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Biosorption Study of Pb(II) Ions onto Treated *Eupatorium adinoforum (AEA)* and *Acer Oblongum (AAO)*: Thermodynamic and Equilibrium Studies

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ABSTRACT
In the present study, dried activated biomass of Eupatorium adinoforum (AEA) and Acer oblongum (AAO) used for removal of Pb (II) from synthetic wastewater. The batch operation was conducted with effect of variation of contact time, biosorbent dose, pH, concentration of metal ions and temperature on biosorption of metal ions on biosorbent. Maximum adsorption was recorded for initial metal ion concentration of 10 mg/l, biosorbent dose of 2.5 gm, at pH 5 with 105 minutes of contact time for activated AEA and AAO biomass. The adsorption equilibrium conditions were well described by Langmuir, Freundlich and Temkin isotherm models. The Langmuir isotherm model has provided a better fit with the experimental data in comparison to that of Freundlich and Temkin isotherm models. Thermodynamic data suggest that the bisorption process was spontaneous, feasible and endothermic. The values of thermodynamic parameters suggest that the biosorption process was spontaneous, feasible and endothermic. The kinetics of the biosorption for the reaction mechanism and types of biosorption process onto activated AEA and AAO biosorbent were also discussed.

Keywords: *metal ions, biosorption, isotherm models, kinetics, ageratum conyzoid (TAC) biomass*

I. INTRODUCTION

Water pollution caused by industrial sewage carrying toxic heavy metal ions is a serious environmental issue. The industrial significance of Lead is its use in batteries, paints, pigments and ammunition, petrol, cables, alloys and steels, plastics, the glass industry and the metal industry [1, 2]. Lead has been introduced in the environment from a variety of sources such as, storage battery, lead smelting, tetraethyl-lead manufacturing and mining, plating, ammunition, ceramic and glass industries. industry, plastics, cables, pigments, and a variety of other anthropogenic wells of heavy metals throughout the environment [1]. Lead is found in the environment in an insoluble form that can cause major health concerns in humans. Lead poisoning is mostly caused by inhaling lead-contaminated dust particles or aerosols, as well as ingesting lead-contaminated food, drink, and paints [1]. The kidney absorbs the most lead in the human body, followed by the liver and other soft tissues including the heart and brain; nonetheless, lead in the skeleton makes up the majority of the body [3]. Lead poisoning is very dangerous to the nervous system. Early indications of lead exposure on the central nervous system include headache, short attention span, irritability, memory loss, and dullness [3, 4]. Encephalopathy, cognitive impairment, behave aural problems, kidney damage, and anemia are all symptoms of excessive lead (Pb) buildup [5]. Lead is a toxic metal that can harm the neurological system and cause mental illness. Long-term exposure to lead can result in nephropathy, gastrointestinal aches, and is especially damaging to women's reproductive function [6, 7]. Lead compounds are poisonous in all forms, but Pb(II) salts and organic lead compounds are the most dangerous. Although Chemical precipitation, filtration, ion exchange, chromatography, and carbon adsorption are some of the methods for removing heavy metals from wastewaters [8-12]. These approaches have a number of drawbacks, including secondary pollutants, high costs, excessive energy usage, and so on [13]. Biosorption is an environmentally acceptable method for removing heavy metal ions from wastewater. In recent years, a variety of biosorbents such as soyabean [14], Algerian pine, beech and fir sawdust's [15], modified Cocoa (*Theobroma cacao*) Pod husk residue [16], Activated Carbon derived from Sugarcane bagasse [17], banana (*Musa paradisaca*)[18], *Rubus ellipticus* [19], *Pyras pashia* [20], and *Urtica dioica* [21] have been employed to remove heavy metal ions from wastewaters.

FT- IR is an important tool for determination of functional group present in biomass. The main objective of this study is to investigate the possibility of activated biomass *Eupatorium adinoforum* (*AEA*) and *Acer oblongum (AAO)* leaves as an alternative low-cost biosorbents for removal of Pb(II) metal ions from synthetic wastewaters.

II. MATERIALS AND METHODS

2.1 Preparation of Adsorbent

The leaves of *Eupatorium adinoforum* (*AEA*) were collected from Almora city area and Eupatorium adinoforum (AEA) leaves were obtained in Almora and Acer oblongum (AAO) leaves were collected in Chopta (Rudraprayag) in Uttarakhand, India. These leaves are professionally cleansed with double distilled water to remove dust and solvent chemicals. The leaves were dried at room temperature for 24 hours before being baked at 60°C (Model: SN-1680, Popular Trader). The dried biomass is crushed into a fine powder in an electric processor. This fine mass was incubated with hot air at 60°C for two days after being treated with N/10 HNO_3 at room temperature for 24 hours. In the oven, it was heated and dried. This treated biomass was sieved to a molecule size of 63 μm in view of smashing and subsequently placed in water/airtight containers for use as an adsorbent. Fourier-transform infrared spectroscopy (FT-IR) spectroscopy was used to detect surface functional groups of the treated adsorbent (Model: spectrum 10 version, PerkinElmer).

