad peak (amorphous hump) between 18° and 26°, 2θ . this side indicated an increase in the amorphous portion of polymer [21] .

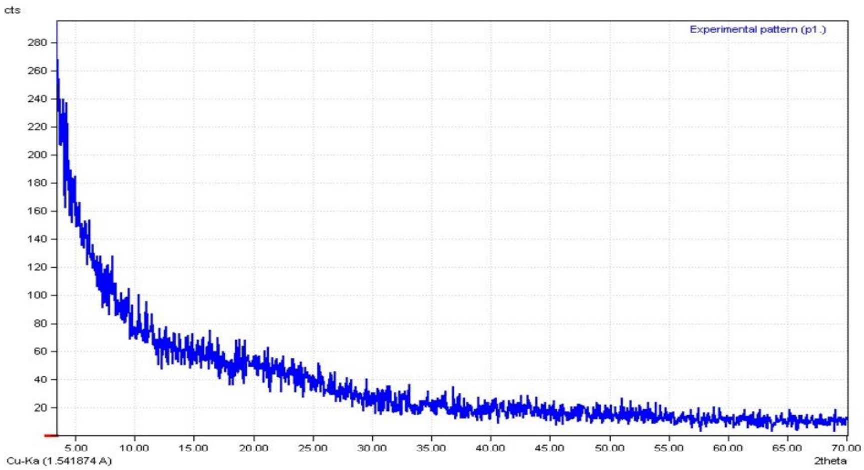


Figure 6. XRD of PVC-g-4-amicacid phenol

SEM images of the raw poly vinyl chloride and grafted 4-amic acid phenol are shown in Figures (7) and (8) . The morphology of poly vinyl chloride and PVC-g-4-amic acid phenol indicate that the raw PVC has grainy texture ,with various site and thick of micro particles . After the grafting modification , the morphological texture of PVC-g-4-amic acid phenol changes with formation of likely regions of lamellar , obviously represented by small crackers . Regions grafting of poly vinyl chloride its original morphology and guide to an increase of surface area , for the use it as desired adsorbent .

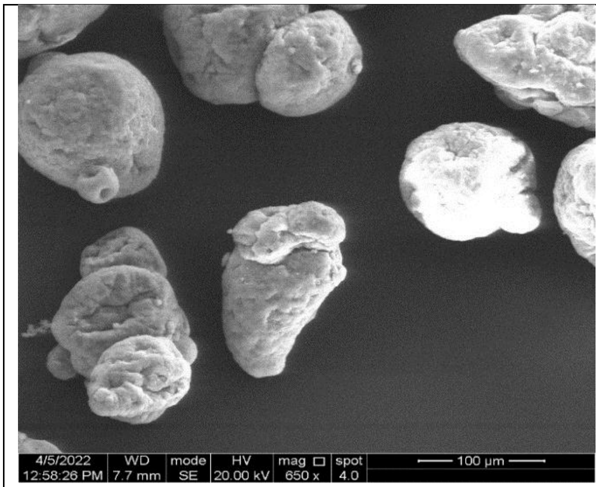


Figure 7. SEM of PVC

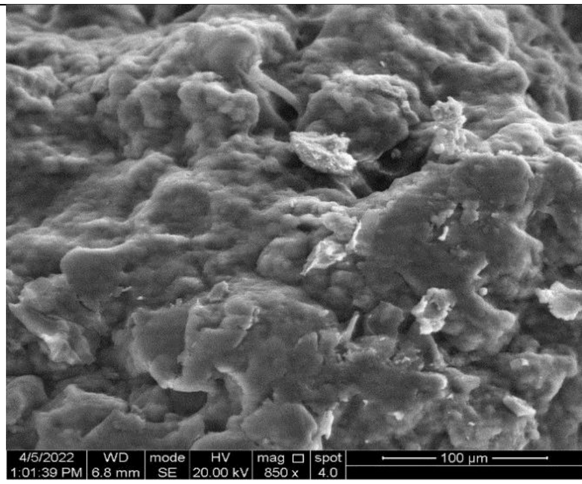


Figure 8. SEM of PVC-g-4-amicacid phenol

Removal of metal ions (Adsorption)

The adsorption percentage of the interaction of PVC-g-4-amicacid phenol with lead ions was determined. An accurate amount of the PVC-g-4-amicacid phenol polymer was suspended with 10 mL of 100 mg/L cation (Pb^{2+}). The amount of non-binding lead ions was determined by atomic absorption spectrometry after equilibrium was reached. The influence of pH, the amount of PVC-g-4-amicacid phenol and time of agitation were studied to measure the optimum conditions for the adsorption of Pb^{2+} ions from aqueous solution.

