Synthesis, Study and Biological Efficacy of Pb+^{2} Ion Removal from Aqueous Solutions using a Novel Interpenetrating Copolymer Network Based on (Acrylic Acid-co-Acrylonitrile)/Phenol-Formaldehyde Semi-IPNs

Nabaa K. Alqurashi[1], Hussain J. Mohammed[2] and Salah S. Al-Luaibi[3]
[1]Department of Chemistry, Faculty of Science, University of Kufa, Najaf, Iraq, Ministry of Education, Al-Najaf, Iraq.
[2]Department of Chemistry, Faculty of Science, University of Kufa, Iraq.
[3]Department of Chemistry, Faculty of Science, University of Basra, Iraq.
E.Mail* : **nabaakareem281@gmile.com**

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ABSTRACT

A novel, cost-effective, and selective method was developed for synthesizing interpenetrating polymer networks (IPNs) to be used as efficient adsorbents for metal ions. The IPNs were successfully synthesized by copolymerization of acrylic acid with polyacrylamide, and synthesized IPNs with phenol formaldehyde were thoroughly characterized using various techniques such as Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), and thermodynamic evaluation Newly synthesized IPNs' adsorption efficiency was measured, with special attention paid to their effectiveness in adsorbing the Pb(II) metal ion. The results clearly indicate that the IPNs exhibit superior adsorption capabilities compared to other materials. Furthermore, a comprehensive adsorption study was conducted to examine the influence of various experimental variables on the adsorption of the Pb (II) metal ion. Parameters such as the adsorption capacity of Pb (II), the impact of pH and equilibrium, and the maximum reaction capacity of the metal ion were thoroughly investigated. Notably, the (AC-co-AN)/resole semi-IPNs demonstrated excellent efficacy in removing bp (II) from aqueous solutions using a bath adsorption process. This highlights the superior adsorption capacity of the IPNs and their potential as effective adsorbents for metal ion. This study also tested an effect (AC-co-AN)/resole semi-IPNs on biological activity.

INTRODUCTION

In recent times, adding a second reactive polymer to a polymer mixture is a popular strategy for improving the mixture's characteristics. interpenetrating polymer network systems (IPNs) (Rui, M *et al.,* 2020, Zengbao, W *et al.,* 2023, Yitian, L ., Weian, H., Xiong, Y ., Ziao, L .and Xushuo, Z ; 2023, Vaneet, K *et al .,*2018, Simon, B *et al .,*2021, Dayanand, M *et al .,*2022,) IPNs are formed when two or more chemically distinct polymer networks intermingle on a molecular scale (Sangemano.M *et al.,* 2012, Chen.S *et al.,*2011, Chen.S *et al.,*2010,).

Various combinations of monomers have been employed to produce IPNs, which involve the overlaying of two or more polymers in a lattice structure, resulting in molecular interlocking (Crivello. J.V,2007, Moussa. K and Decher. C, 1993, sangermano.M *et al.,*2014, decker. C *et al.,* 2001, Rajaraman.C *et al.,*1999, Jain. Y *et al.,*2013, Carioscia A.J *et al.,*2007, Dragan.S.E *et al.,*2014,lee .Y *et al.,*2008,Xiao.P *et al.,*2014,).

In this study, we prepared an IPN material with the intention of investigating its capacity to effectively remove ions at lower concentrations. IPNs have garnered attention due to their superior properties compared to individual polymers or polymer blends. Dental composites, damping composites, artificial teeth, tires, medical equipment, and drug delivery systems can all benefit from IPNs because of their broad glass transition temperature for energy absorption and vibration damping. IPNs provide for more precise regulation of drug delivery by modifying matrix-drug diffusion, polymer dissolution and erosion rates, and pH and temperature sensitivity. controlled release of drugs or biologically active substances (Rudin. A,1999, Sperling. L.H,2001).

Dental applications have also embraced the use of IPNs in the form of synthetic teeth and cavity fillers, offering benefits like reduced shrinkage, improved bonding, and decreased temperature sensitivity. However, the multifaceted nature of IPNs, stemming from diverse chemistries, processing conditions, kinetics, and thermodynamic instabilities, presents challenges in their study (Yang. J,1996). The advantage of the present work is to obtain interpenetrating polymer network IPNs containing different moieties of the backbone in order to raise the capacity and selectivity to remove heavy metal ions. Minimum inhibitory concentration (MIC) is the lowest concentration of a chemical, usually a drug, which prevents visible *in vitro* growth of bacteria or fungi. MIC testing is performed in both diagnostic (Pfaller. M. A, 2010) and drug discovery laboratories.

MATERIALS AND METHODS
General Procedures:

In this experiment, commercially available solvents and chemicals of the highest analytical grade, such as those produced by Sigma-Aldrich and Fluka, were employed. At the University of Kufa's Faculty of Science, an infrared spectrometer (a Bruker Alpha FT-IR spectrometer) was used to capture spectra.

The Department of Chemistry in the Faculty of Sciences at the University of Tehran in Iran used Rigaku equipment for X-ray diffraction (XRD) analysis and a BRUKER X FLASH6l 10 device for energy-dispersive X-ray spectroscopy (EDX). The University of Kufa's School of Pharmacy used a Shimadzu AA-6300 Flame Atomic Absorption Spectrophotometer for its analyses. Additionally, S50 was analyzed by scanning electron microscopy (SEM) at the University of Kufa's Faculty of Science's Materials Science/EFI laboratory.

Synthesis of Poly (acrylic acid-co-acrylonitrile):

A three-neck round-bottom flask was used to synthesize poly (acrylic acid-co-acrylonitrile) by combining 0.1 mole of acrylic acid and 0.9 mole of acrylonitrile. The mixture was dissolved in 100 ml of distilled water. To initiate the reaction, an emulsion containing 0.01 g of ferrous chloride initiator and 0.01 g of potassium persulfate as co-initiator was added to the solution, along with three drops of soap solution. The reaction mixture was refluxed for three hours at

65°C. After the completion of the reaction, the copolymers were washed several times to remove impurities. Subsequently, they were dried for three hours at 50°C, resulting in the formation of a light pink solid. The yield of the acrylic acid - acrylonitrile copolymer was determined to be 1.18 g.

Synthesis of Phenol Formaldehyde Resin (Resole):

To synthesize phenol formaldehyde resin (Resole), 0.2125 moles of phenol were dissolved in 100 ml of a 37% formaldehyde solution. The mixture was prepared in a three-neck round-bottom flask. Next, 10% sodium hydroxide was added gradually to the mixture until the pH reached 11. The resulting solution was then heated at 70°C while continuously stirring. After cooling, 5% phosphoric acid was employed to neutralize the solution. To separate the resulting mixture, tetrahydrofuran (THF) was used as a separating agent in a separating funnel. The separated solution was subsequently evaporated, and the resin was dried at 50°C for 3 hours, resulting in the formation of a dark orange phenol formaldehyde resin. The yield of the resin was 4.5 g.