2.2 Preparation of Adsorbate

The chemicals used were of analytical reagent quality. In distilled water, a stock solution of Pb(II) in 1000 mgL^{-1} of their different salts as $Pb(NO_3)_2$ was created. The pH of these solutions was tuned to four using N/10 NaOH or N/10 HNO3 solutions and a digital pH meter (Model: Systronic 361). These stock solutions were utilized to deliver synthetic wastewater. In synthetic wastewater, lead ionic concentrations vary from 10 to 50 mgL^{-1}.

2.3 Biosorption Experiments

The biosorption experiments were carried out with 100 mL of standard solution in 250 mL conical flask. The experimental conditions employed to investigate the effects of adsorption dose, agitation period, pH, beginning metal ion concentration, and temperature on metal ion biosorption are listed in Table 1. The solution was shaken at 170 rpm for 45 min and then filtered by using Whatman No. 42 filter paper. The filtrate was digested with conc. HNO_3. The digested solution was analyzed by atomic absorption spectrophotometer (Optima 4300DV ICP, Perkin Elmer Boston, MA). The adsorption efficiency of mixed ions was calculated using eqn. 1:

$$\text{Adsorption efficiency} = \frac{(C_i - C_e)}{C_i} \text{ x } 100 \qquad \ldots.(1)$$

where C_i is the initial concentration of metal ion (mgL^{-1}) and C_e is the equilibrium concentration of metal ion (mgL^{-1}).
Table 1 Batch adsorption experimental conditions

Experimental parameter	Ms (g /100ml)	t (min.)	pH	Initial metal ion in equimolar concentration C_0 (mgL^{-1})	Temperature (^0C)
Effect of adsorbent mass (g)	0.5-2.5	30	4	10	22
Effect of contact time, t (min.)	1.00	15-105	4	10	22
Effect of pH	1.00	30	1-9	10	22
Effect of metal concentration, C_0 (mgL^{-1})	1.00	30	4	10-50	22
Effect of temperature, (^0C)	1.00	30	4	10	15-75

III. RESULTS AND DISCUSSION

FT-IR and SEM used for the changes in biosorbent before and after biosorption. The effect of the variation of amount of biosorbent, contact time, temperature, pH and concentration of metal ions in removing the Pb(II) metal ions from synthetic wastewater using *AEA* and *AAO* biomass have been studied by batch operations.

3.1 Characteristics of the *AEA* and *AAO* Biomass

3.1.1 FT-IR Analysis (Characterisation of Functional Groups)

The FT-IR study reveals a number of functional group present in the *Eupatorium adinoforum* and *Acer oblongum*. In order to determine, the main functional groups of activated *AEA* and *AAO* biosorbents that participate in Pb (II) ion sorption, FT-IR spectra were recorded before and after sorption of Pb (II) ions onto activated *AEA* and *AAO* biomass Figure 1A. The sharp absorption bands of activated AEA biomass at 3743, 2363, and 2922 cm-1 are attributed to stretching vibration bands of N-H, aliphatic C-H, and NH2 [22], respectively. The presence of the O-H group in biosorbent is indicated by the absorption bands at 3836, 3615, and 3515. The bending vibrations C-O, C-O-H, and C-C are ascribed to the peaks at 1461, 1239, and 1023, which are all connected to saccharide structure [23, 24]. After biosorption of the Pb (II) ion onto activated AEA (AEA-Pb) biomass, these absorption bands change.

In Figure 1B for activated *Acer oblongum*, the broad peaks in the region of 2916 and 2949 cm^{-1} are characteristic of C-H group in the aliphatic compound. The peaks at 1611, 1516 and 1439 cm^{-1} are related to the N-H stretching vibrations in tertiary amine. The formation of $–CH_2–O–CH_2–$ linkage is appeared at 1085–1104 cm^{-1} [25]. These shifts may be due to the changes in counter ions associated with the ether and amine group suggesting that these groups are predominant contributors in metal ion uptake [26]. The absorption band of –C–O was decreased due to the formation of complex between atom oxygen and Pb (II) [27]. Obvious changes in the FT-IR spectra were found at the wave numbers of 3810, 3742 and 3280 cm^{-1} that appeared after Pb (II) adsorption [28]. Which indicate that the metal ions adsorption affected the chemical bonds in biosorbent.

