



Kinetics Study of Heavy Metal Removal from Synthetic Aqueous Solutions Using Modified Poly(Methylmethacrylates)

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Article's Information	Abstract
Received: 26.12.2024 Accepted: 04.03.2026 Published: 15.06.2026	The investigative results from the elimination of the cadmium (II), nickel (II), and lead (II) ions into solution form utilizing p-aminoacetophenone modified poly (methylmethacrylates) are presented in the current paper. Fourier transform infrared spectroscopy (FTIR) was employed to characterize the modified polymer. The pH level in the solution, the time of the interaction, the starting concentration of a heavy metal and the dosage of adsorbent were all examined to better comprehend the adsorption procedure. Three models were utilized to examine the adsorption isotherm. Results showed that improved polymer could adsorb higher concentrations of heavy metal (II) ions. The PMMA-p-aminoacetophenone was found to have a maximum adsorption capacity of 8.9605, 15.552 and 7.2939 mg/g for cadmium (II), lead (II), nickel (II) ions respectively.
Keywords: Modified poly(methylmethacrylates), Adsorption, Metal ions. Kinetics.	

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1. Introduction

Wastewater created by manufacturing processing, or other institutional, commercial, and agricultural operations, as well as any operation that discharges effluent in addition to household or sanitary wastewater, is classified as industrial wastewater [1]. Wastewater contains both organic and inorganic chemical contaminants. The basic components of organic food are carbs, lipids, and protein. Among the inorganic pollutants that can be detected in wastewater are ammonia, nitrogen organic compound, nitrites, nitrates, and heavy metals [2]. Owing to the growing utilization of chemicals and metals in process industries, huge amounts of wastewater containing hazardous heavy metals have been produced. These metals persistence and non-degradability provide challenges for environmental disposal. Furthermore, hazardous liquid wastes are produced by extractive metallurgical, mining, and mineral processing activities [3]. Adsorption is the term used to describe

the rise in reactant concentration on the catalyst surface. This leads to either the fast advancement of reactions as well the overlapping of liquid-liquid, liquid-solid, gas-liquid, and gas-solid phases. Lack of an overlay structure causes the linkages in the surface layer to become disorganized. Since of this, the surface layer is referred to as being surface active since it has higher levels of energy. However a wide surface area with numerous active sites besides a porous structure are essential characteristics of effective Adsorbents [4]. Because of its affordability and convenience of use, adsorption is regarded as a very effective technology for treating water [5]. It involves the absorption and immobilization of contaminants within an adsorbent through associated processes such as structure adsorption, surfaces precipitation, partitioning, and surface adsorption [6]. There are two primary categories for adsorption. The first kind is where the intermolecular forces play a role in physical adsorption, also known as physisorption, in which

hydrogen bonds and Van der Waals forces induce the adsorbent and adsorbate to bind. While the second kind of adsorption, known as chemical adsorption or chemisorption, creates covalent forces via the sharing or exchange of electrons between the adsorbent and the adsorbate [7]. Adsorbents with nitrogen groups, for instance amine, hydrazine, thioamide, and imidazoline groups, not only chelate cationic metalation but also adsorb anionic adsorbates concluded electrostatic interaction [8]. Adsorbents with carboxyl, sulfonic, and phosphonic groups remove adsorbates concluded ion exchange [9]. Specifically, one of the best groups for eliminating heavy metal ions from aqueous solutions is an amine group [10]. The characteristics of an adsorbate material, including its form, size, concentration, as well as presence of polar groups, influences the interaction between the adsorbent surface with the adsorbate molecules. The interference involving the surface adsorbent and adsorbate particles, which results in the selective absorption of one of the constituents, is influenced by increases in molecular weight, polar group solubility [11]. Polymethylacrylate (PMA) hydrazide derivative was developed and used to remove (Cu^{2+}) via Langmuir isotherm formulation which provided the most accurate description of the adsorption process according to pseudo-first-order reaction model [12]. A double network made of (EDTA) cross-linked chitosan and N, N-methylene (acrylamide) cross-linked PAA. Numerous adsorption considerations were examined, for example the quantity of adsorbent, the pH, and the time [13]. Heavy metal ions are adsorbed by carboxyl functionalized magnetite nanoparticles (CMNP) [14]. The novel adsorbent CS-MA-DETA was first produced by grafting methyl acrylate and (DETA) onto chitosan (CS). Adsorption tests were conducted in Pb^{2+} and Cd^{2+} solutions [15]. It was effective, present modified lignin into the system. A significant adsorption capacity of 399.0 mg/g was displayed carboxyl and amine groups of adsorption with Cu (II) [16]. FTIR was used to study the modified poly (amidoamine)-graft-PMMA magnetic nanocomposite. The capability of the adsorbent to remove lead was experienced at altered pH values, initial lead concentrations, and contact time; the result is (310 mg/g) [17]. The current study examined the behavior of the adsorbent and the kinetics of metal ion adsorption onto a poly (methyl methacrylate) that is modified by the addition of a functional group (p-aminoacetophenone). Furthermore, the impact of pH, adsorbent quantity, and initial concentrations were examined. Using experiment data, pseudo first order and pseudo

second order adsorption kinetics were computed. The isotherm of the adsorption hypothesis based on Langmuir, Temkin and Freundlich was calculated.

