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Potential of Pistachio-Hard Shell Based Thiosemicarbazone-Acetophenone for Pb^{2+}Metal Sorption: Kinetic Studies, Isotherms Modeling and Optimization

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Abstract

The batch studies conducted in the present work provide significant information regarding the adsorption of Pb^{2+} onto Pistachio-Hard shell-grafted-Thiosemicarbazone acetophenone. The sorption kinetics, isotherms and thermodynamics of Pb^{2+} onto adsorbent surface modified thiosemicarbazone acetophenone has been assessed under various operation conditions such as contact time, initial concentration of Pb^{2+}, pH of the solution, temperature and adsorbent dosage. The FT-IR results of Pistachio-Hard shell - grafted-Thiosemicarbazone acetophenone showed that biomass has different functional groups and these functional groups are able to graft with Pb^{2+} in aqueous solution. The removal process reached maximum which was 97.08%. Equilibrium data fitted well with Freundlich isotherm model (1/n<1). Also, Kinetic data were best described by the pseudo-second order model. Thermodynamic studies showed that sorption of Pb^{2+}ions were endothermic, spontaneous, and feasible. Finally, the optimum dosage of the modified adsorbent was 0.165g for adsorption process at pH 5.

Introduction

Simulated wastewater is one of main problems facing the mankind. These contaminations emanate both from agricultural and industrial activities [1]**.** Thus, removal of these toxic pollutants from wastewater and industrial wastes has become a priority to environmentalists and technologist worldwide [2]. The occurrence of heavy metal ions such as mercury, cadmium and lead…etc within the environments at level above regulated amounts are regarded as risk to aquatic and human lives due to its kidney, gastrointestinal and nervous system disruptions [3]. Lead, is an element which has been used by mankind for centuries, can be regarded as a longstanding environmental contaminant.

Heavy metals are released into the environment in a number of ways; by petrochemicals, photographic materials and explosive manufacturing, process industries engaged in lead acid batteries, pulp and paper, refineries, printing, pigments, ceramics, glass, paint, metal, phosphate fertilizer, oil, electronics, wood production and also combustion of fossil fuel, forest fires, mining activity, automobile emissions, sea spray and sewage wastewater [4], [5] and [6]. The existence of lead in drinking water even at low concentration may cause diseases such as encephalopathy, nephritic syndrome, hepatitis and anemia [7] and [8]. Lead is non-biodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain, and can be readily absorbed into the human body. Even a very small amount can cause severe

physiological or neurological damage to the human body. It is a general enzyme inhibitor and metabolic poison, also causing semi permanent brain damage and mental retardation in young children [9].

Recent studies have established that adsorption using natural materials is one of the promising techniques, because of its simple design, ability to eliminate a wide range of pollutants from wastewater, availability, eco-friendly nature and low investment cost [10] and [11]. The key factors in the selection of the raw material are economy, eco-friendly, processability, cost effective adsorbent and consistency of the material. Biomass has a very complex structure but the main constituents of a plant cell wall are cellulose, hemicelluloses and lignin that make biomass a natural composite material. Generally, these structures are composed of 70-90% cellulose and hemicelulose and the remaining lignin molecules. The cellulose hemicelluloses are tightly bound to lignin molecules mainly by hydrogen bonds and some covalent bonds [12] and [13].

Literature has shown that, there is no report on the removal of Pb^{2+} from industrial wastes using surface modification of pistachio-hard shell based Schiff base. The biomass is covered by a kernel and a hard coat, named pistachio-nut shells. The chemical composition of pistachio shells determined previously in literatures [13].

The scope of this work is to develop effective adsorbent that are stable and to evaluate the performance in the adsorption of lead ions from aqueous solution. The experiments assess the adsorption of Pb2+and the stability of modified Pistachio-hard shell. Further, this study has been focused on water treatment application. To accomplish this, the experiments were performed in laboratory scale with aqueous solutions of Pb2+ ions. Also, this work demonstrates that the Pistachio-Hard shell-grafted-Thiosemicarbazone acetophenone is a good adsorbent for wastewater treatment in term of mechanical stability and lead removal at different pH and temperature.

The experiments were repeated three times and average values were reported. Further, the error bars for the figures were so small as to be smaller than the symbols used to plot the graphs and, hence, not shown.

Material and Methodology

A. *Chemicals and Instruments Used*

All materials and reagents used were of analytical grade and used without further purification. BDH, Sigma-Aldrich, Merck, Molekula and Scharlau. BUCHI Melting point (B-545), Oven (Desert chamber pro), pH meter (pH/ion 510), infrared spectrum (KBr disc by Thermo Mattson 300 FT-IR spectrophotometer), UV-Vis spectrophotometer (Aglient Technology Cary UV-Vis spectrophotometer) and incubator shaker (GFL 3031) are used for characterizing and determination of synthesized compounds.

Preparation of synthetic wastewater

Synthetic wastewater samples were prepared by using analytical grade lead nitrate (99 %Sigma-Aldrich) by using double distilled water. The stock solution was prepared by dissolving the salt $Pb(N0_3)_2$ in double distilled water, which contains 1000 mg/L. Working solutions of 10, 25, 40, 80, and 100 mg/L were prepared by dilution. The pH was adjusted using 0.1M NaOH and 0.1M HCl solutions. The concentration of Pb^{2+} was measured using UV-Vis spectrophotometer.

Synthesis of the Schiff base (Thiosemicarbazone Acetophenone TAE)

Acetophenone were mixed in 1:1 molar ratio in ethanol with thiosemicarbazide. The resultant mixture was refluxed for 5 hours. After removing the excess ethanol by evaporation, the resulting precipitate was filtered off and re-crystallized from ethanol, the melting point was 117-119°C [1].

B. Preparing of Pistachio-hard shell-graft-thiosemicarbazone acetophenone composite matrix(PH-g-TAE)

The pistachio-hard shell used in this work was obtained from peeling the nut fruits which was obtained from the local market. The hard external peel was milled using house mill and then sieved into different

particle sizes the fraction 250 µm < d < 500 µm was selected [9] and [10]. The sieved pulverized hard shell was washed with double distilled water many times for dust and fine removals. The prepared hard shell was dried at105°C over night, cooled and stored in a desiccators until required for use. The adsorbent was prepared by mixing 1g/250ml solution by treating with thiosemicarbazone (0.5% w/v) stirring at 35°C for period 3hrs. After the treatments, the material was filtered and washed with double distilled water to remove an excess of chemicals. Finally, the modified adsorbent kept in air-free oven monitored at 105°C.