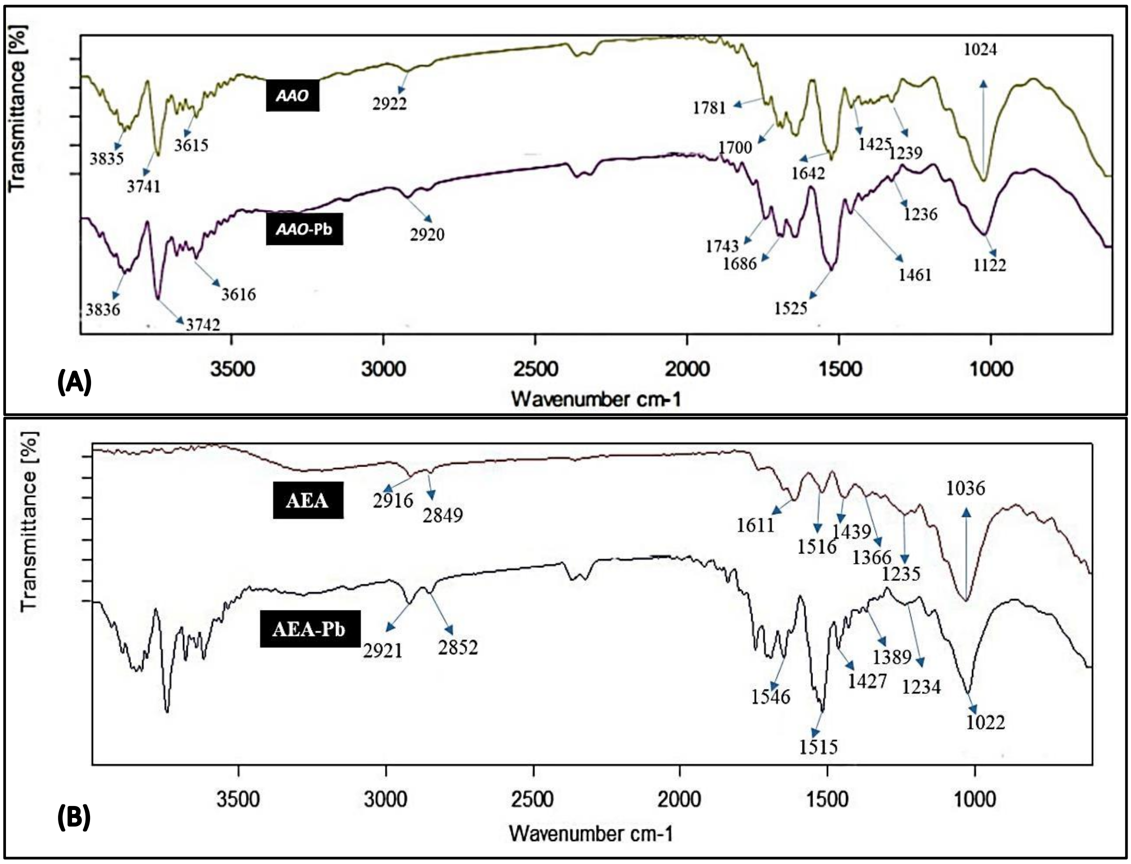

Figure 1

3.1.2 SEM Analysis (Characterisation of Surface Morphology)

Scanning electronic microscopy (SEM) analysis is one of the useful characterization techniques applied for the analysis of surface morphology, properties, porosity and texture morphology of biosorbent [29, 30]. The irregular, rough and porous structure of the activated *Eupatorium adinoforum (AEA)* and *Acer oblongum (AAO) biomass* is shown in Figure 2 A and Figure 2 C, which are one of the criteria of high adsorption capacity and favourable for adsorption process.