2. Experimental part

2.1. Material

Analytical grade chemicals and reagents were employed in this study. $\text{Pb}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, $\text{CdCl}_2 \cdot \text{H}_2\text{O}$, polymethylmethacrylate (PMMA) and 2-propanol were purchased from Sigma-Aldrich p-aminoacetophenone was procured from Fluka. HCl and NaOH were also procured from Biochem. Stock solutions of 1000 mg/L Pb and Ni ions were prepared in deionized water via dissolving a suitable quantity of $\text{Pb}(\text{NO}_3)_2$, and $\text{Ni}(\text{NO}_3)_2$, $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ salts. Adjustments were made to the pH of the solution by adding either HCl (0.1 mol/L) or NaOH (0.1 mol/L).

2.2. Instruments

Atomic absorption spectrophotometer type AA-7000(Shimadzu, Japan) was used for determination of the concentrations of Pb^{2+} , Cd^{2+} and Ni^{2+} . Three replications were used to determine the metals, the percentage RSD did not exceed 5%. IR spectra were collected using FT-IR 8300 Spectrophotometer Shimadzu. WTW inoLab pH 7110 Benchtop Meter, (Germany) used in every experiment. Water Bath with Shaker type BS-11,230 VAC-50 Hz, (Korea) was used.

2.3. Preparation of the modified polymer

A mixture of 2.0 g polymethylmethacrylate and 40 mL isopropanol was stirred until the solution became clear, and then p-aminoacetophenone 0.2 g was added. The mixture was refluxed for 24 hours, the solvent was evaporated, and the modified polymer was collected [18,19].

2.4. Experimental procedures for batch adsorption

The adsorption studies were completed using a series of flasks, each one contains 20 mL of a solution containing 10 mg/L of metal ion. The solutions were stirred at 150 rpm at 25 OC. After that, the solutions were filtered. Further research was carried out to examine the effect of an absorbent dosage, pH of the solution, contact time and initial metal ion concentrations. Using an adsorbent dose of 50 mg and an adsorbate volume of 20 mL at certain concentration, the adsorption process was carried out in batch mode as a function of contact duration, pH and starting metal ion concentrations. Following the achievement of the equilibrium time, the liquid phase was obtained and evaluated. The starting metal cation concentration

was varied from 10 to 80 ppm, the solid-liquid contact duration was varied from 5 to 40 min, the pH was modified from 4 to 7, to conduct adsorption equilibrium tests. The values for Cd (II), Ni(II), Pb(II) ions have been determined by collecting filtrates of water and using atomic absorption spectrometry. The adsorption capacity of the sorbent material, expressed as Q_e (mg/g), and the percentage of metal ion removal were considered using equations (1) and (2) [20].

$$Q_e = \frac{V(C_o - C_e)}{m} \quad \dots (1)$$

$$R\% = \frac{(C_o - C_e)}{C_o} \times 100 \quad \dots (2)$$

The initial equilibrium levels of metal ions before and after the adsorption process are represented by the symbols C_o and C_e , respectively. V (L) represents the volume of the solution, m (g) represents the quantity of the material being adsorbed.

3. Results and Discussion

3.1. Characterization

Fourier transform infrared spectroscopy (FT-IR) has been used to investigate the differences between the functional groups of PMMA before and after the modification. As seen in Figure 2, the infrared spectrum of polymethyl methacrylate (PMMA) shows a carbonyl stretching vibration at 1721cm^{-1} , 2943cm^{-1} and 2854cm^{-1} for the symmetric and asymmetric stretching vibration of CH_2 aliphatic. 1138cm^{-1} of stretching C-O-C , 749cm^{-1} of C-H out-of-plane [21], the two bands at 980 , 1238cm^{-1} of (C-C) [22]. The spectrum of PMMA-*p*-aminoacetophenone (Figure 3) shows a band at 1660cm^{-1} , 1597cm^{-1} that of (C=C) , band at 3039cm^{-1} (aromatic C-H) [23]. A band at 3230cm^{-1} of (NH) stretching of amide, the overlap bands at 1724 - 1680cm^{-1} of $-\text{C=O}$ of ester and amide respectively. On the other hand, the bands at 983 , 1239cm^{-1} refer to (C-C) . bands at 1273 , 1386cm^{-1} of (C-N) whereas the 1142cm^{-1} of C-O-C , 2957 , 2851cm^{-1} of (Aliphatic $-\text{CH}$) [24].

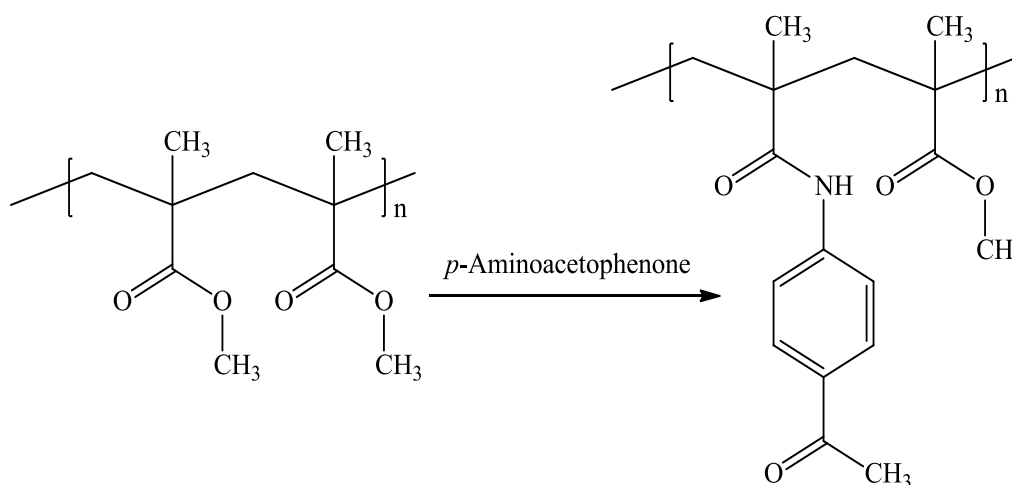


Figure 1. The structure of modified (PMMA) with *p*-aminoacetophenone.