Batch experiments

In this work, surface modified cross-linked Schiff base obtained using thiosemicarbazone acetophenone was grafted onto the surface backbone of the biomass, and entrapped physically within the composite matrix to produce highly effective adsorbent. Pistachio-hard shell mainly composed of cellulose or cellulose derivatives are one of the widely examined biopolymers, due to its non-toxic nature, availability and high adsorption capacities [10]. Thiosemicarbazone acetophenone, main inorganic component of bones and teeth, has displayed high adsorptive capacity for removal of lead ions from contaminated effluents [11].

The adsorption capacity, mechanism and operation parameters such as contact time, adsorbent dosage, initial dye concentration, adsorption temperature and pH of dye solution were explored in detail. Adsorption kinetic, thermodynamic and isotherm models were used to analyze the equilibrium data.

C. Optimization of Pb^{2+} ions sorption and determination of the adsorptive Capacity

The key factors affected the sorption process which optimized on lead such, temperature (298, 303 and 313) K, pH (2, 4, 6, 8 and 10), biomass (50, 100, 150 and 200) mg, contact time (2, 4, 6, 8 and 10) hrs and initial Pb^{2+} concentrations (25, 40, 100 and 150) $mg.l^{-1}$.

After the modification of the surface biomass has been done, the optimum weight of the modified biomass was suspended in 100ml of a solution containing different Pb^{2+} concentrations and the solution was continuously stirred on a shaker (180 rpm) at 30°C for the optimum contact time [12]. After the contact time reached, the supernatant liquid was collected by filtered through 1 µm filter membranes and analyzed for Pb^{2+} ions using UV_Vis spectrophotometer [13]. Furthermore, all the sorption experiments were repeated twice to confirm the results. Also blank (without biomass) experiments were conducted to ensure that no adsorption had taken place on the walls of the apparatus used.

The amount of Pb^{2+} adsorbed to the modified biomass was calculated by the following equation [9]:

$$q = (C_i - C_f)\frac{V}{m} \quad (1)$$

$$\%\,\text{Removal} = \frac{C_i - C_f}{C_i} \times 100 \quad (2)$$

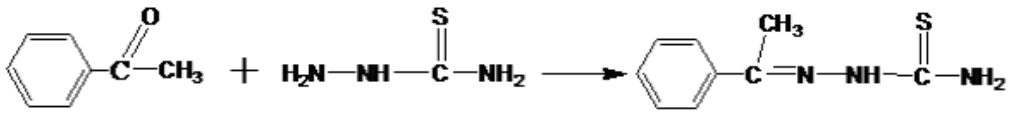
Where: q= Pb^{2+} uptake (mg of Pb^{2+}/g of adsorbent), V = Pb^{2+} solution volume (ml), C_i= initial Pb^{2+} concentration in the solution (mgl^{-1}), C_f= final Pb^{2+} concentration in the solution (mgl^{-1}), m = amount of the added PHTAE as a biomass (mg) and R = removal percentage.

Results and discussion

A. Characterizations of FT-IR

1. Characterizations of FT-IR for Identification of Schiff base (TAE)

Scheme (1) illustrates the synthesis of Schiff base TAE



Scheme-1: Synthesis of TAE

Absorption stretching band were detected at 1679.66 cm^{-1} in FT- IR spectrum which assigned to C=N and the disappearance of C=O stretching band, these are evidences on the forming of the structure of TAE. The bands at 1093.90 and 1073.69 cm^{-1} indicate the C=S stretching. While the bands at 3147.18 and 3208.50 cm^{-1} were assigned to stretching vibration mode of NH_2. Figure1showed absorption bands at 3408.20cm^{-1} and 1587.04 cm^{-1} which indicate the stretching and bending vibration of N-H [1]. The C-H bending for mono substituted aromatic appears at 688.49 and 763.39cm^{-1}[3].