Synthesis of Interpenetrating Polymer Networks Semi-IPNs:

We took equal amounts of the resole and the copolymer (AC-co-AN) in a 1:1 ratio. The two components were thoroughly mixed together and then cured at a temperature of 80°C for a duration of 3 hours. After curing, the mixture was finely ground to achieve a homogeneous consistency.

Experiments:

Adsorption was used to determine how much metal ions were taken in. The first step involved putting 0.1 g of (AC-co-AN)/resole semi-IPNs into a conical flask. Then, at a pH of 4.0, mL of a metal ion solution (Pb2+) containing 100 mg/l was added. The temperature and speed of the shaking were set at 180 rpm and 25° C for the mixture. At 0.25, 0.5, 1, 2 and 3-hour intervals, samples were obtained to determine the concentration of leftover metal ions.

Lead ion (Pb2+) absorption by (AC-co-AN)/resole semi-IPNs was studied by adding 0.1 g of dried (AC-co-AN)/resole semi-IPNs to 10 mL of metal ions at various concentrations (100 mg/l) and pH 4.0 in a series of flasks. After 2 hours on a shaker at 180 rpm and 25°C, the flasks were considered to have reached equilibrium. The concentration of metal ions in the solutions was determined after the solid was filtered. Experiments on the absorption of metal ions were also done at a constant 25°C and pH of 7. Experiments were conducted by mixing 0.1 g of dry (AC-co-AN)/resole semi-IPNs with 10 mL of a metal ion solution (Pb2+) containing 100 mg/l for 2 hours at 180 rpm. Before adding the metal solutions, the (AC-co-AN)/resole semi-IPNs were suspended at three different pH levels: 2, 6, and 8 Equation () was used to determine the adsorption efficiency of (AC-co-AN)/resole semi-IPNs.

percent adsorption formula: $(C_i - f_i) / C_i \cdot 100$ …… **(1)**.

Where: The concentration of the metal ion before adsorption is denoted by C_i (mg/l) The concentration of the metal ion in the solution after adsorption is denoted by the symbol C_f (mg/l).

An absorption spectrophotometer (model AA-6300 by Shimadzu) was used to evaluate the effectiveness of the adsorption process.

Biological Efficacy:

Testing the Ability of Interpenetrating Polymer Networks Semi-IPNs to Inhibit the Growth of Microbes (bacteria): First, we choose the type of test for this process, which is:

Minimum Inhibitory Concentration (MIC): The MIC is determined by preparing a dilution series of the chemical, adding agar or broth, then inoculating with bacteria or fungi, and incubating at a suitable temperature. The value obtained is largely dependent on the susceptibility of the microorganism and the antimicrobial potency of the

chemical, but other variables can affect results too. The MIC is often expressed in micrograms per milliliter (µg/mL) or milligrams per liter (mg/L).

Broth Dilution Assay: The MIC is determined by examining tubes containing the microbe and a dilution series of antimicrobial agents for turbidity.
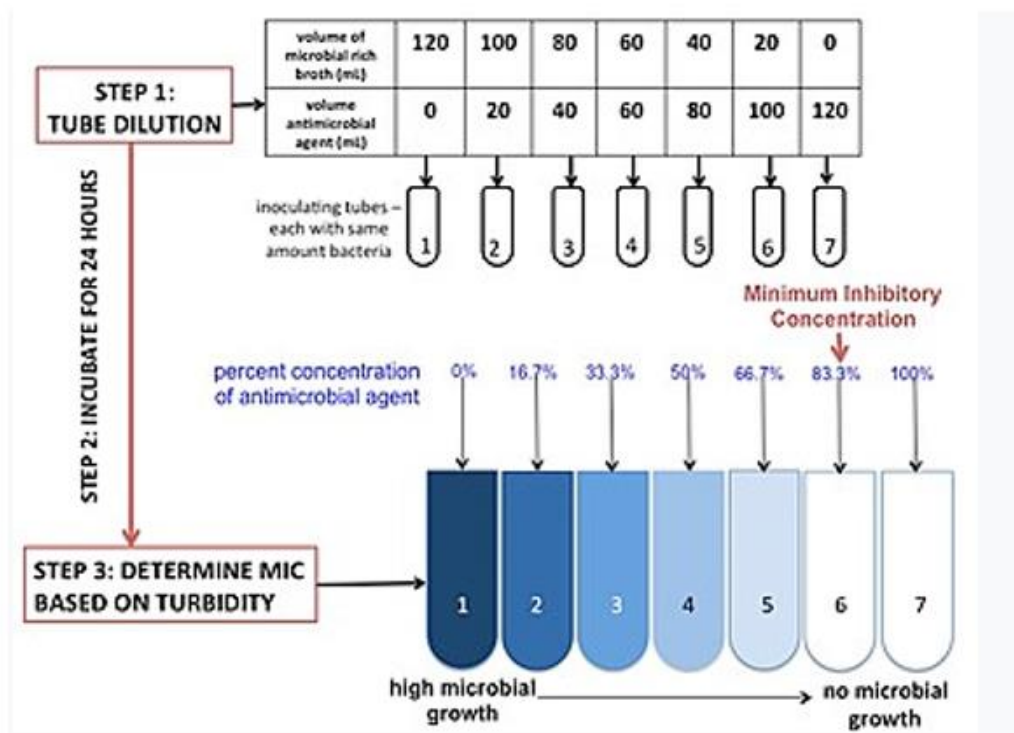
Scheme 1: Broth dilution assay.

There are three main reagents necessary to run this assay: appear in (scheme 1) the media, an antimicrobial agent, and the microbe being tested. The most commonly used media is cation-adjusted Mueller Hinton Broth, due to its ability to support the growth of most pathogens and its lack of inhibitors towards common antibiotics. Depending on the pathogen and antibiotics being tested, the media can be changed and/or adjusted. The antimicrobial concentration is adjusted to the correct concentration by mixing stock antimicrobial with media. The adjusted antimicrobial is serially diluted into multiple tubes (or wells) to obtain a gradient. The dilution rate can be adjusted depending on the breakpoint and the practitioner's needs. The microbe, or the inoculating agent, must come from the same colony-forming unit and must be at the correct concentration. This may be adjusted by incubation time and dilution. For verification, the

positive control is plated in a hundredfold dilution to count colony-forming units. The microbes inoculate the tubes (or plate) and are incubated for 16–20 hours. The MIC is generally determined by turbidity.

So, we will use in this test:
1- The media Mueller Hinton Broth.
2- The antimicrobial agent is the poly (Acrylic acid -co Acrylonitrile)/resole-semi-IPNs.
3-The microbe used Streptococcus pyogenes.Here, for the purpose of dilution, DMSO (Dimethyl sulfoxide) will be used because the IPNs do not dissolve in water.