3.2. Effect of adsorbent amount

The following dosages of PMMA-*p*-aminoacetophenone were used to study the influence of dosage on the removal % besides adsorption capacity (Q_e): 0.05 g, 0.06g, 0.07 g, 0.08 g, 0.09 g, and 0.1 g in a 20 mL solution with 10 mg/L of metal ion, every other variable was kept constant during the experiment. The outcomes exhibited that while more adsorbent was employed, the proportion of metal ions removed [25]. As seen in Figure 4, the observed reduction in adsorption capacity in conjunction with consecutive increases in mass

doses exceeding 2.5 g/L for every ion may result from partial agglomeration of adsorbent particles. This partial aggregation reduces the effective surface area that facilitates the adsorption process. Another explanation for this phenomenon might be that more sorption sites become available as the dose of sorbent is increased. This therefore results in certain adsorption sites remaining unsaturated during the whole adsorption procedure. This might be caused by the fact that the solution contains insufficient metal ions relative to the binding sites that are currently present [26].

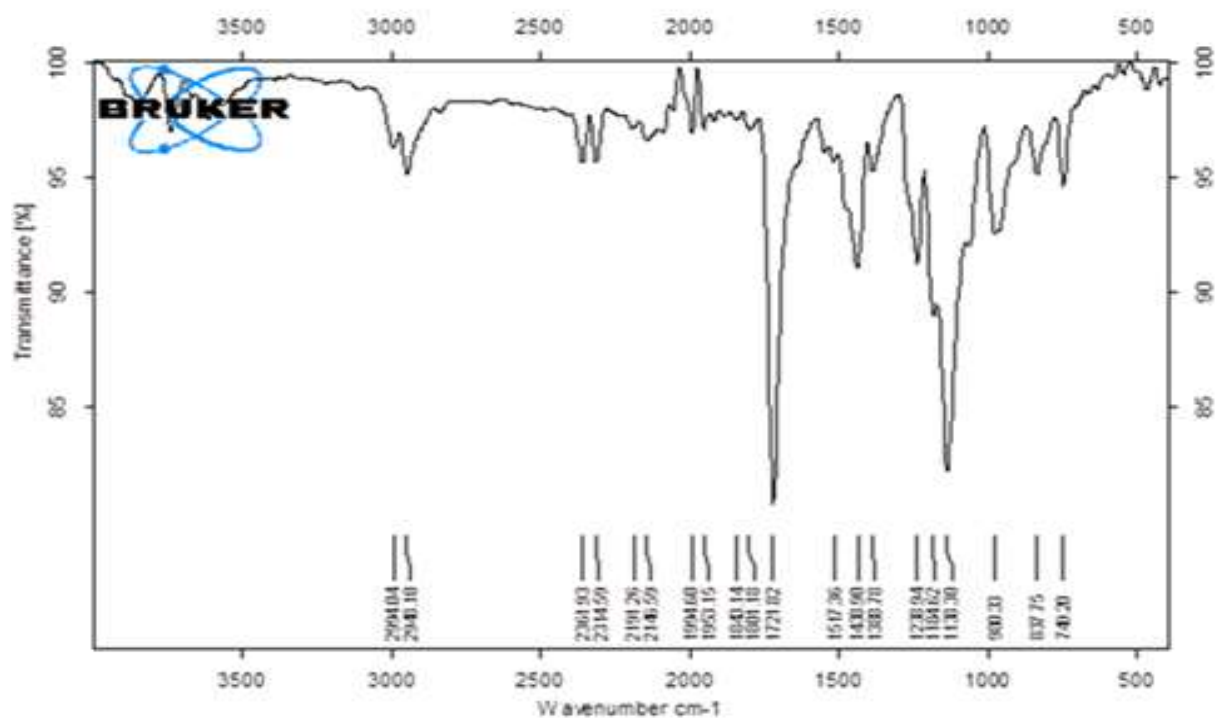


Figure 2. FTIR spectrum of polymethylmethacrylate (PMMA).