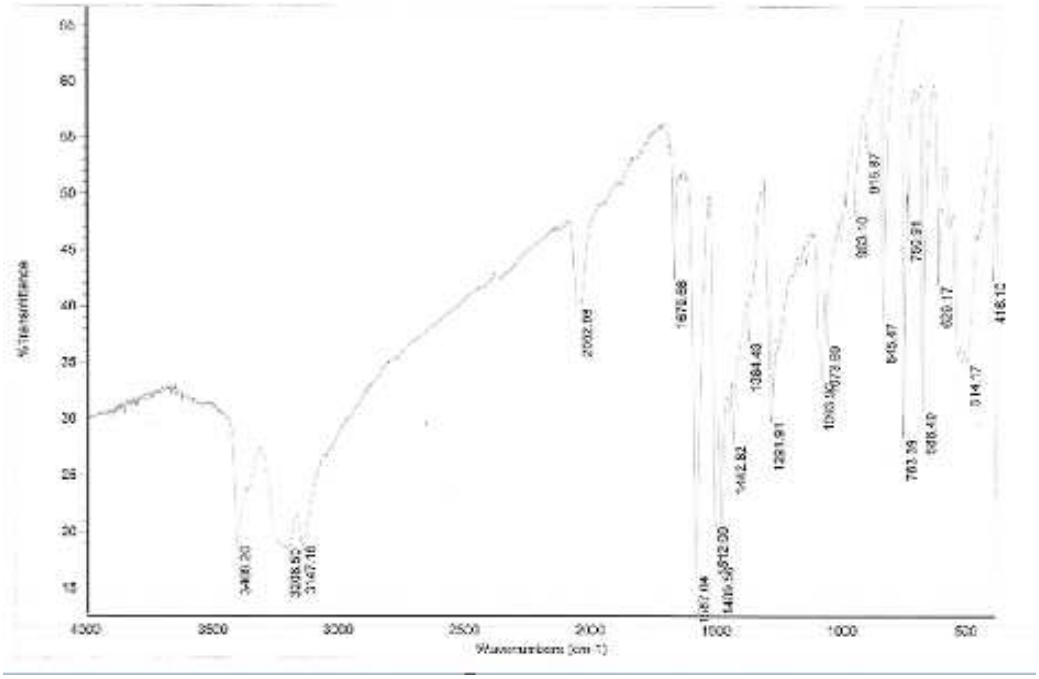


Figure-1: FT-IR spectrum of TAE

2. FT-IR Identification of TAE -wall pistachio

The term "lignocellulosic biomass" is used for softwood or hardwood of the high plants. Cellulose, hemicellulose and lignin are main components of the lignocelluloses. The functional groups of these components are Hydroxyl group, Aromatic ring, Carbon to carbon linkage, Ester bond and Ether (glucosidic) linkage [3]. In the FT- IR spectrum of TAE-wall pistachio has a new strong wide band at 3419.99 cm^{-1} assigned to OH stretching vibration, and the two peaks at 2926.09, 2853.83 cm^{-1} assigned to stretching vibration of aliphatic CH_2 are evidences of bonding TAE with wall pistachio. A strong band at 1746.78 cm^{-1} assigned to stretching vibration of ketone group. The position of C=N band of the TAE appear at 1635 cm^{-1}.The presence of O-H broad band hides the stretching band of N-H, but appears bending vibration at 1558cm^{-1}[3].

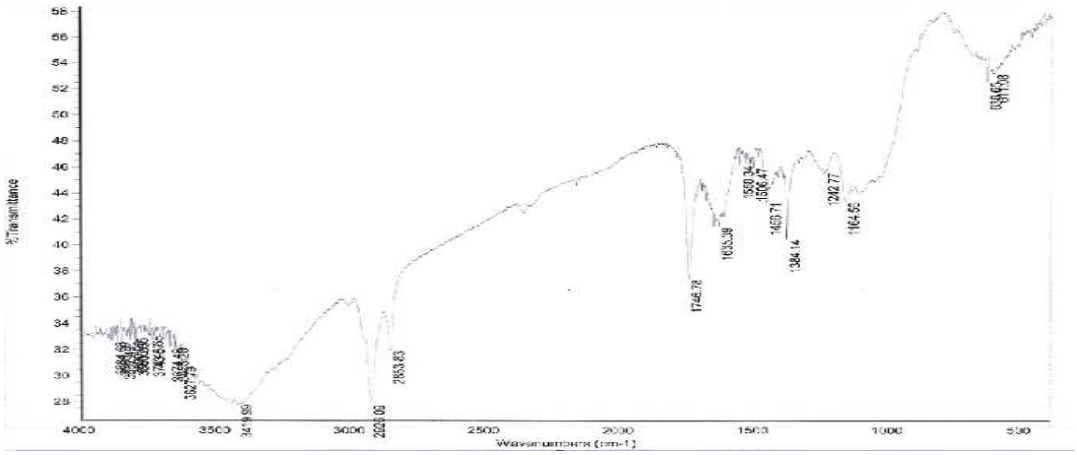


Figure-2: The FT-IR spectrum of TAE-wall pistachio

3. FT-IR Identification of TAE-wall pistachio–Pb

FT-IR spectrum can provide the basic information about the adsorption of Pb on TAE-wall pistachio surface. The position of C=N band of the TAE-wall pistachio is shifted towards higher wave number that appear at 1653.05 cm^{-1} indicating coordination via the nitrogen atom. The appearance of band at 419.53 cm^{-1} confirms the Pb-N bond. The C=S stretching is shifted towards higher wave number that appear at 1084, 1102 cm^{-1}, it indicates that sulfur coordinate with the Pb^{2+} ions [3].

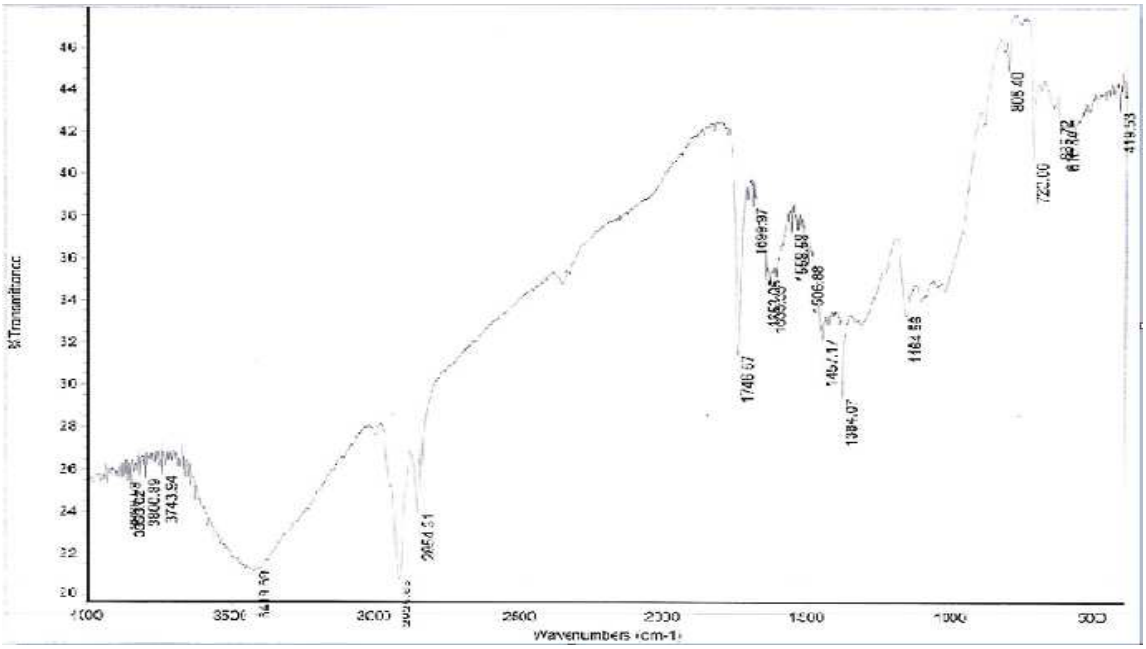


Figure-3: The FT- IR spectrum of TAE-wall pistachio-Pb

B. Effect of contact time on removal process

The effect of contact time on the adsorption of the Pb^{2+} from the solution is shown in Figure-4; however the uptake of Pb^{2+} ions increases at the contact time. Moreover, the adsorption was very fast from the first30 min. However, equilibrium was attained in 2h. Further increase in contact time to 24 h, the percentage adsorption decreases very slowly [15] and [16]. Therefore, the contact time can be optimized to 2h.In addition, at equilibrium was achieved no more increase observed.