RESULTS AND DISCUSSION

The first step of this research focused on synthesizing the equation for (AC-co-AN)/resole semi-IPNs. This was achieved by reacting acrylic acid-co-acrylonitrile with phenol formaldehyde in a 1:1 ratio. The resulting product is the (AC-CO-AN)/resole semi-IPNs, as depicted in reaction schemes 2, 3, and 4.
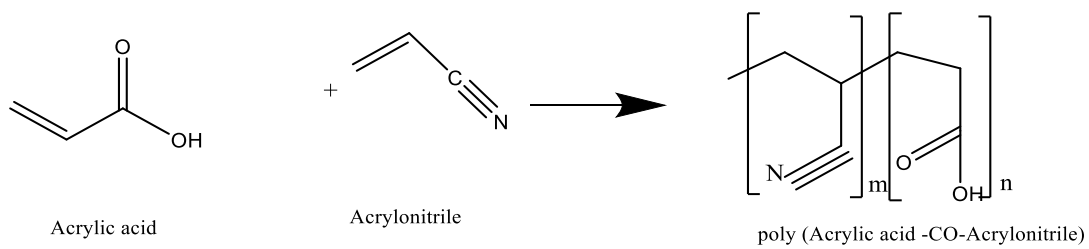
Scheme 2. Equation reaction of Acrylic acid and Acrylonitrile as copolymer**.**
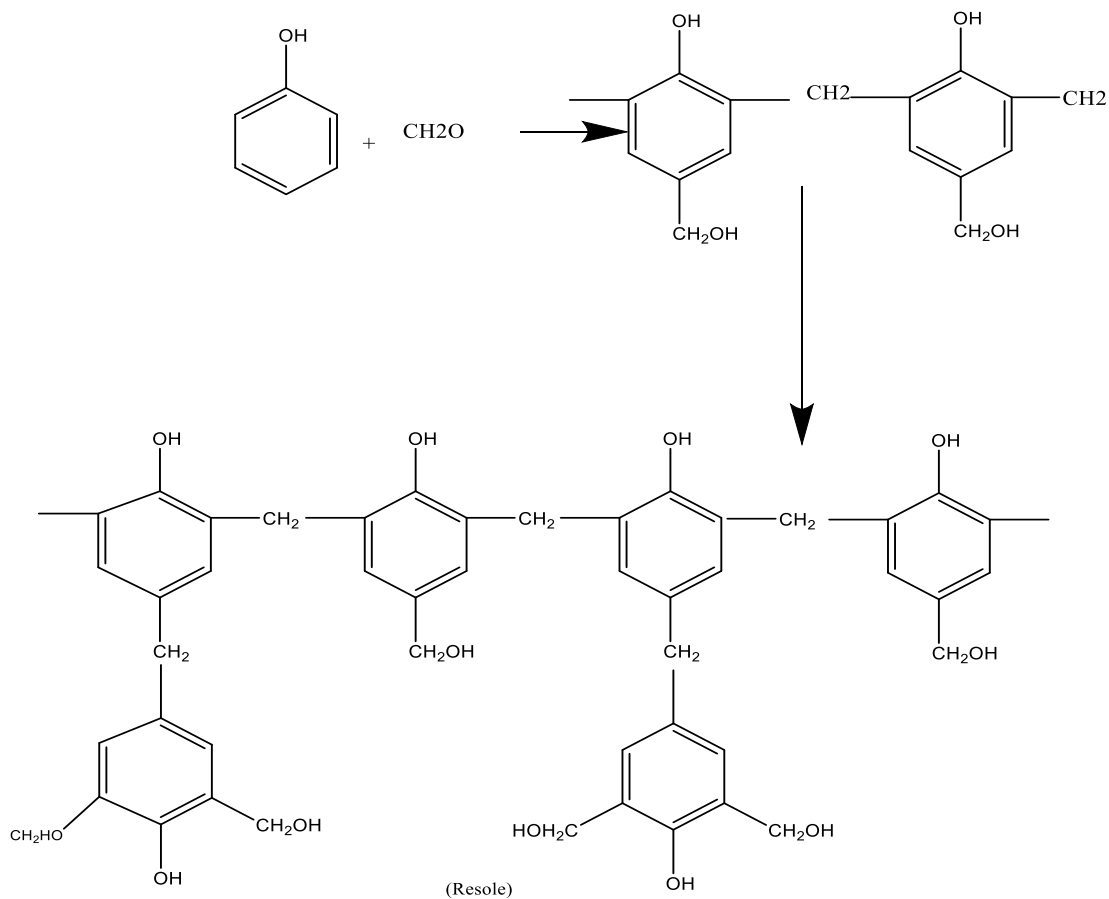
**Scheme 3.** Equation reaction of phenol formaldehyde as resin**.**
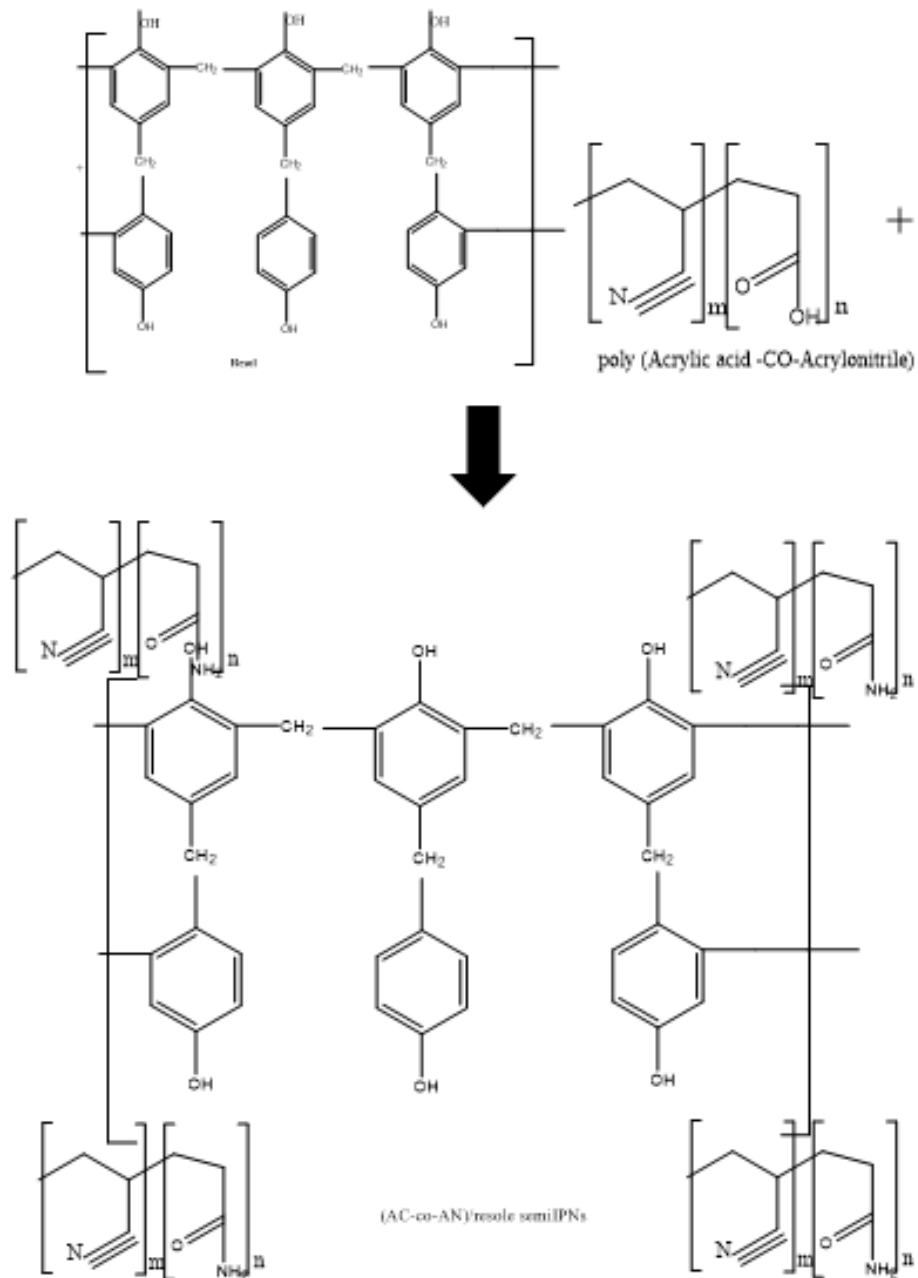
Scheme 4. Equation reaction of (AC-co-AN)/resole semi-IPNs.