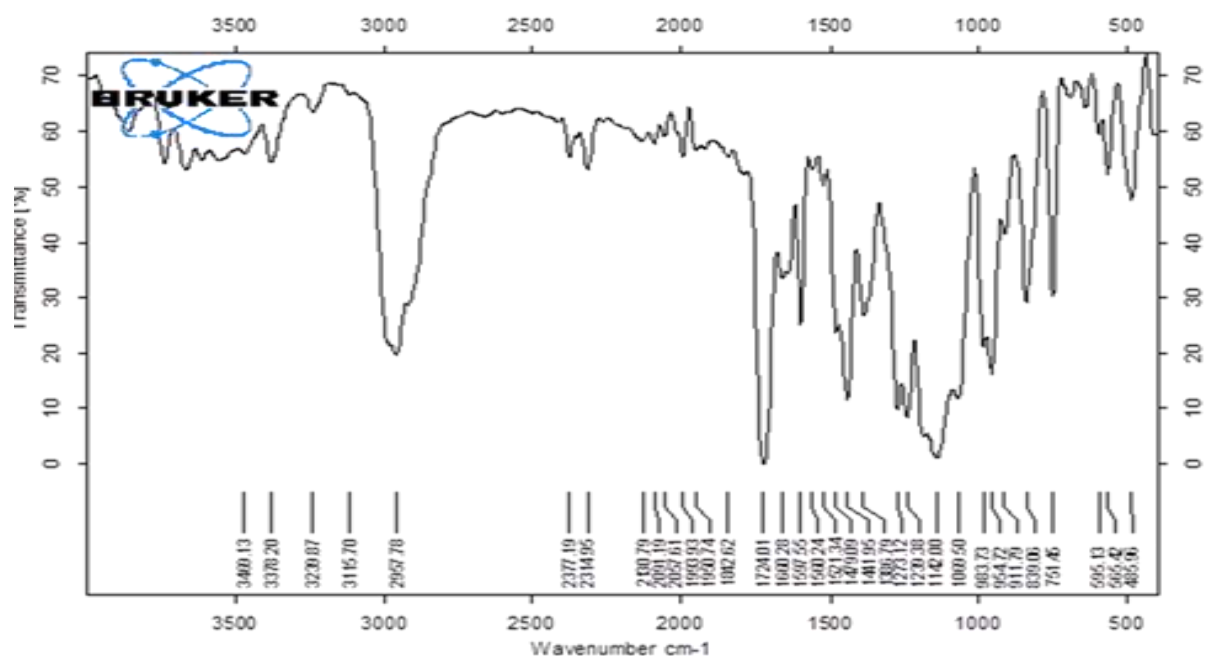


Figure 3. FTIR spectrum for modified (PMMA) with *p*-aminoacetophenone.

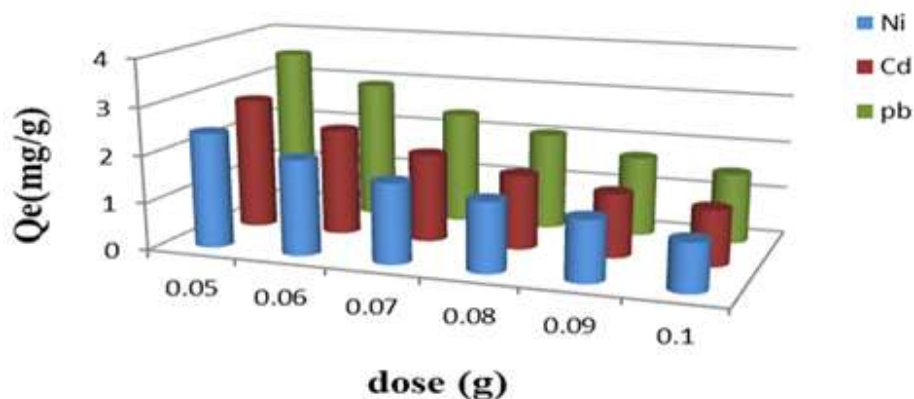


Figure 4. PMMA-*p*-aminoacetophenone dosages impact on Q_e (mg/g) (298 K, 150 rpm, pH: 4-5, 30 min).

3.3. Effect of the pH

The pH of the solution has a considerable effect on the adsorption behavior since it affects the solubility of the metal ions as the functional group (carbonyl oxygen) for the adsorbent that are used. This means that a key element influencing adsorption behavior is the pH of the solution [27]. Intrinsically, the ideal pH range must be maintained during the adsorption process. An examination on the effect of pH on adsorption method was conducted ideal pH is (5-

5.5), and the results are displayed in Figure 4. Since at low pH levels, positively charged metal ions are electrostatically repelled by the high H^+ ion concentration at the interface, preventing them from approaching the polymeric surface [28]. On the other hand, metal hydroxides begin to precipitate in the solution at the greatest feasible pH level, which is about greater than seven, which aids in slowing down the adsorption process [29].

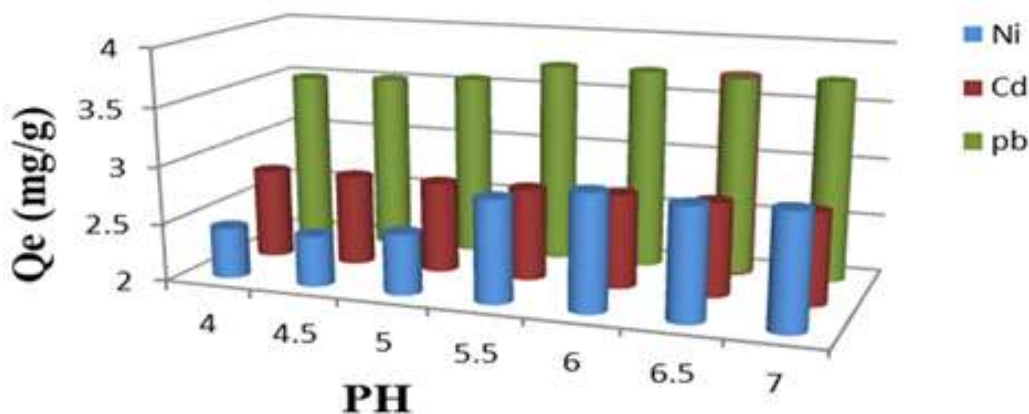


Figure 5. Impact of pH on adsorption.