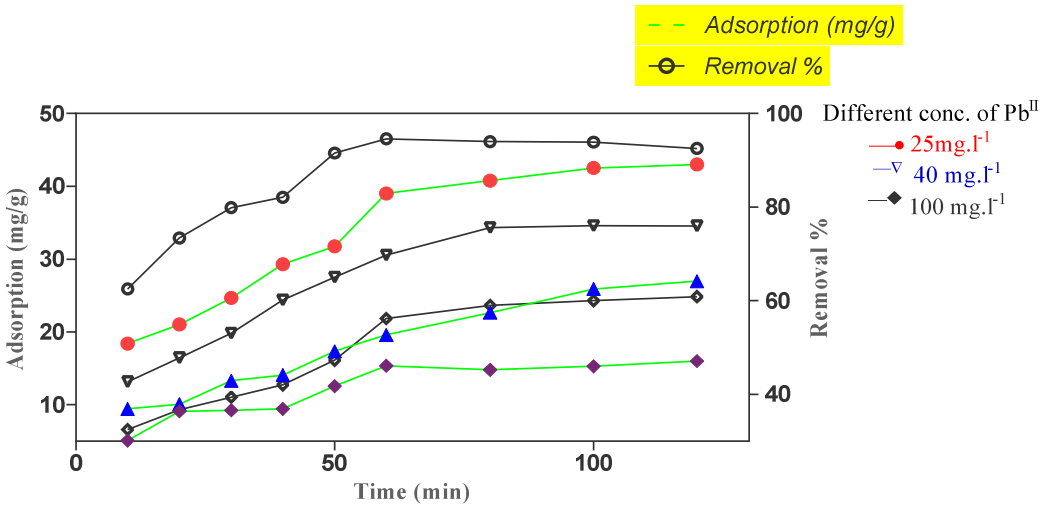


Figure-4: Effect of contact time on removal of Pb^{2+} at different concentrations

The removal percentage of Pb^{2+} increased from (62.54 to 92.55%), (42.71 to 76.00%) and (32.49 to 60.01%) at 25, 40 and 100 $mg.l^{-1}$initial lead concentration respectively. Observable, removal percent was not noticed after contact time of 2h, and this demonstrate that the free sites at the surface of PHTAE have been occupied.

C. Effect of PH-g-TAE dosage on removal process

The dependence of PH-g-TAE dose (25 to 150 mg) loading on the adsorption at different concentration of Pb^{2+} (25, 40, 100 $mg.l^{-1}$) is presented in (Figure: 5a and 5b). It is readily understood that the adsorbent dosage significantly influenced the intensity of lead ions sorption [17]. Moreover, the removal of Pb^{2+}ions increased with increasing of PH-g-TAE loading can be attributed to larger surface area and availability of more active sites [18]. The results indicated that the removal of Pb^{2+} from aqueous solutions was maximal at higher adsorbent dosage and the optimum dose studied for the removal Pb^{2+} ions is 0.165g. However, figure-5b shows the uptake percentage was varied from 49.5 – 97.08% at initial concentration of 25 mg/L.