The FTIR:

The spectrum of (AC-co-AN)/resole semi-IPNs Figure. 1 showed that the revealed two distinct absorption bands at 3259.80 cm^{-1} and 2967.22 cm^{-1}, attributed to (OH) and (CH). (C≡N) carboxyl and (C=O) acrylic acid absorption bands were detected at 1733.08 cm^{-1} and 1685.71 cm^{-1}, respectively.
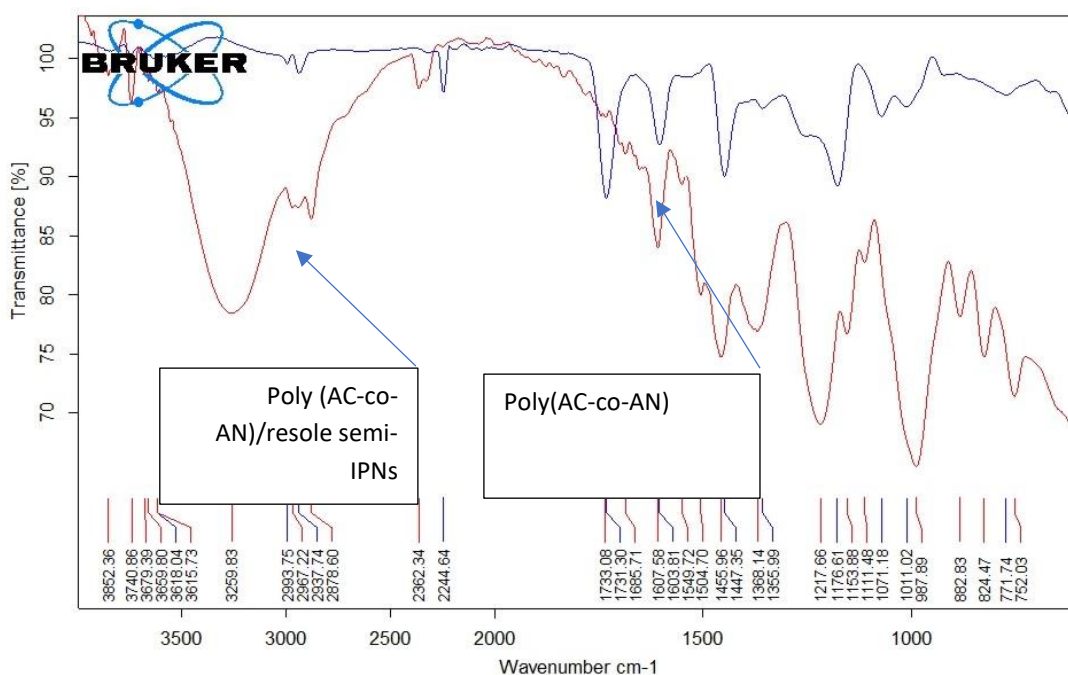
Fig. 1: IR spectra for polymer (AC-co-AN), (AC-co-AN)/resole semi- IPNs**.**

Thermal Analysis (TGA and DSC):

Thermogravimetric analysis (TGA) is a technique widely used to investigate the thermal characteristics of polymers. It allows for the determination of polymer stability by measuring the decomposition temperature. Another technique, called differential scanning calorimetry (DSC), analyzes the changes in heat flow as temperature varies, providing valuable information about the polymer's behavior during heating or cooling.

In the case of Copolymer (AC-co-AN) and (AC-co-AN)/resole IPNs, TGA and DSC revealed three distinct thermal events, as shown in Figure 2. The first event, occurring below 130°C, is attributed to the desorption of moisture and evaporation of residual traces. Between 130°C and 320°C, the weight loss of poly (AC-co-AN) is primarily due to the decarbonylation of the polyacrylic moiety. On the other hand, for IPNs, the main weight loss occurs between 180°C and 400°C, as depicted in Figure 3. At higher temperatures, intramolecular interactions and cross-linking of the polymer become evident, leading to significant weight loss (Li, H *et al.,*2008, Shen, X.Y., G.I. Gong and Wang, D., 2008, Henrici, O.G., and Olive, S., 2005, Nurettin, S., Pekel, N., and Gaven, O., 1999,).