3.4. Effect of the time

The effect of time (5, 10, 15, 20, 25, 30, 35, 40 min.) on the adsorption of metal ions by PMMA-*p*-aminoacetophenone was illustrated (Figure 6). The adsorption effectiveness increases linearly with the duration of the experiment because of the interaction that occurs between the Cd (II), Ni(II) and Pb(II) ions and the surface of the substance that

adsorbs. The adsorption material and the Cd (II), Ni(II) and Pb(II) ions reached a condition of equilibrium around thirty minutes. The adsorbent particles pack in over time, covering the adsorption sites. About 30–35 min equilibrium is reached, and the adsorbents active sites are saturated, or exhausted [30].

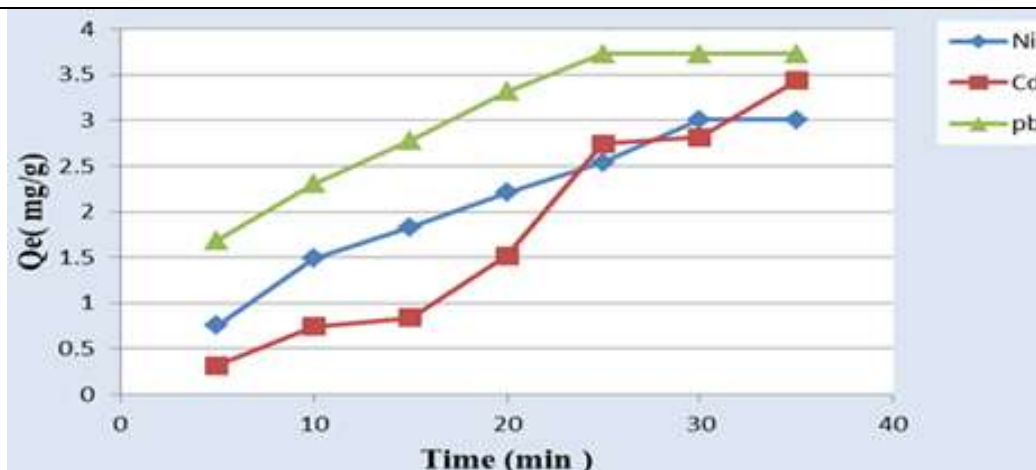


Figure 6. Effect of time (min) on adsorption capacity.

3.5. Adsorption Kinetics

To examine the absorption performance of metal ions, research has been done on their adsorption kinetics. About 30 minutes, the adsorption rose significantly before steadily trending in the direction of equilibrium. A possible explanation for this phenomenon is that as the adsorption capacity rose, fewer sites became available, which therefore caused the rate to decrease. In the beginning, there were quiet many sites accessible [10]. The following equations may be used to explain the conventional approaches for fitting kinetic information: eq. (3) denotes the pseudo first order equation (PFO), and eq. (4) denotes the pseudo second order (PSO). The following equations might be used to characterize these models.

$$\ln(q_e - qt) = \ln q_e - k_1 t \quad \dots (3)$$

$$\frac{t}{qt} = \frac{1}{k_2 qe^2} + \frac{t}{qe} \quad \dots (4)$$

The adsorption capacity at time (qt) also at equilibrium (qe) [31]. The capacity for sorption on the solid phase constitutes the basis for a second order equation. It makes general behavioral estimates. It also resembles to the idea which states that rate-determining sorption is chemisorption [16]. The results demonstrated that the P.S.O. equation was more successful in matching the experimental data in relations of coefficients. Additionally, there was a significant connection between the calculated Qe values and the experimental outcomes (Qe, exp). Because of this, the adsorption of metal ions resembled the P.S.O. model, which was created in accordance with the chemisorption theory, which includes valency forces through electron sharing as well as exchange between the adsorbent and substrate. One benefit of

using this type of model is that it may be estimated Qe instantly, avoiding the need to know details, also provides an initial adsorption rate [32].

3.6. The isotherm of adsorption and metal ion concentrations effects

The effect of an initial metal ion concentration (10–80 mg/L) on the adsorption capacity of PMM-p-aminoacetophenone was studied under the ideal pH, adsorbent dosage, and duration as mentioned. The strong force produced by the initial concentration of metal ions helps to overcome any mass transfer barrier of metal ions throughout the two phases. Consequently, the outcomes show that adsorption capacity grows proportionately according to the starting metal ions concentration, since most binding sites are empty, this rise can be explained by competition for the binding sites that are accessible, after which it either stays the equivalent or somewhat alterations and this is since the sorption sites of the modified polymer have saturated [33]. On the other hand, selecting the appropriate isotherm adsorption model over a range of concentrations offers a clear picture of the surface [34]. Model of isotherm have been examined by means of models: Freundlich, Temkin and Langmuir.

3.6.1. Langmuir isotherm

The Langmuir isotherm variable is generated by the fifth equation, which is found by a plot of $1 / Q_e$ against $1 / C_e$. As a result, a completely uniform adsorption surface is where adsorption occurs [35].

$$\frac{1}{Q_e} = \frac{1}{b Q_{max} C_e} + \frac{1}{Q_{max}} \quad \dots (5)$$

The $1/Q_e$ vs $1/C_e$ plot was used to determine the numerical values associated with the Langmuir parameters b and Q_m . Table 2 displayed: Q_m , b , and the correlation coefficient (r). The Langmuir model showed high values of (r) more than (>0.96) for Pb^{2+} , Ni^{2+} and Cd^{2+} ions. A homogeneous surface experiences sorption due to complexation, which is caused via coordination or ion exchange routes, as

indicated by the Langmuir isotherm model fit. There are no noticeable interactions amongst the adsorbate throughout this process; instead, metal ions are adsorbed as a monolayer. Furthermore, the values for equilibrium constant RL range between 0 and 1, indicating that the adsorption is favorable [36].