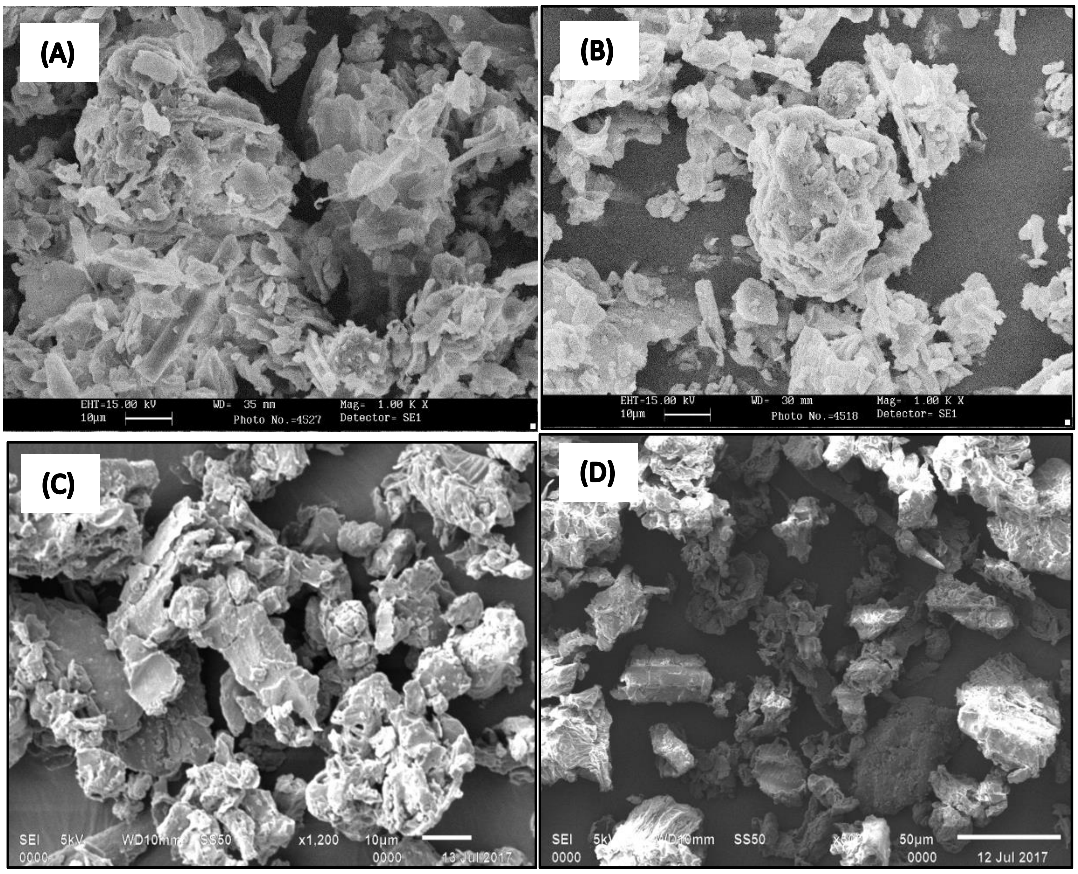

Figure 2: SEM image of (A): unloaded *Eupatorium adinoforum (AEA)* (B): Lead loaded *Eupatorium adinoforum (AEA)* biomass. (C) unloaded *Acer oblongum (AAO)* biomass (D) Lead loaded *Acer oblongum (AAO)* biomass

3.2 Biosorption of Pb (II) Metal Ions

Biosorption study of Pb (II) metal ions onto activated *AEA* and *AAO* biomass is carried out by batch experiments and process parameters used were pH, contact time, biosorbent dose, initial metal ion concentration and temperature.

3.2.1 Effect of solution pH

In Figure 3, For activated *AAO* biosorbent, the removal percentage increased pH from 1 to 5. The removal percent of Pb(II) ions was 25.7 % and 10.1% for *AEA* and *AAO* biosorbent respectively at pH 1. It increased to 58 % and 38% for *AEA* and *AAO* respectively at pH 3. For *AEA*, the maximum removal percent of Pb(II) ion was found to be 92.4 % and for *AAO* 85% at pH 5. After pH 7 a steady decrease to 81% for *AEA* and 65% for *AAO*. It decreased to 78 % for *AEA* 60.1% for *AAO* at pH 9. The maximum adsorption of lead ions is obtained at pH 5.0. It was show that the activated *AEA* biomass was more efficient biosorbent as compared to activated *AAO* biomass for the removal of Pb(II) ion from synthetic waste water and the optimum pH 5.

Experimental results exhibited that the percentage removal and adsorption capacity of the Pb(II) ions increases with an increase in solution pH from 1 to 5. After pH 5 the percentage removal and adsorption capacity decreases. The minimum biosorption at low pH is due to high concentration and high mobility of hydrogen ions. The hydrogen ions are preferentially adsorbed rather than the metal ions. At higher pH values, the lower number of hydrogen ion and greater number of ligands with negatives charges results in greater metal ions biosorption [31]. The maximum adsorption of metal ions is obtained at pH 5.0 [31]. Above pH 5 a steady decrease of adsorption of metal ions can be related to the precipitation of metal hydroxide [32, 33].