The DSC curves of poly (AC-co-AN) exhibit a decrease in released heat as the acid content of the copolymer increases. Furthermore, these curves become broader, indicating changes in the polymer's thermal behavior (Somaye, A *et al.,* 2016,). The DSC curve of IPNs displays two peaks: the first one is a wide endothermic peak occurring at 125.6°C, corresponding to dehydration. The second exothermic peak, observed in the temperature range of 330°C to 400°C, signifies the degradation of the main structure of IPNs. The weight loss between 150°C and 320°C is attributed to the degradation of the chain structure of (AC-co-AN) copolymers (Wenj, Y *et al.,*2021)
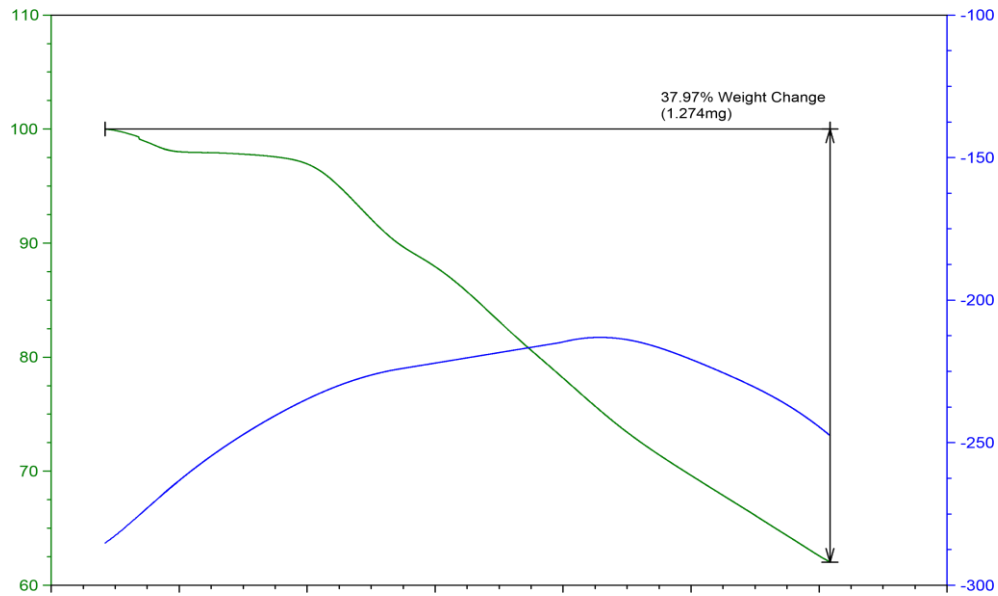
**Fig. 2.** Thermogravimetric and differential Scanning Calorimetry profiles for poly (AC-co-AN)**.**
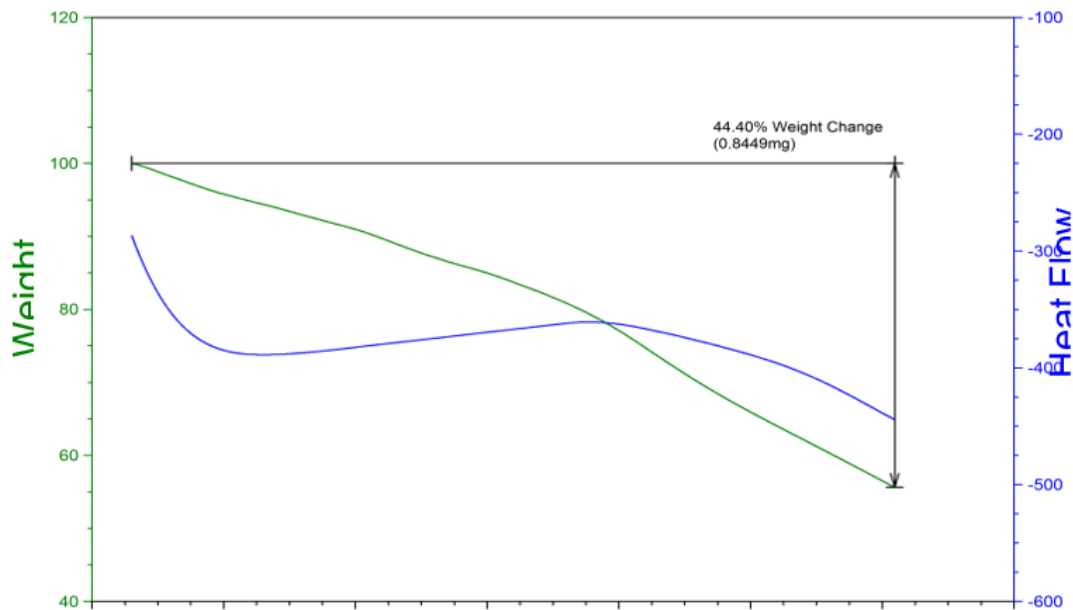
Fig. 3. Thermogravimetric and differential Scanning Calorimetry profiles for poly (AC-co-AN)/resole semi- IPNs.

X-Ray Diffraction:

Measures enable the determination of the relative proportions of crystallinity within the interconnected network sites in relation to copolymers, as well as facilitate the exploration of complexation phenomena. Figure (4), presents the diffraction model for poly (AC-co-AN). In the case of poly (Ac-co-AN), it was observed that peaks appeared at 2ɵ values of 18.2 and 25. The first peak corresponds to the crystalline regions of the (AC-co-AN) copolymer, while the second peak indicates the presence of the amorphous phase (Silva, M. A. *et al.,* 2011) This copolymer exhibits a semi-crystalline nature with low crystallinity index. The IPNs (Interpenetrating Networks) formed by poly (AC-co-AN) exhibit a modified diffraction pattern. This pattern shows a reduction in the intensity of the peaks at 2ɵ values of 25 and 18, along with the emergence of new peaks at 2ɵ values of 32°, 46°, and 57° (Fig. 5). These results suggest that the structure of the IPNs possesses a higher degree of crystallinity compared to the poly (AC-co-AN) copolymer.
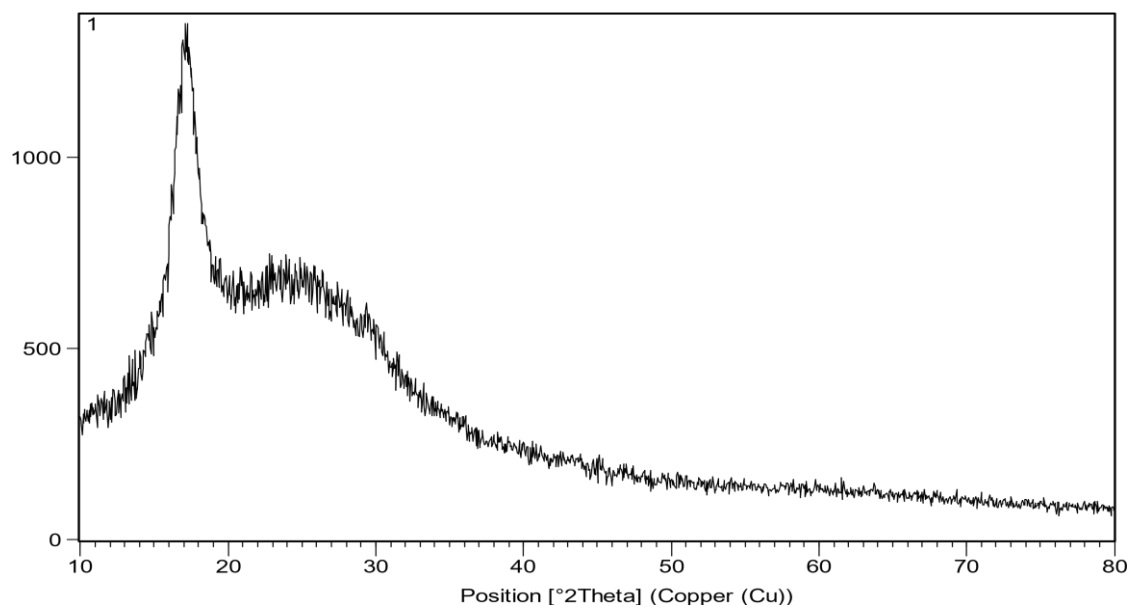
Fig. 4. XRD of poly (AC-co-AN).
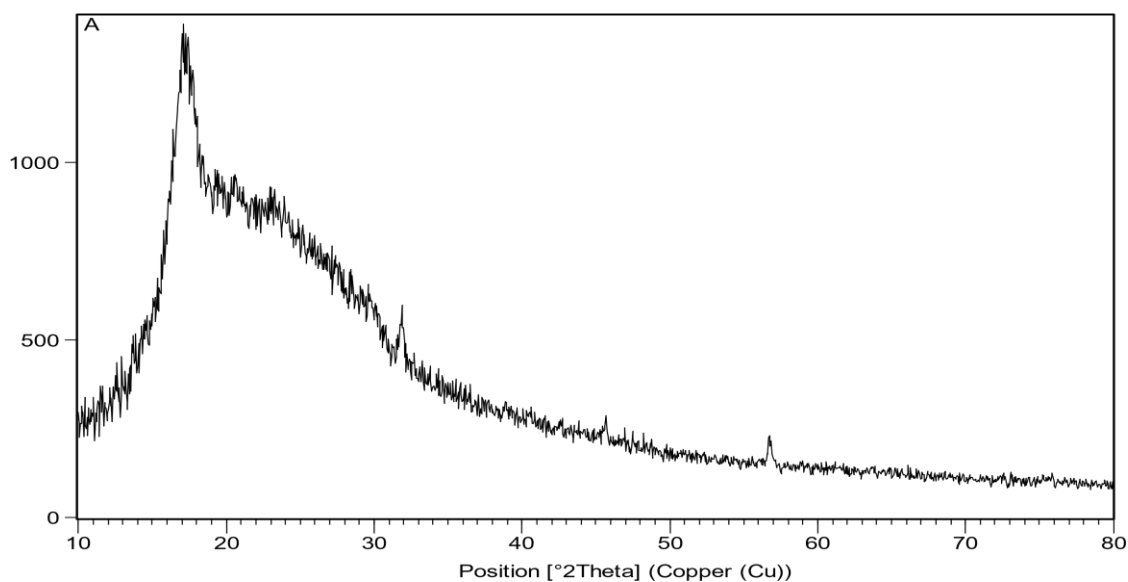
Fig. 5: XRD of poly (AC-co-AN)/resole semi- IPNs**.**