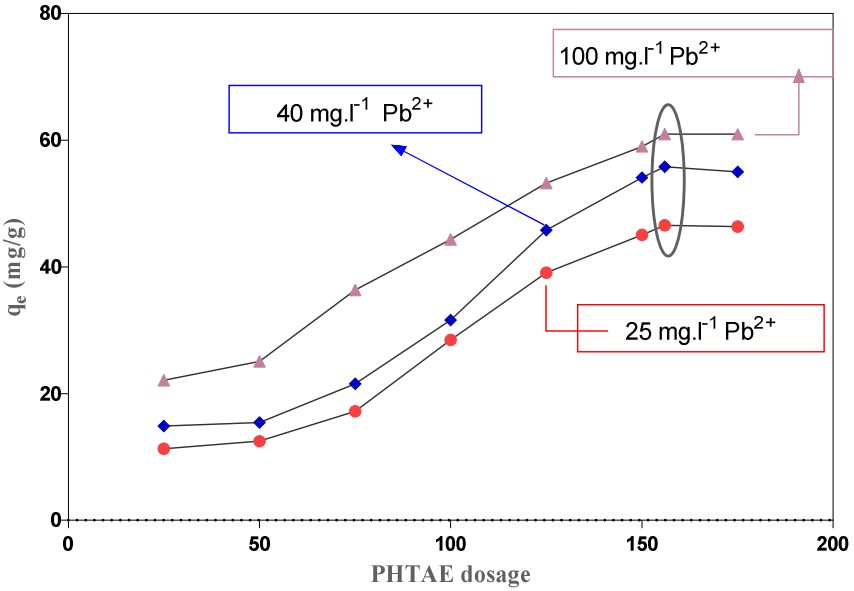


Figure-5a: Effect of PH-g-TAE dosage onto Pb^{2+} sorbent

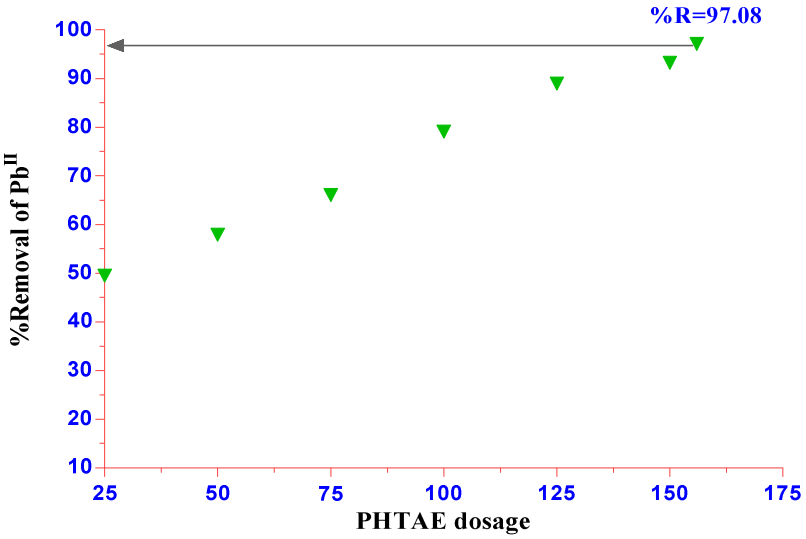


Figure-5b: Removal percentage of Pb^{2+} initial concentration 25 mg/L at pH 5

D. Effect of pH

The pH of the solution is one of the important factors in controlling the adsorption process and particularly on the adsorption capacity. Difference pH will affects the adsorptive processes via dissociation of functional groups (TAE-Pb) on the active sites of adsorbent and, this leads to a shift in reaction equilibrium and kinetics of the adsorption process. Here, the adsorption of Pb^{2+} on the activated Surface-g-Thiosemicarbazone from the aqueous soloution was evaluated from solution at different pH levels covering a range of 1-9. Moreover, as shown in figure-6, the adsorption capacity increases as the solution pH increases the maximum adsorption was acquired at pH 5 for both concentrations 25 and 40 mg/L of Pb^{2+}solution and fixed adsorbent (PH-g-TAE) dosage 0.165g. The highest efficiency was noticeable at 97.08 - 83.9 % for (25-40) mg/L respectively was obtained at pH 5. In addition, the removal of Pb^{2+} ions is pH dependent, at lower (pH< 3) H^+ from hydronium ions compete with positively charges of Pb^{2+} for the Surface-g-TAE which would prevent Pb^{2+}ions from reaching the binding sites of the adsorbent induced by the repulsive forces[19]. In this work, removal process indicated that in the highly alkaline solutions and highly acidic solutions adsorption was decreased. Probably it is linked with a different charge on the surface of PH-g-TAE. Nevertheless, the main idea to investigate the effect of pH on the PH-g-TAE and its adsorption conducts; we determine the point of zero charge (pH_{pzc}) by the salt addition method as shown in figure-7. At pH_{pzc} (which is pH_{pzc}= 4) the surface of the adsorbent has zero potential charge. However, below the pH_{pzc} the surface of PH-g-TAE becomes positively leads to formation a positive barrier on the surface of the adsorbent and electrostatic repulsion between PH-g-TAE and $Pb^{2+}$and the metal cations have limited access to the surface of the adsorbent result in a decrease in the adsorption capacity of Pb^{2+}, and above pH_{pzc} the surface of the adsorbent have more adsorption sites may increase the electrostatic interaction caused increment of adsorption capacity [20].

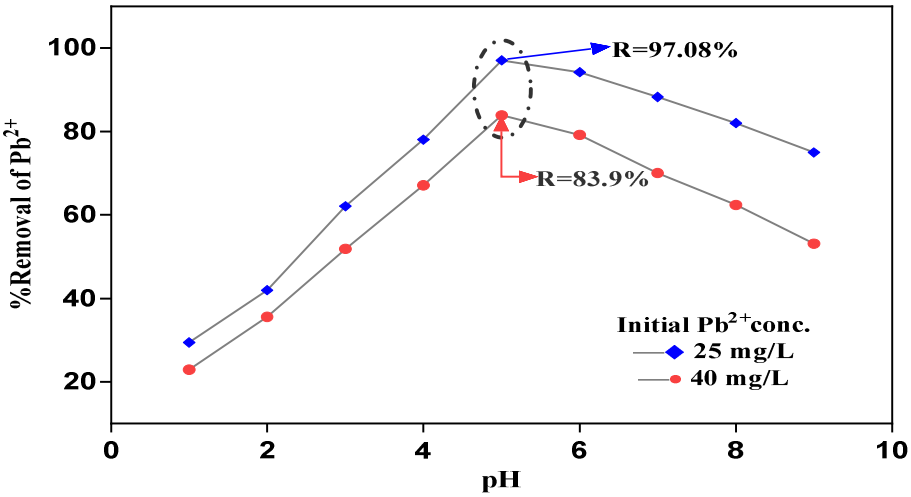


Figure-6: Effect of pH on removal of Pb^{2+} ions (adsorbent dose 0.165g, mixing rate 180 rpm, time 2h)

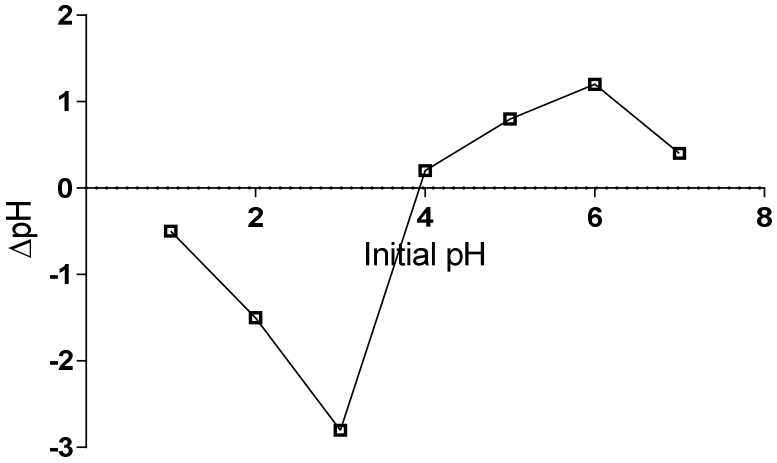


Figure-7: pH_{pzc} determination by salt addition method

E. Effect of temperature

In order to evaluate the effect of temperature on removal of Pb^{2+} ions from aqueous solutions, adsorption experiments were performed, at 298, 303 and 313 K. Other parameters remained the same. As can be seen in figure-8, the increment of the adsorption capacity with increasing the temperature could be due to the availability of a high number of active sites on the surface of PH-g-TAE. Nevertheless, increasing temperature may produce more freely available sites via the breakage of inner bonds. Such a result confirms the adsorption process is endothermic.