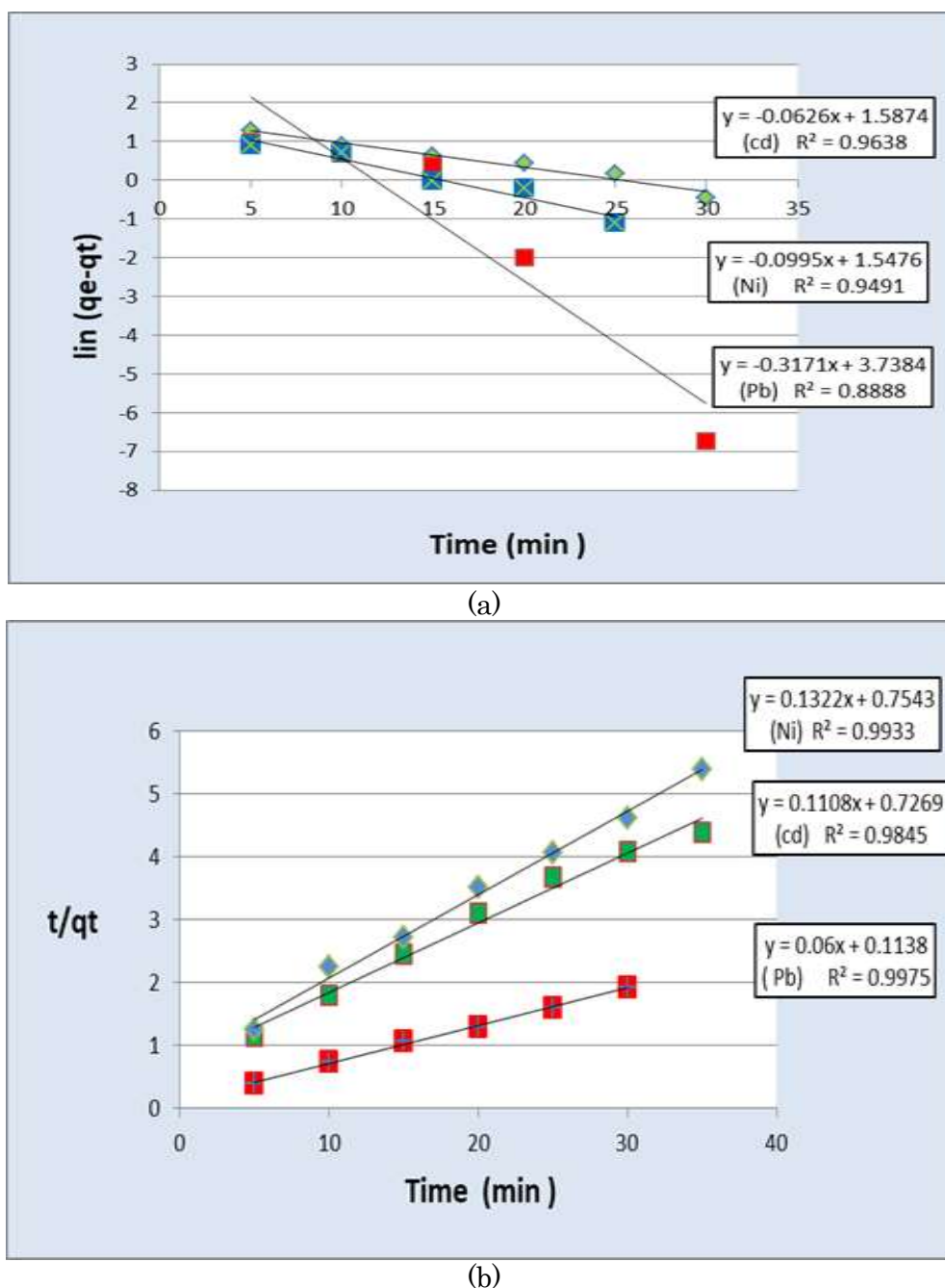


Figure 7. Plots of (a) the pseudo first order kinetics (b) the pseudo second order kinetics for adsorptions on PMMA-PAAP (dose 2.5 g/L; 60 mg/L Pb^{2+} , 30 mg/L Cd^{2+} , 30 mg/L Ni^{2+} ; $T = 25^\circ C$).