Effect of pH

The influence of pH on the removal of metal ion was examined. The concentration of H+ ions increases with the acidity of the solution, and the removal of metal ions depends on the available oxygen atoms in amic acid , which have affinity for the lead ions . The presence of more H^+ ions would compete with the pb^{2+}ions and hence decrease the adsorption rate. Therefore, determining the optimal pH of the solution is of great interest. The effect of H^+ ion concentration on metal removal was studied in the pH range of 3–7. The effect of pH on the removal of Pb^{2+} ions by the PVC-g-4-amicacid phenol is shown in Figure 9. The adsorption of metal cations decreased at a lower pH value (pH 3) because a higher H^+ concentration reduces metal cation adsorption. The adsorbent surface surrounded by H+ and metal ions becomes positively charged; thus, electrostatic repulsion takes place, and the metal ions cannot reach the functional groups of the active site [22]. The removal of metal ions increased with increasing pH because the number of protons decreased and the heteroatoms (oxygen)of the adsorbent had more non-bonding electrons on their active sites. As a result, the metal ions would be strongly attracted by the adsorbent. The highest adsorption of metals was observed at pH 7. Thus, pH 7 was chosen as optimal pH for the other measurements.

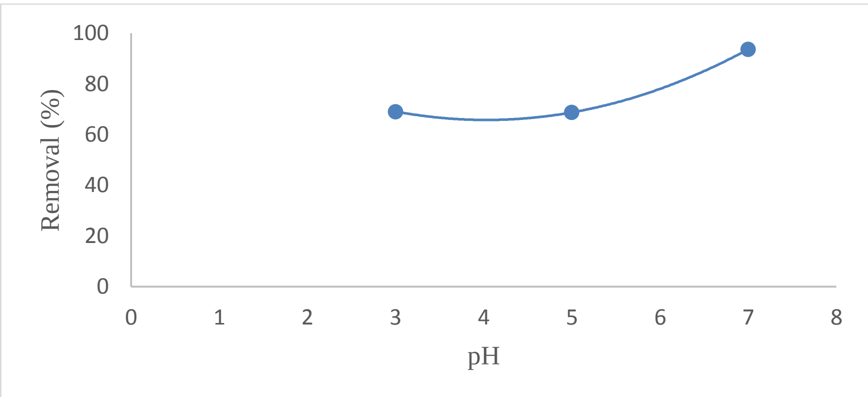


Figure 9. Effect of pH on adsorbtion of lead ions on PVC-4-amicacid phenol

Effect of PVC-g-4-amicacid phenol weight

The availability of active site for the removal of metal ions is affected by PVC-g-4-amicacid phenol weight. The effect of PVC-g-4-amicacid phenol amount on the removal of Pb^{2+} ions was investigated with varying PVC-g-4-amicacid phenol quantity from 0.05 g to 0.15 g in 10 mL of 100 mg/L metal ion solutions as shown in figure 10 .

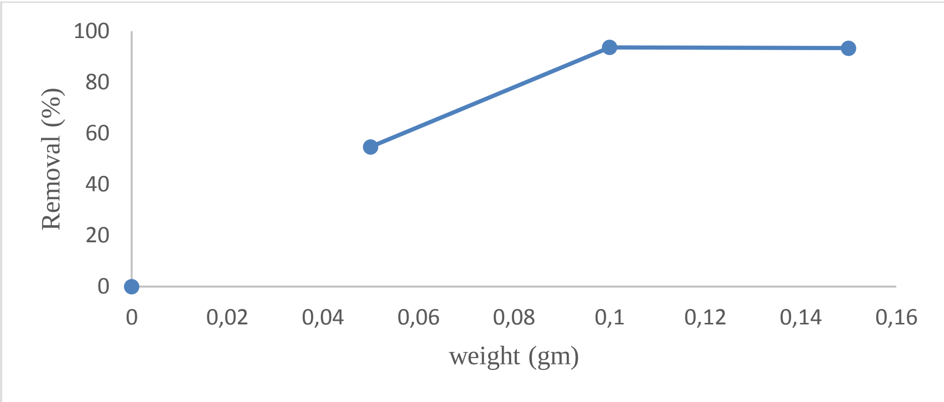


Figure 10. Effect amount of PVC-4-amicacid phenol on the adsorption of lead ions

The percentage of the removal of metal ions increased as the amount of adsorbent rose until 0.1 g and then became constant with further increase in adsorbent dose .This result suggested that the active site was blocked up to 0.1 g of adsorbent, which is the maximum amount required for the efficient removal of metal ions. However ,accumulation took place when the quantity of the adsorbent was increased [23]. Therefore, 0.1 g of adsorbent was selected for further removal experiments. PVC-g-4-amicacid phenol could be decided that PVC-g-4-amicacid phenol had a significant potential benefit for the removal of Pb^{2+} ions from aqueous solution.