In order to describe the thermodynamic parameters of the adsorption of Pb^{2+}on PH-g-TAE adsorbent, the standard Gibbs free energy change (ΔG°) of the adsorption process can be calculated from Van't Hoff equation [21] and [22].

$$\Delta G^{\circ} = -2.303RT \log K_d \quad (3)$$

$$K_d = \frac{q_e}{C_e} \quad (4)$$

The Entropy change (ΔS°) and Enthalpy change (ΔH°) (i.e. heat of adsorption) are related with the Gibbs free energy by the equation [22]:

$$\log K_d = \frac{\Delta S^{\circ}}{2.303R} - \frac{\Delta H^{\circ}}{2.303RT} \quad (5)$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \quad (6)$$

Where K_d is equilibrium constant of Van't Hoff equation, R is the universal gas constant 8.314 (J/mol. K) and T is the temperature (K). C_e is concentration of Pb^{2+} ions at equilibrium(mg/L) and q_e is the amount of adsorbate (Pb^{2+}), ΔG° is Gibbs free energy change (KJ/mol),ΔS° is Entropy change (KJ/mol. K)and ΔH° is Enthalpy change (KJ/mol). A plot of log K_d against 1/T is given a straight line, ΔH° and ΔS° can be determined from intercept and slope, respectively. The value of free energy (ΔG°) was calculated by using Eq. (5) and (6). Consequently, the obtained data are tabulated in table 1.

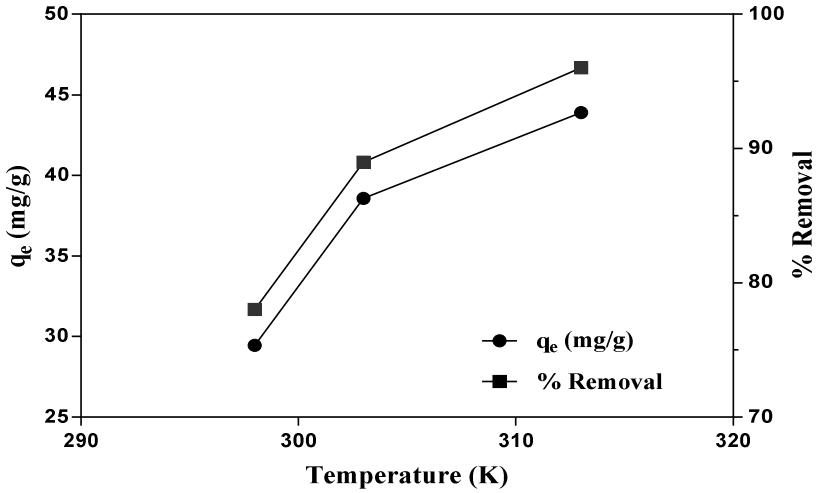


Figure-8: Effect of temperature on removal of Pb^{2+}in aqueous solution, (Adsorbent dose 0.165g, initial conc.25 mg/L, pH = 5)

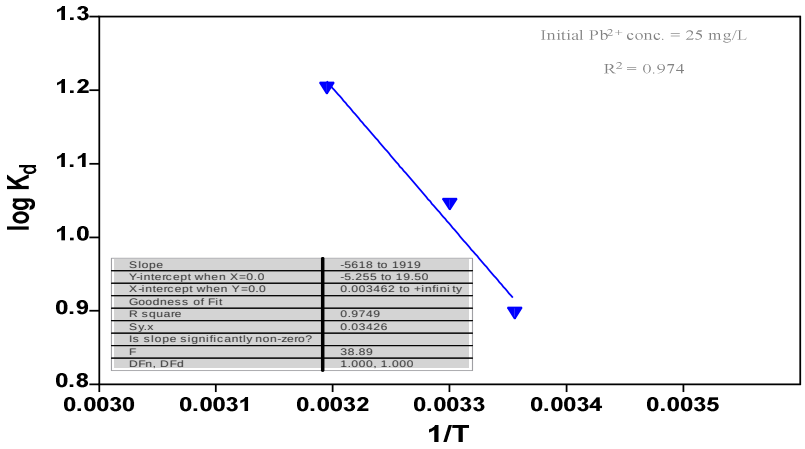


Figure-9: Thermodynamic evaluation of Pb^{2+} adsorbed onto PH-g-TAE

Table-1: Thermodynamic studies of Pb^{2+} ions on PH-g-TAE as a function of temperature

T(K)	*K_d Log K_d*	*ΔG °(Kj/mol)*	*ΔH °(Kj/mol)*	*ΔS °(Kj/mol. K)*	
298	*7.90*	*0.897*	*5.66*		
303	*11.10*	*1.045*	*6.83*	*29.31*	*0.114*
313	*15.98*	*1.203*	*8.37*		

The positive value of ΔH° confirm the adsorption of Pb^{2+} on PH-g-TAE is endothermic process, the overall ΔG° were negative during the removal processes as indicated in table-1; this agree to a spontaneous nature and feasibility of the adsorption process. In addition, more negative which provide the uptake of Pb^{2+} ions become more spontaneous with increase in temperature [23] and [24].

F. Dynamic studies

The most important vital to demonstrate the control of adsorption system is kinetic. The kinetic models are used to describe the experimental data in order to examine the mechanism of the Pb-adsorptive process on the chemically modified pistachio-hard shell [25]. In this case many models have been tests to express the mechanism of Pb^{2+} ions sorption onto PH-g-TAE, and to design an effective, fast and optimized treatment plant, these models including the pseudo-first order kinetic, the pseudo-second order kinetic and the Weber-Morris intraparticle diffusion model, which are given by equations (7), (8) and (9), respectively[4] and [25].

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \tag{7}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{8}$$

$$q_t = K_3 t^{1/2} + K_d \tag{9}$$

Where, q_e and $q_t$are the amount of Pb^{2+} adsorbed per unit of mass (mg/g) at the equilibrium and time t (min), respectively. K_1 (min^{-1}) is the rate constant of pseudo-first order kinetic, K_2 (g/g.min) is the rate constant of pseudo-second order kinetic, K_3 ($mg/g.min^{1/2}$) is the intraparticle diffusion rate constant and K_d can be determine from intercept of a plot of q_t vs $t^{1/2}$ and gives an idea about thickness of a boundary layer.