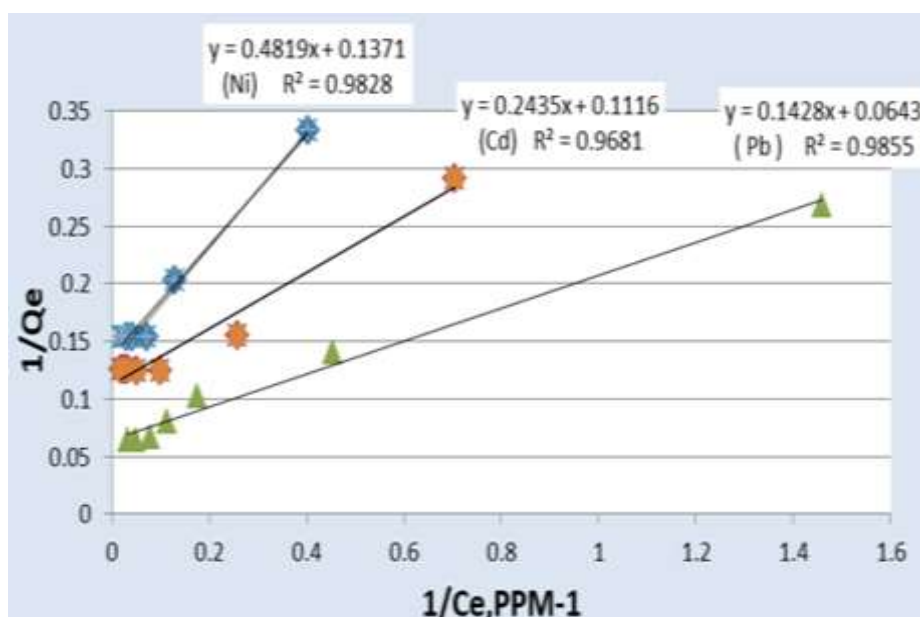


Figure 8. Langmuir isotherm model for adsorption of Ni(II), Cd(II) and Pb(II) (50mg PMMA-*p*-aminoacetophenone, pH 5-5.5, 25°C).

The findings demonstrated that the adsorption capacity of lead ions was better than that of cadmium ions and nickel ions. The decline in Q_m (mg/g) is explained by the characteristics of individual metal ions, including electronegativity, ionic potential, radius, charge, and electron configuration. The capacity of an atom to draw electrons towards itself in a covalent connection is known as electronegativity, and it is a chemical feature. Consequently, the electrostatic interaction between the dissolved ions and the surface charge has a greater impact on the surface complexation process. Pb^{2+} (2.33) has a somewhat stronger electronegativity than Cd^{2+} (1.69) and Ni^{2+} (1.91), meaning that lead ions interact strongly with the surface groups on the adsorbents surface, an additional consideration is the ionic radius. More water molecules are drawn to the smaller ions with the identical valency because they have greater

charge densities, leading to an increased hydrated radius. Consequently, Pb^{2+} has a lower hydrated radius due to its greater ionic radius (1.21 Å) than Cd^{2+} and Ni^{2+} , making the adsorbent and these ions interact less strongly [37]. Another factor for clarification, the Pb(II) ion has a higher affinity to misplace water molecules from the aquo-cations due to its single ion hydration enthalpy, which is around -1,481 kJ/mol, compared to -1,807 kJ/mol for the Cd(II) ion. As well, this makes interaction easier for the Pb(II) ion and the surface of the adsorbent [15].

3.6.2. Freundlich isotherm

Its foundation is the asymmetric dispersion of adsorbates brought about by multilayer adsorption, which was clarified as follows:

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad \dots (6)$$

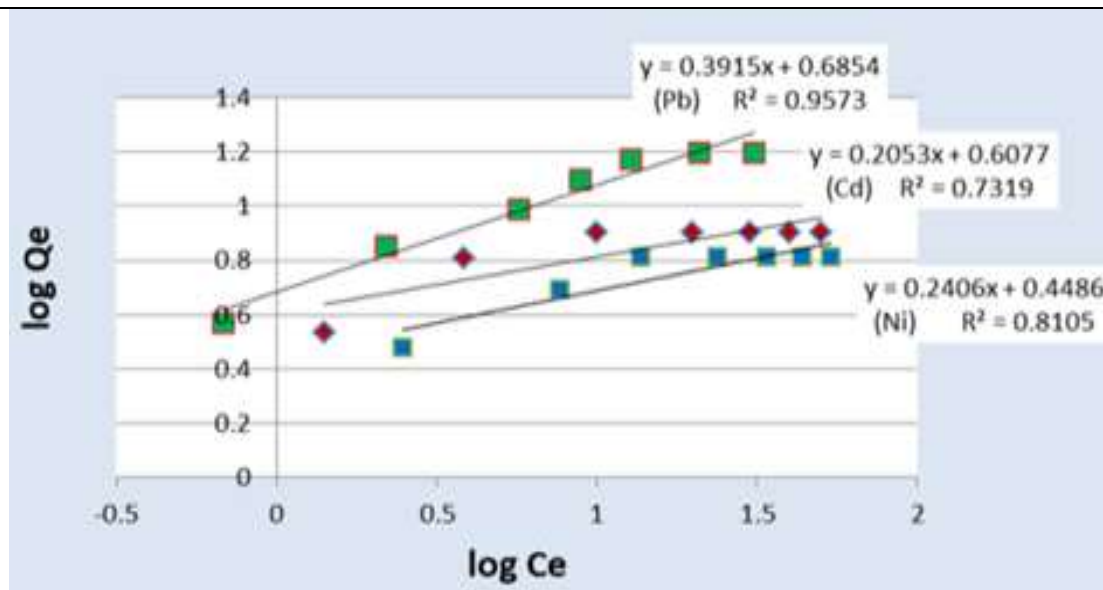


Figure 9. Freundlich isotherm model for adsorption of Ni(II), Cd (II) and Pb(II) (50mg PMMA-*p*-aminoacetophenone, pH 5-5.5, 25°C).

The Freundlich isotherm variables were shown to be predictable by plotting of $\log Q_e$ against $\log C_e$, shown in figure (8). Initial concentration is represented by C_e (mg/l), adsorption capacity is denoted by K_f , and equilibrium adsorption capacity is characterized by q_e . The adsorption intensity is characterized by $(1/n)$; if $1/n < 1$, the system is

regarded as favorable. Moreover, $1/n$ is a heterogeneity factor [38].