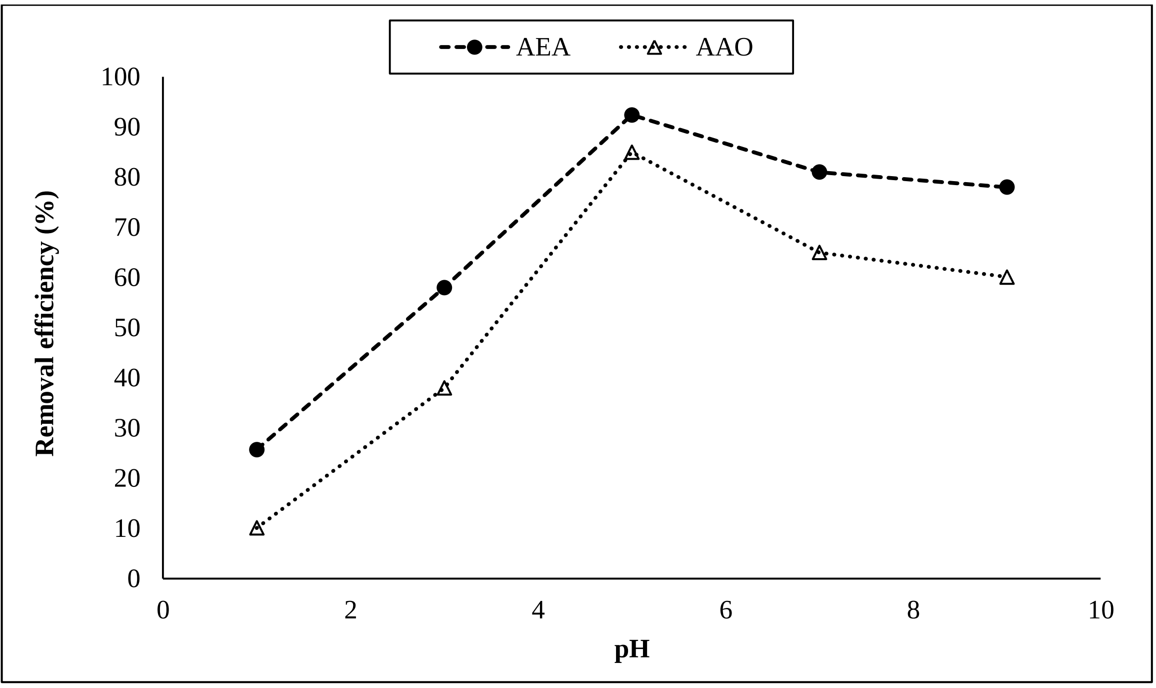

Figure 3: Effect of solution pH on adsorption of Pb (II), metal ions onto activated *AEA and AAO* biomass: (experimental conditions: initial concentration of metal ions 10 mg/L; 1 g *AEA* and *AAO*; contact Time 30 min.; temperature 295 K; agitating speed:170 rpm)

3.2.2 Effect of Biosorbent Dose

For *AEA* biosorbent, the removal efficiency of Pb(II) ions is found to be 81% at 0.5 g of biosorbent dose. This removal efficiency reaches 92.4 % at biosorbent dose 1 g. It increases to 95.7 % at biosorbent dose 2.0 g. The removal efficiency attains maximum value of 96.01 % at 2.5 g of biosorbent dose. The amount of lead ion adsorbed per unit mass q_e from 1.62 mg/g to 0.364 mg/g for 0.5 g and 2.5 g of *AEA* biosorbent dose respectively.

The removal efficiency of lead ion onto activated *AAO* biosorbent, is 75 % at 0.5 g of biosorbent dose. On increasing biosorbent dose to 1g, it becomes 86 %. It increases to 90.02% at 1.5 g of biosorbent. It is observed that after 1.5g of biosorbent dose gradually increases the removal efficiency. The removal percent obtained was 92.32 % for 2.0 g and 93.31 % for 2.5 g of biosorbent dose. Adsorption capacity q_e decreases from 1.5 to 0.373 mg/g with increase of the biosorbent dose from 0.5 to 2.5 g. It was observed that the Pb (II) ion removal efficiency increases with increase biosorbent dose from 0.5 to 2.5 gm of activated *AAO* biomass.

The percentage removal and adsorption capacity of Pb(II) onto activated *AEA* and *AAO* biosorbent with different doses of biosorbent are shown in Figure 4 (A)and Figure 4(B) which indicated that the activated *AEA* is more efficient in comparison to activated *AAO* biosorbent for the removal of lead.

Initially the removal efficiency rapidly increased with biosorbent dos4e after 1.5 g of biosorbent dose it increases gradually, this is due to the availability of more active sites [34, 35]. However, for the same dose the adsorption capacity q_e of Pb(II) ions decreases with increase in metal biosorbent ratio. It may be due to aggregation resulting from high sorbent dose. The aggregation would lead to a decrease in total surface area of the sorbent and results to increase in diffusional path length [36].