FESEM:

Field emission scanning electron microscopy (SEM) was utilized to observe the surface morphology of the copolymer consisting of acrylic acid and acrylonitrile (AC-co-AN), as well as the interpenetrating polymer networks (IPNs) of (AC-co-AN) and resolve semi.

Figure (6) demonstrates that the (AC-co-AN) samples exhibit a distinct irregular granular structure. The microbeads display a spherical shape, which is advantageous for surface adsorption. The surface morphology of

(AC-co-AN) is characterized as smooth. However, upon the conversion of (AC-co-AN) to (AC-co-AN)/resole semi-IPNs, the surface morphology becomes rougher. The introduction of resole into (AC-co-AN) further contributes to an increase in surface roughness. Figure (7), illustrates that the particle size of the poly (AC-co-AN)/resole semi-IPNs is approximately 216 nm, which is larger compared to that of poly (Ac-co-AN) measuring approximately 210 nm (Ramya, R., *et al.,*2011).
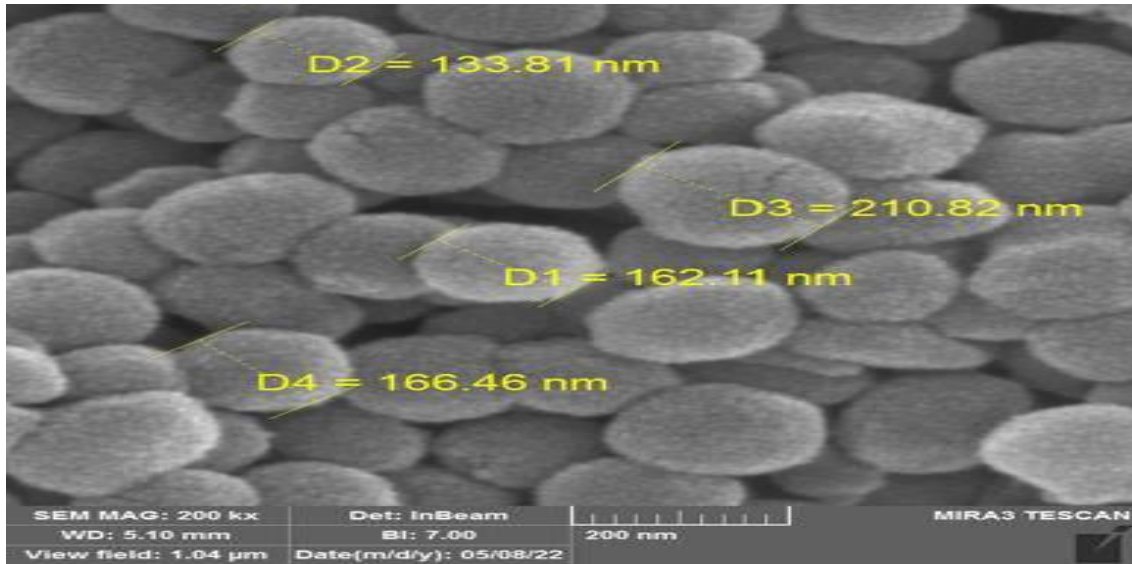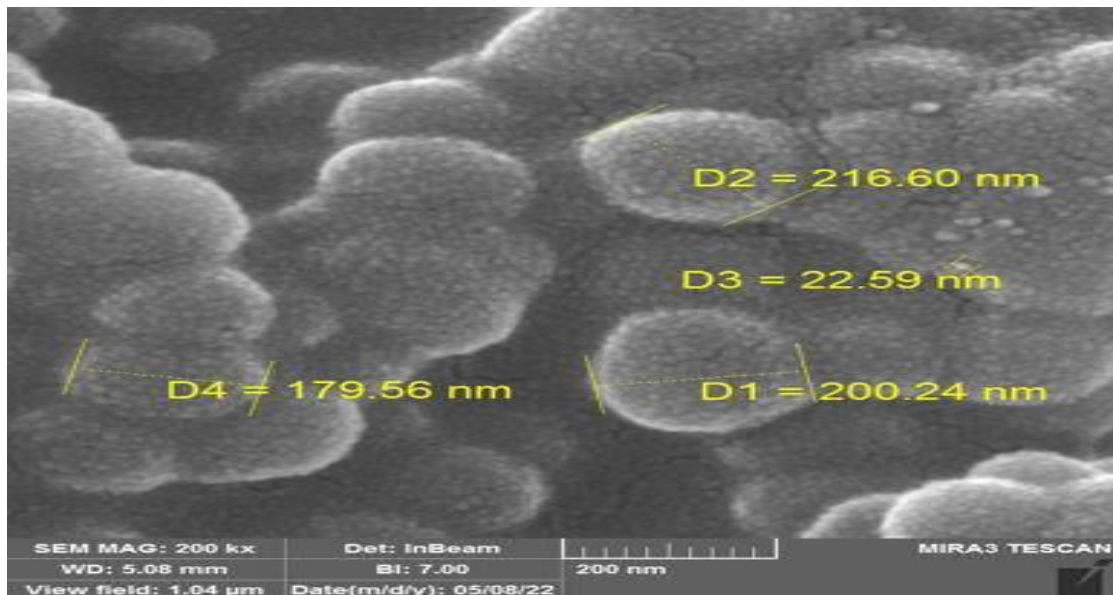
Fig. 6. SEM of poly (AC-co-AN**).**

Fig. 7. SEM of poly (AC-co-AN)/resole semi- IPNS.