3.6.3. Temkin isotherm

Temkin isotherm possibly will be attained via beneath equation:

$$Q_e = BT \ln AT + BT \ln C_e \quad \dots (7)$$

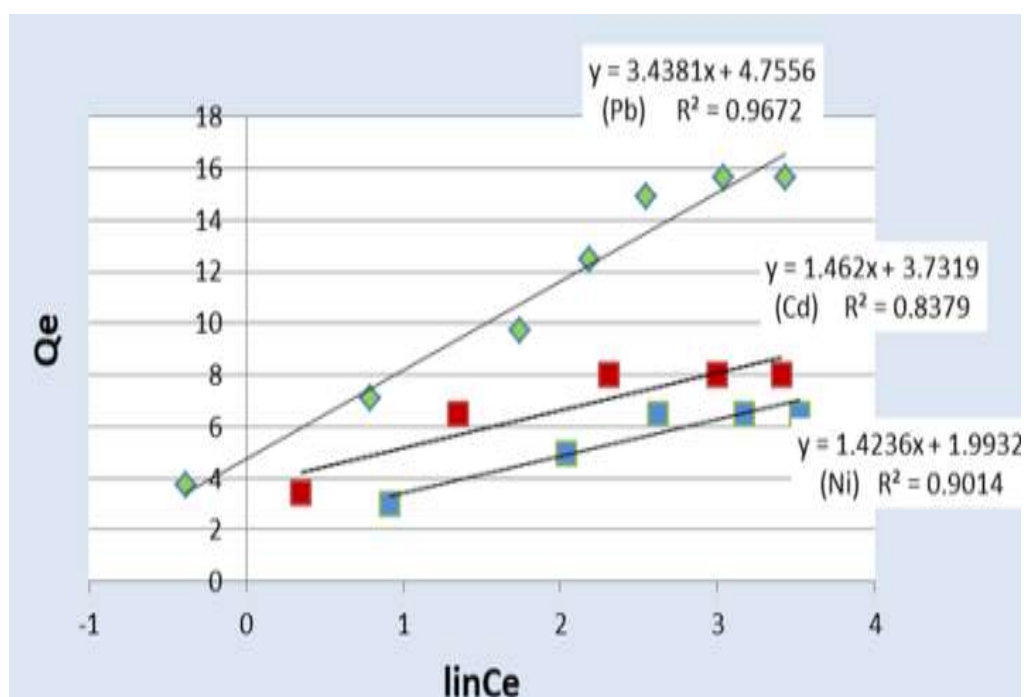


Figure 10. Temkin isotherm model for adsorption of Ni(II), Cd(II) and Pb(II) (50mg PMMA-*p*-aminoacetophenone, pH 5-5.5, 25°C).

Temkin isotherm constants (AT) was evaluated which is the equilibrium binding constant. Also calculated (BT) which is related to heat of adsorption. The fact that metal ions like Pb(II) have a stronger affinity for carbonyl oxygen and NH than metal ions like Cd(II) may help to explain why the adsorption capacity follows the order of Pb(II) >

Cd(II). However, larger metal ions, for instance Pb(II), can more readily reach PMMA-*p*-aminoacetophenone active sites than smaller metal ions, such as Cd(II), which would improve Pb(II) binding to PMMA-*p*-aminoacetophenone [39].

Table 1. parameter of heavy metal ions adsorption kinetic and correlation coefficients (R^2) on PMMA-*p*-aminoacetophenone at 25°C.

Heavy metal	Pseudo-first-order kinetics			Pseudo-second-order kinetics			Experimental result q_e (mg/g)
	$k_1 \text{ min}^{-1}$	q_e (mg/g)	R^2	$k(\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1})$	$q_e(\text{mg} / \text{g})$	R^2	
Cd(II)	0.0626	4.891	0.9638	0.0169	9.025	0.9845	7.9968
Pb(II)	0.3171	42.030	0.8888	0.0316	16.666	0.9975	15.6472
Ni(II)	0.0995	4.700	0.9491	0.0231	7.5642	0.9933	6.4952

Table 2. Characteristics of the Freundlich, Temkin and Langmuir adsorption isotherms.

Heavy metal	Langmuir isotherm			Freundlich isotherm			Temkin isotherm		
	Q_m mg/g	B L/mg	R	K_f mg/g	n	R	AT (L/g)	BT (J/mole)	R
Cd(II)	8.9605	0.4583	0.9681	4.0522	4.870	0.7319	12.839	1.462	0.8379
Pb(II)	15.552	0.4502	0.9855	4.8461	2.554	0.9573	3.987	3.4381	0.9672
Ni(II)	7.2939	0.2844	0.9828	2.8093	4.156	0.8105	4.055	1.4236	0.9014

4. Conclusions

Polymethylmethacrylate (PMMA) and *p*-aminoacetophenone were condensed to prepare modified polymers, which were then identified using FT-IR spectroscopy. Sequel to that, these polymers were effectively used for permitting the adsorption of Cd^{2+} , Pb^{2+} , Ni^{2+} ions in aqueous solutions. Study was conducted on variables that are critical for effectively removing heavy metals, such as pH, contact time and modified polymer dosage. In comparison of three adsorption isotherm, the correlation coefficient shows that the Langmuir adsorption model's isotherm further accurately describes the adsorption of metal ions. The maximal adsorption capacity of PMMA-*p*-aminoacetophenone was reported to be 8.9605, 15.552 and 7.2939 mg per 1 g of modified polymer at 25°C for Cd (II), Pb (II) and Ni (II) respectively. The pseudo second-order kinetics of adsorption processes were apparent.

Conflict of Interest: The authors declare that there is not any conflict of interest.

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