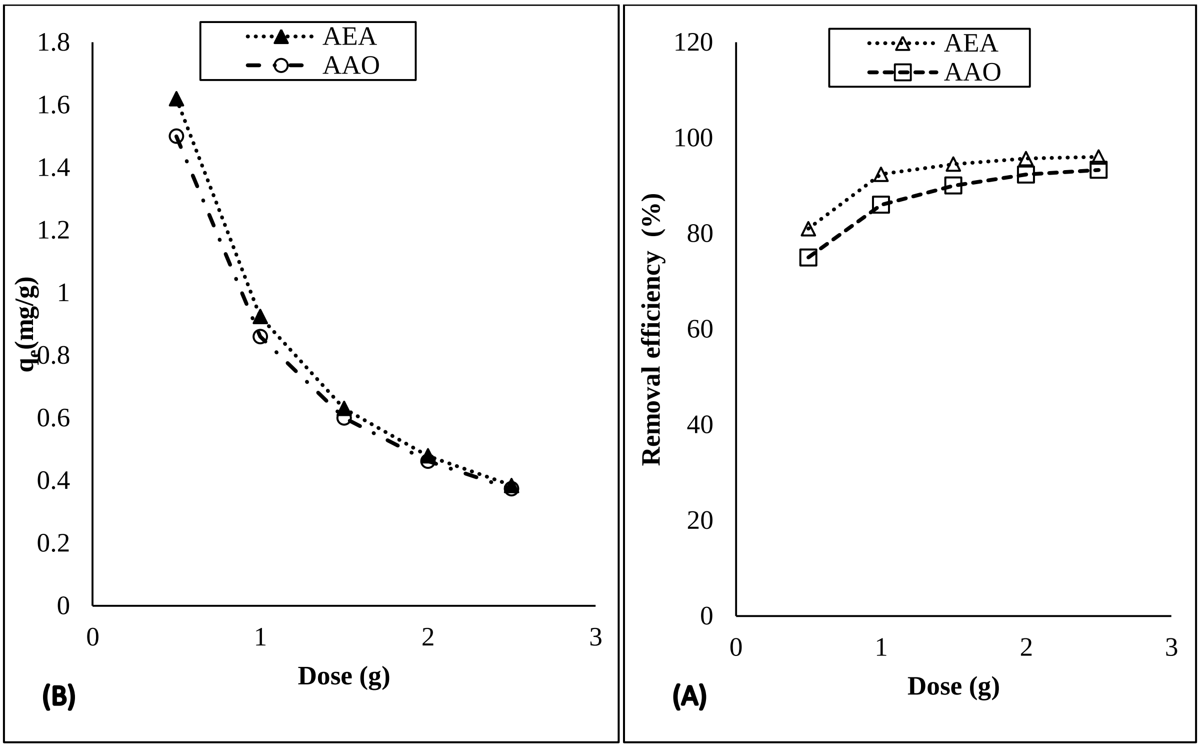

Figure 4: Effect of biosorbent dose of Pb (II), metal ions onto activated *AEA* and *AAO* biomass: (experimental conditions: initial concentration of metal ions 10 mg/L; pH 5.0; contact Time 30 min.; temperature 22 °C; agitating speed 170 rpm)

3.2.3 Effect of Initial Metal Ion Boncentration

For 10 mg/L of Pb (II) ion biosorption, the maximum removal efficiency was found 92.2 % and 83% for *AEA* and *AAO* biomass respectively. It decreased to 76.65% and 69.45 % onto *AEA* and *AAO* for 20 mg/l of lead ion concentration. For 50 mg/L, it becomes 63.3 % and 55.32% for *AEA* and *AAO* biosorbent respectively. At the same time absolute amount of Pb (II) ions absorbed per unit of adsorbent increases from 0.92 mgg^{-1} to 3.16 mgg^{-1} when the metal ion concentration increases from 10 to 50 mgL^{-1}. The adsorption capacity (mgg^{-1}) reverse trend of removal efficiency. In 50 mgL^{-1} lead ion concentration adsorption capacity was 3.168 and 2.766 for *AEA* and *AAO* respectively. It was observed that the Pb (II) ion removal efficiency increases with increase biosorbent dose from 0.5 to 2.5 gm of activated *AAO* biomass.

It is evident that on increasing metal ion concentration from 10 to 50 mg/l, the percentage removal of Pb (II) ions decreases. This is due to the fact that for a given adsorbent dose the total number of available adsorption sites is fixed thereby adsorbing almost the same amount of adsorbate. Thus resulting in a decrease in the removal of adsorbate corresponding to an increase in initial adsorbate concentration i.e. saturation of the adsorbent [37]. The equilibrium uptake has been increased with increase in initial metal ion concentration from 10 to 50 mg/l (Table 6.7 and Table 8.8). This is due to increasing concentration gradient which acts as increasing driving force to overcome the resistances to mass transfer of metal ions between the aqueous phase and the solid phase [38].