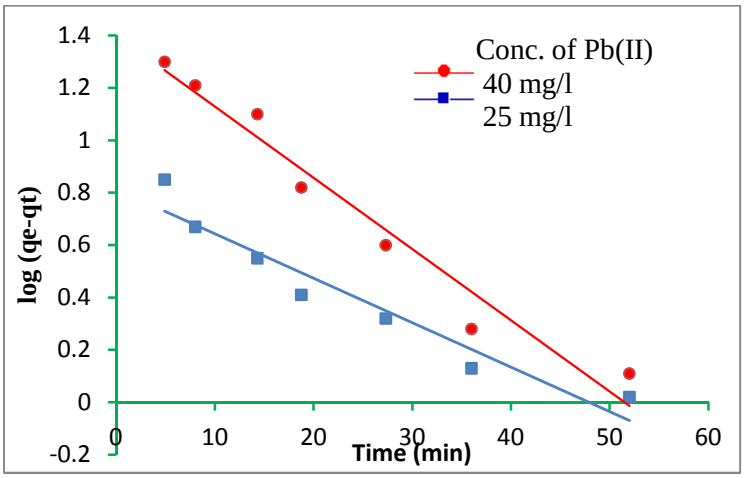


Figure-10: Pseudo-first order kinetic model of the uptake of Pb^{2+}

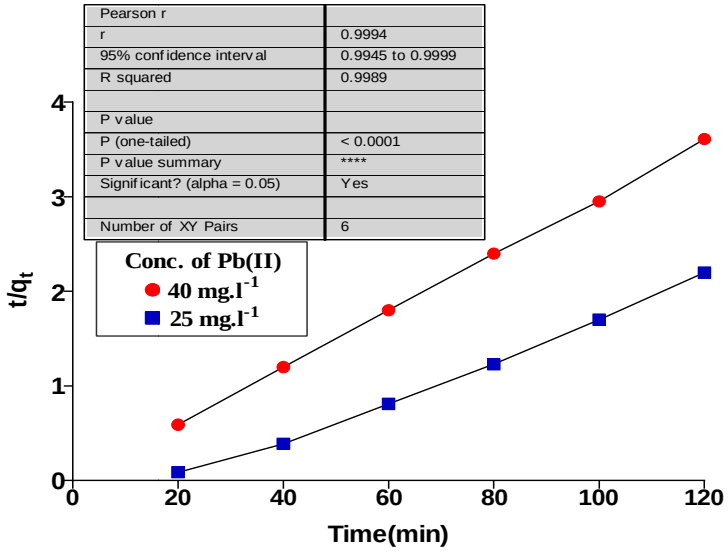


Figure-11: Pseudo-second order kinetic model of the uptake of Pb^{2+}

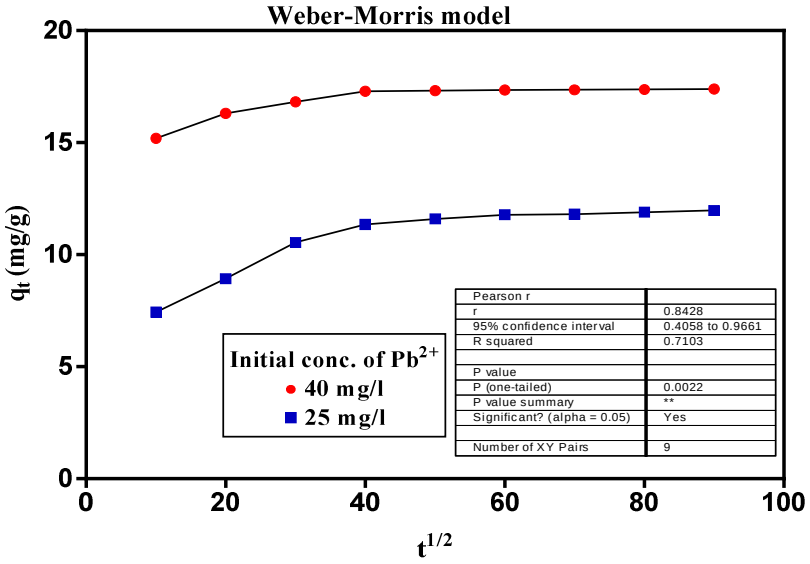


Figure-12: Intraparticle diffusion kinetic model of Pb^{2+} on PH-g-TAE

As can be seen from the above figures, it is clear that the adsorption dynamics of Pb^{2+} on PH-g-TAE fitted well to the pseudo-second order kinetic model. In addition, this model gives the best fit to experimental data of Pb^{2+} ions which investigated in this work, also have higher coefficient of determination value (R^2=0.9994) for all concentrations studied in compare with the coefficient of determination value (R^2=0.9580) obtained by pseudo-first order kinetic model. Nevertheless, the theoretical values of qe mostly agree with the experimental data as tabulated in table-3, both facts suggest that the pseudo-second order kinetic model is more likely to predict the kinetic behavior for the whole range of time studied. That means the rate of occupation of adsorption sites is proportional to the square number of unoccupied sites, because the pseudo-second order model is based on a second order mechanism [26] and [27]. Furthermore, figure-12 shown that the final sorption equilibrium was the intraparticle diffusion initiates to slow down due to quit low concentration of Pb^{2+} ions left in the solution.

Table-3: Kinetic parameters and Weber-Morris model for Pb^{2+} onto PH-g-TAE

Conc. of Pb^{2+} mg/l	***$q_{exp.}$ mg/g***	***Pseudo-first-order kinetic model***			***Pseudo-second-order kinetic model***			***Intraparticle diffusion model***		
		$q_{e\ (cal)}$	***K_2***	***R^2***	***$q_{e\ (cal)}$***	***K_2***	***R^2***	***K_3***	***R^2K_d***	
25	*23.54*	*15.74*	*30.55*	*0.9575*	*19.63*	*47.58*	*0.9990*	*4.32*	*0.710*	*21.30*
40	*27.14*	*21.60*	*31.82*	*0.9580*	*25.30*	*81.06*	*0.9994*	*5.644*	*0.713*	*3907*

G. Sorption isotherm modeling

Adsorption isotherms are significant data to realize the mechanism of sorption system from a physicochemical view. The adsorption capacity of adsorbent can be also characterized by the equilibrium adsorption isotherm [28]. In this work, two widely model isotherm were applied which fit the experimental data are namely Langmuir and Freundlich isotherms. Moreover, the liner forms of both models are represented as follows [16] and [22]:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \tag{10}$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{11}$$

Where, C_e is concentration of Pb^{2+} at equilibrium in (mg/l), q_e is the amount of Pb^{2+}adsorbed onto PH-g-TAE per unit mass, K_L is the Langmuir constant, q_m is the maximum adsorption capacity in (mg/g), K_F and n are Freundlich constants which giving an indication of how the adsorption process is favorable. However, all resulted data are obtained for each isotherms model are summarized in table-4.