Removal of Metal Ions (Adsorption):

The percentage of adsorption for the interaction between (AC-co-AN)/resole semi-IPNs and lead ions was quantified. The (AC-co-AN)/resole semi-IPNs were precisely dispersed in a 10 mL solution containing 100 mg/L of cations (Pb2+). The impact of pH, the quantity of AC-co-AN/resole semi-IPNs, and the duration of agitation on the adsorption of Pb2+ ions from aqueous solutions were examined.

Study of Adsorption Isotherms:

By appropriately diluting the original solution, we created five solutions of (Pb+2) with concentrations of 5, 10, 20, 30, and 40 ppm. These solutions were prepared in accordance with the desired concentrations for studying the adsorption isotherm of the chosen adsorbent. The best conditions were reached by fine-tuning the pH, adsorbent dose, adsorbent particle size, agitation speed, temperature, and contact time After that, we filtered the suspensions and analyzed the filtrates with a flame atomic absorption spectrophotometer to see how much (Pb+2) was left. Standard linear equation (2) for the Langmuir isotherm construction:

$1/q = 1/(b\ q_m\ C_e) + 1/q_m$ ……… **(2)**

The Langmuir isotherm parameters are q_m (mg g-1) and b (L g-

1), and 'q' (mg g-1) indicates the amount of adsorbed metal ions, 'Ce' (ppm) represents the equilibrium concentration of the metal, and 'b' (L g-1) represents the surface area. The slope and intercept of a linear plot of 1/q versus 1/Ce were used to generate these values Using the same linear standard equation (3), we may visualize the Freundlich isotherm:

Log q = log KF + (1/n)*log (1/Ce) ……….. (3)

The Freundlich isotherm constant, KF, can be calculated from the intercept, and 1/n is derived from the

slope of the linear plot of log q versus log Ce to complete the equation.

Table 1. Adsorption Freundlich and Langmuir constant parameters.

Freundlich Isotherm Parameters	Pb $^{+2}$
^{1}/n	3.645
Kf	1.045
R^2F	0.9657
Langmuir Isotherm Parameters	Pb^{+2}
Qm (mg g-1)	12.555
b (L g–1)	3.950
R^2 L	0.7664
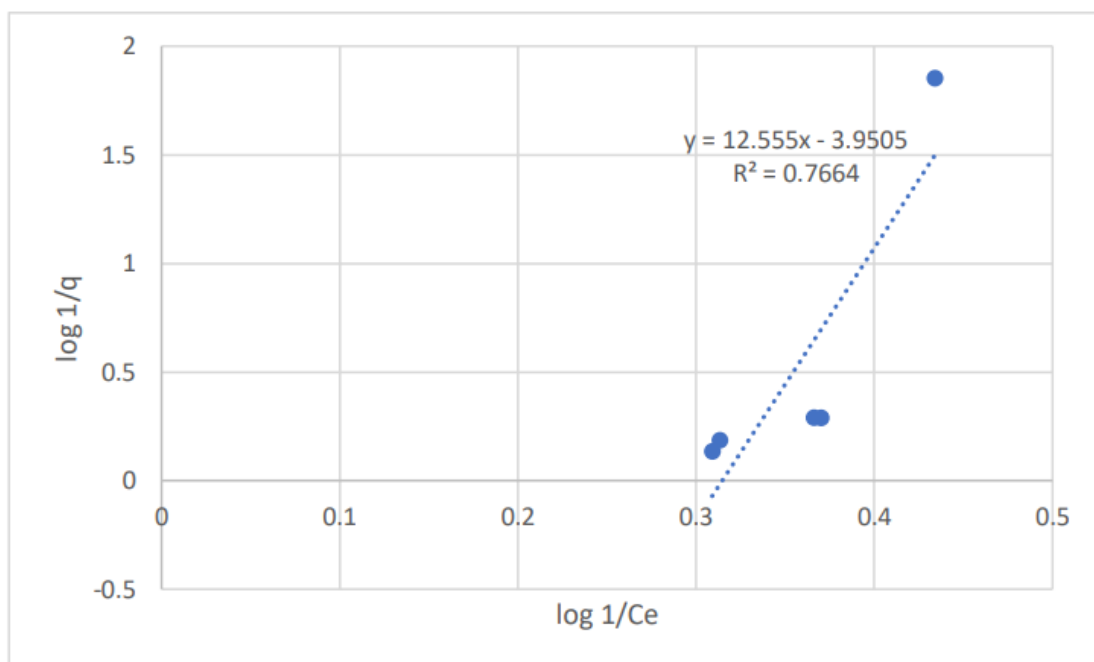
Fig. 8. Langmuir adsorption isotherm for metal adsorption by poly (AC-co -AN)/resol semi-IPN's) at pH=4, shaking rate of 180 rmp, amount of adsorbent 0.1g.
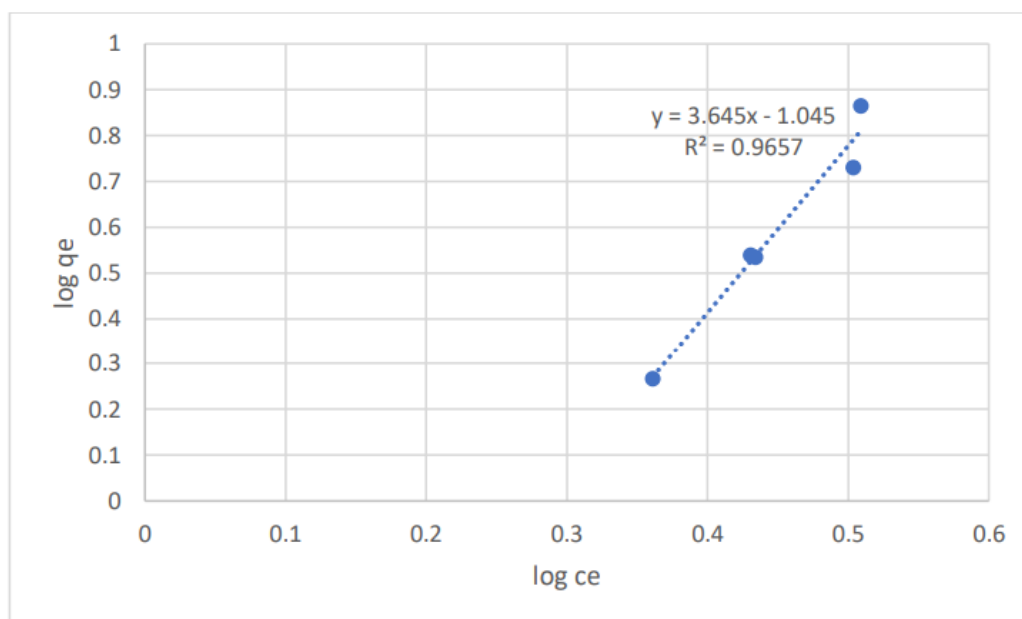
Fig. 9. Freundlich adsorption isotherm for metals adsorption by poly (AC-co - AN)/resole semi-IPN's) at pH=4, shaking rate of 180 rmp, amount of adsorbent 0.1g.