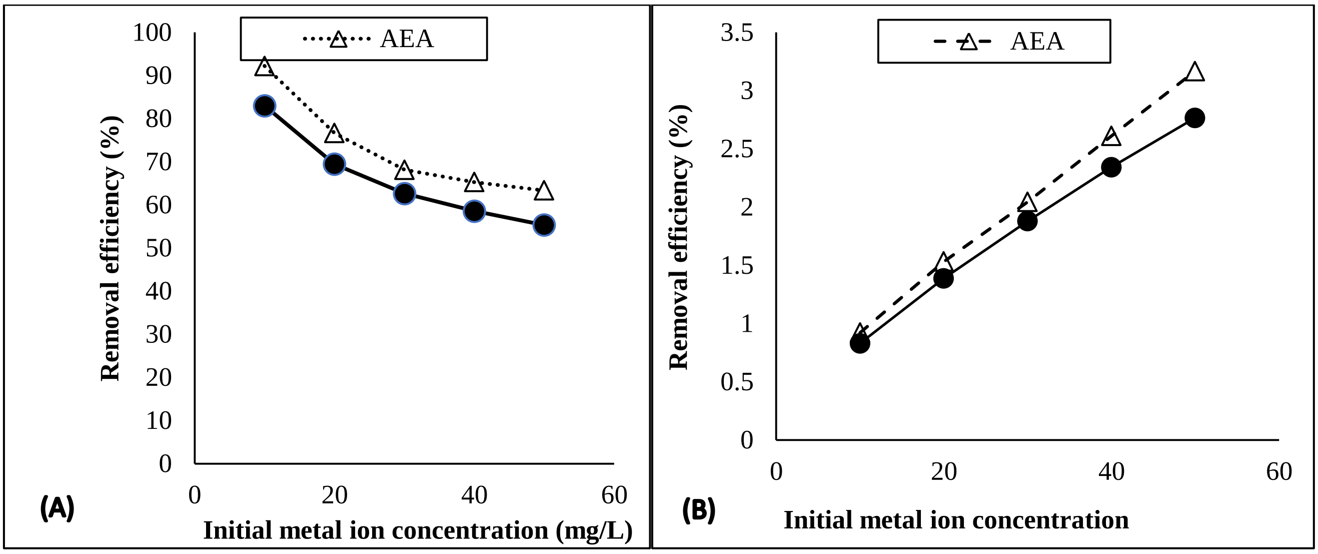

Figure 5: Effect of initial metal ion concentration on adsorption of Pb (II) metal ion onto activated *AEA* and *AAO* biomass: (experimental conditions: pH 5; 1gm dose of biomass; contact time 30 min; temperature 22 ^{0}C; agitating speed 170 rpm)

3.2.4 Effect of Contact Time

The effect of contact time on the adsorption of Pb (II) ions onto *AEA* and *AAO* was investigated with different initial Pb (II) ion concentration (10–50 mg/L), and shown in Figure 6 and Figure 6.10. The effect of contact time from 15 to 105 minutes in the removal of Pb(II) ion has been examined with 1 g of biosorbent dose at 22 ^{0}C. The initial concentration of lead ion was kept 10, 30 and 50 mg/L keeping the agitation speed to 170 rpm.