Effect of time on adsorption

Contact time is an important parameter in the adsorption process as it provides an idea of the equilibrium time for the adsorption process. Contact time was studied at different durations ranging from 30 min to 240 min to study the effect of time on the removal of metal ions by PVC-g-4-amicacid phenol . The removal percentage of the metal ions (Pb^{2+}) as a function of time is demonstrated in Figure 11.

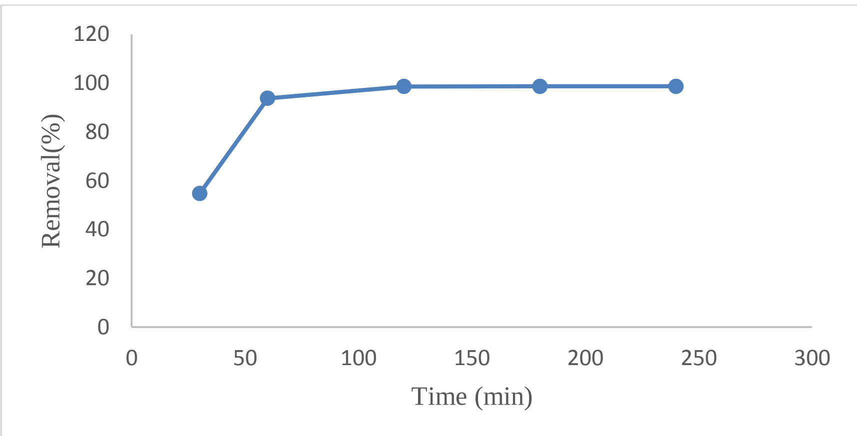
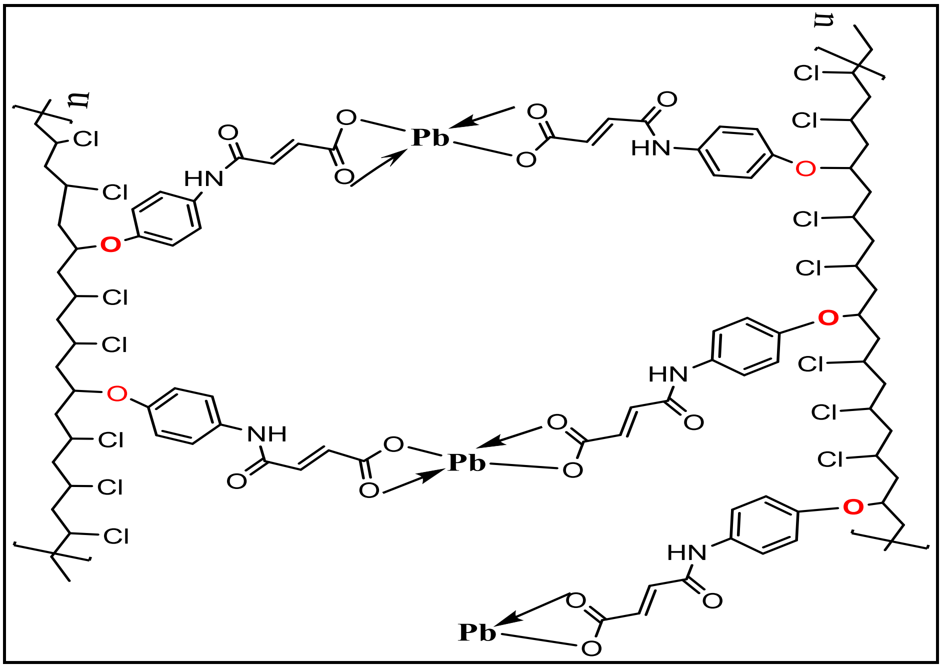


Figure 11. Effect of PVC-g-4-amicacid phenol amount on adsorption

The removal percentage rose with increasing adsorption time to 240 min . No remarkable variation on the adsorption percentage was detected after240 min, and this finding indicated that equilibrium was reached. In other words, the adsorbent surface and the surface adsorption sites have become saturated and occupied by the metal ions. Thus, this period was used as the optimum contact time for all further experiments.



Scheme 3. Adsorption of lead ions by PVC-g-4-amicacid phenol

Conclusions

The application of grafting to the chemical modification of polyvinyl chloride was effective, but with an associated degradation. As expected heavy metal ion adsorption of PVC-g-4-amicacid phenol. Also, to achieve higher pb^{+2} uptake by PVC-g-4-amicacid phenol , one requires to work under condition : pH=7 , time = 60min , temperature = 25^0C. Finally, The adsorption results suggest the utilization of the PVC-g-4-amicacid phenol
As a chelating with excellent adsorption.

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