Adsorption Isotherms:

The metal ion concentrations were varied as 5, 10, 20, 30, and 40 ppm while maintaining a constant adsorbent dosage of 0.1 g and an optimal pH of 4. These conditions facilitated the investigation of the adsorption capacity of the metal in this study. Figures (8 nd 9), present graphical representations of the Langmuir and Freundlich isotherms, respectively, along with their associated parameters. The Freundlich isotherm demonstrated higher correlation coefficient (R^2) values compared to the Langmuir isotherm, indicating that the Freundlich model provides a better fit to the data, as determined through linear regression analysis. This observation supports the notion that the Freundlich isotherm can effectively describe the adsorption of metal ions (Pb+2) from solutions onto the surface of the poly (AC-co-AN) or resole semi-IPNs developed in this study when employing the multilayer mode rather than the monolayer mode. The linear applicability of the Freundlich isotherm over the Langmuir equation makes it more suitable for describing the adsorption process of the investigated ions and IPNs (Sangeetha, V.; 2013,).

Effect of PH:

The study investigated the impact of pH on the removal of metal ions. As the solution becomes more acidic, the concentration of H+ ions increase. The removal of metal ions is influenced by the availability of oxygen atoms in acrylic acid, which possess an affinity for lead ions. The presence of an increased number of H+ ions compete with the pb2+ ions, leading to a decrease in the adsorption rate. Consequently, determining the ideal pH of the solution becomes crucial. To explore the relationship between H+ ion concentration and metal removal, pH levels ranging from 2 to 8 were examined. The Figure (10) illustrates the way Pb2+ ions are eliminated depending on the pH using the (AC-co-AN)/resole semi-IPNs. Notably, the adsorption of metal cations displayed an increase within the pH range of 4 to 6. Under these acidic conditions, the ion undergoes complete dissolution, resulting in a more stable binding with the IPNs. However, beyond a pH of 6, lead hydroxide ions commence precipitation. The highest metal adsorption occurred within the pH range of 4 to 6. Consequently, a pH of 4 to 6 was determined as the optimal range for subsequent measurements.
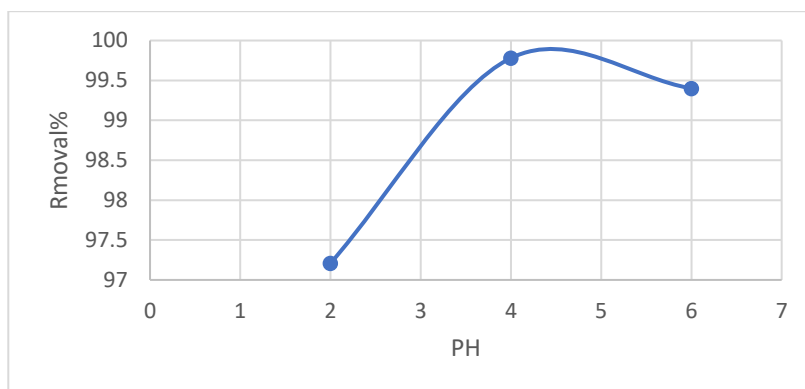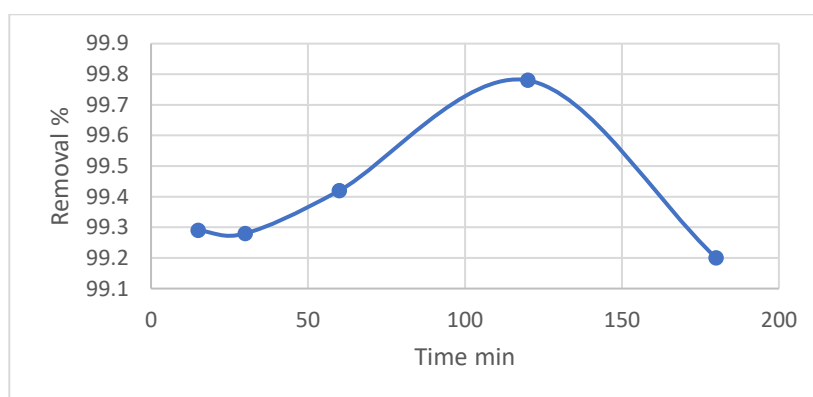
Fig. 10: Effect of pH on adsorption of lead ions on (AC-co-AN)/resole semi- IPNs**.**

Effect of Time on Adsorption:

The contact time serves as a vital parameter within the adsorption process, offering insights into the equilibrium duration required for optimal adsorption. An extensive investigation of contact time was conducted, spanning various intervals from 15 minutes to 180 minutes, with the intention of assessing the influence of time on the efficacy of metal ion removal utilizing (AC-co-AN) /resole semi-IPNs. Figure (11) illustrates the graphical representation of the removal percentage of metal ions (specifically Pb2+) as a function of time.

Fig. 11: Effect of Time on Adsorption of lead ions on (AC-CO-AN)/resole semi-IPNs.

Study the Effect of Biological Efficacy:

After conducting the work method used in the dilution of IPNs and testing its effectiveness in inhibiting bacteria and preventing their growth, it was found in the end that the IPNs were used separately. He has the ability to inhibit the growth of bacteria at a different concentration level. Where this appeared by preventing the growth or reproduction of bacteria used in this test and as follows.

The poly (Acrylic acid-co Acrylonitrile)/resole-semi-IPNs, showed results with a high effect by inhibiting the growth of bacteria at a concentration level of, 4, i.e., in the fourth tube, (MA, W., (2006).

CONCLUSION

The results reveal that (AC-co-AN) or resole semi-IPNs may successfully remove Pb (II) from aqueous solutions. The adsorption of these metals was studied under a variety of conditions, including contact time and pH.

A solution's optimal pH for absorbing Pb (II) from an aqueous solution The Freundlich multilayer sorption model was used to predict the sorption of Pb (II) by AC-co-AN/resole semi-IPNs. IPNs he has high effectiveness and effect in inhibiting Streptococcus pyogenes bacteria.

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