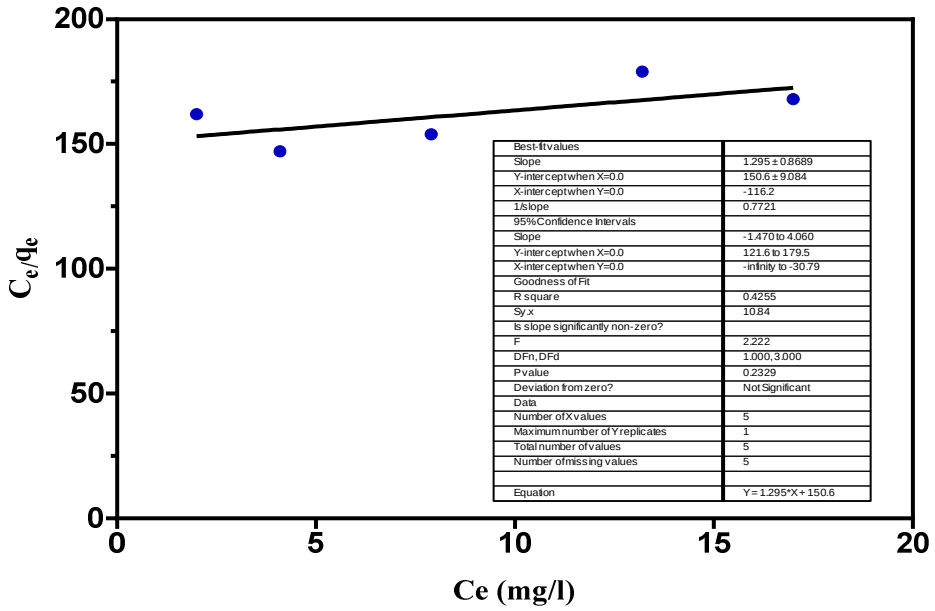


Figure-13: Isotherm model of Langmuir for Pb^{2+} sorption

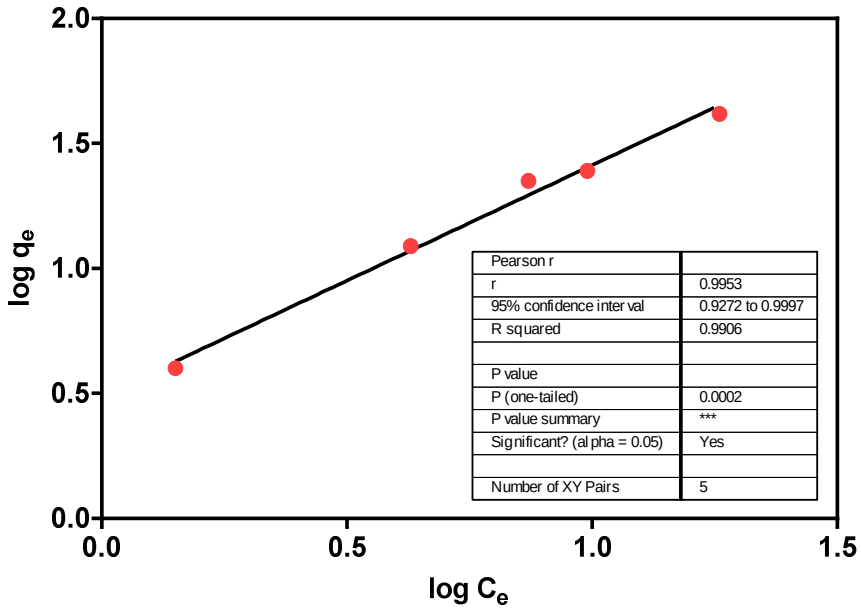


Figure-14: Isotherm model of Freundlich for Pb^{2+} sorption

From above figures, the Freundlich isotherm model showed best fit to adsorption data which have highest coefficient of determination (R^2=0.9906) might be availability of heterogeneous surface with different classes of PH-g-TAE sites caused physically interaction with Pb^{2+} ions from the solution . Also, table-4 revealed that the values of constants (K_F and n) at maximum uptakes given by Freundlich models are in good agreements with experimental capacities calculated from the isotherms. The value of (1/n=0.293) showed the most important consequence of isotherm of non-linearity of the Freundlich type when (1/n<1).

Table-4: Isotherm parameters of Pb^{2+}sorption

Langmuir		***Freundlich***	
Parameter	*value*	*Parameter*	*value*
q_m	*47.022*	*n*	*3.410*
K_L	*25.731*	K_F	*6.130*

Conclusions

Modified agricultural by- product materials have been utilized as effective and high potential adsorbent for removal of Pb^{2+} from aqueous solutions. In addition, the synthesis of Schiff base (Thiosemicarbazone acetophenone) was loaded successfully on the surface of the adsorbent to increase the ability and efficiency for removal of Pb^{2+} from aqueous solutions. Thus, the adsorption process were investigated and characterized by FT-IR technique. Furthermore, dynamic studies, isotherm modeling and optimization were performed. It was found that the Pb^{2+}sorption were rapidly increased at the initial stages and the maximum sorption was observed at pH5 and the highest removal percentage of Pb^{2+} was 97.08%. On the other hand, the thermodynamic parameters showed that the adsorption process becomes more randomness and feasibility with increasing in temperature due to negative values of $\Delta G°$ and endothermic adsorption confirmed by the positive values of $\Delta H°$. Thus, the uptake of Pb^{2+} by PH-g-TAE obeyed pseudo-second-order kinetic model and the modified surface of PH-g-TAE is heterogeneous with high capability of adsorption sites according to Freundlich isotherm.

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