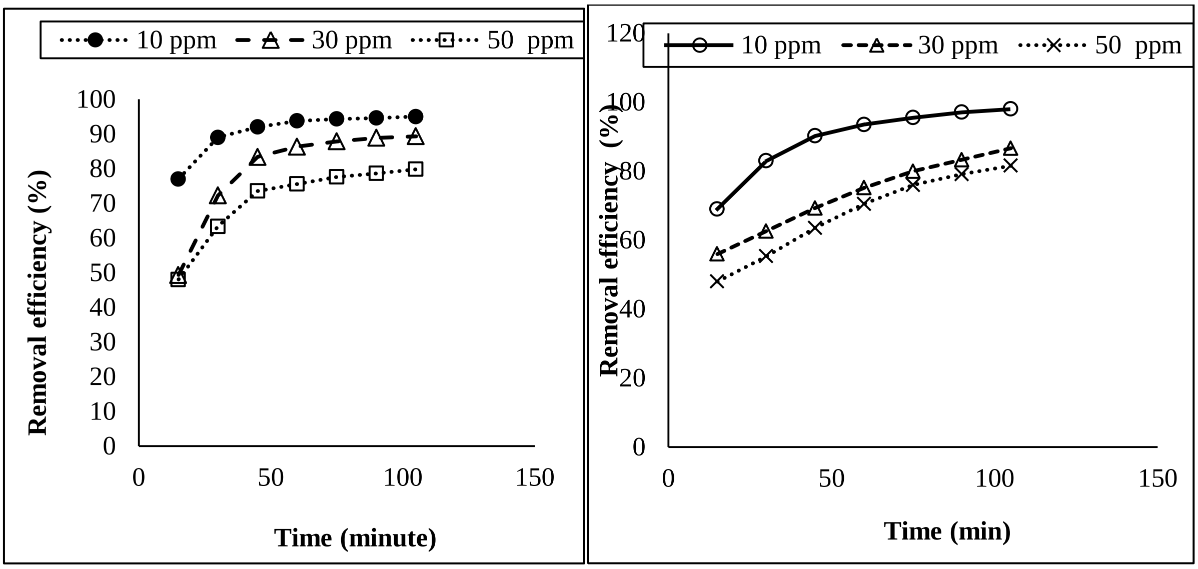

Figure 6: Effect of contact time and initial Pb (II) ion concentration adsorption biosorption onto (A) activated *AEA* biomass*:* (experimental condition: biosorbent dose 1gm/100 ml; temperature 22 ^{o}C; pH 5), (B) activated *AAO* biomass: (experimental condition: biosorbent dose 1gm/100 ml; temperature 22 ^{0}C, pH 5; agitation speed 170 rpm).

For 10 mg/L of Pb(II) ion with AEA, the removal percent was found to be 76% at contact time of 15 minutes. This reaches 89% at 30 minutes and 93.77% at 60 minutes. The metal uptake by biosorbent also increases from 0.76mg/g to 0.922mg for 15 minutes to 105 minutes.

At a contact duration of 15 minutes, the removal efficiency of 30 mg/L of Pb(II) ion onto AEA biosorbent was 49.33 percent. After 45 minutes of contact time, the biosorption percentage climbed to 83.67 percent. The removal efficiency increased gradually from 87.85 percent to 89.33 percent. when the interaction time is raised from 75 minutes to 105 minutes.

For 50 mg/L of Pb (II), the removal percentage achieved on AEA biosorbent was 48 percent after 15 minutes of contact time and climbed to 63.3 percent after 30 minutes. At 45 minutes, the removal efficiency climbed to 73.56 percent, progressively increasing to 75.58 percent at 60 minutes. It reached to 77.58 % at 75 minutes of contact time and it increased to 78.62 at 90 minutes. Finally, removal efficiency reached to 79.8% at 105 minutes.

In case of 10 mg/L of Pb (II) onto AAO biosorbent, the removal efficiency is increased 0.69 mg/g at 15 min to 0.9901 mg/g at 105 min. The adsorption capacity and% removal efficiency increase with increasing the contact time which reached to equilibrium within 105 minutes. After 90 minutes, the surface pores of biosorbent may be occupied and the Pb(II) ion requires more driving force to enter into the interior of the adsorption site after equilibrium [310]. The equilibrium adsorption capacity of the have increased with an increase initial Pb (II) ion concentration, while the percentage removal of Pb (II) ion showed the opposite trend. The values of qe increased from 0.48 to 0.771 mg/g for AAO biosorbent of contact time from 15 to 105 minutes.

This may be attributes to the initial concentration which provides an important driving force to overcome all mass transfer resistances of Pb(II) ions between the aqueous and solid phase, hence a higher initial concentration of Pb (II) ions will enhance the adsorption process [39]. The result shows that for all of initial metal ion concentrations the equilibrium is reached in the same time. The time required to attain the equilibrium time and the amount of metal adsorbed at that equilibrium time reflected the maximum metal adsorption capacity under these particular conditions [40]. *AEA* have better removal efficiency of Pb(II) as compared to *AAO* biosorbent.

3.2.1.1 Effect of Temperature

Biosorption of Pb (II) ion onto *AEA* and *AAO* biomass as biosorbent was investigated at five different temperatures ranging from 15 ^{0}C to 75 ^{0}C. Experiments with *AEA* biosorbent showed that the removal efficiency of Pb (II) ion decreased after 45 ^{0}C. The removal efficiency was 76.9 % at 15 ^{0}C which reaches to 85.8 % at 30 ^{0} C. The maximum removal percent achieved was 94.3 % at 45 ^{0}C, which decreased to 67.5 % at 60 ^{0}C and further removal percent decreased to 45.8 % with increase in reaction temperature at 75 ^{0}C.

The data obtained from the adsorption of Pb (II) ion onto the *AAO* showed that the removal efficiency decreases after 15 ^{0} C, the maximum percentage removal is achieved at 15^0 C, which is 90.2 %, which further decreases to 78.8 % at 30 ^{0} C. The removal efficiency was 69.9 % at 45 ^{0}C which reaches to 90.1 % at 45^0 C; however, it decreases to 22.8% at 75^0 C. The removal efficiency of 53.5 % for Pb (II) ion is recorded at 60 ^{0}C, finally it achieved a minimum removal percent of 40.1 % at 75 ^{0}C. The optimum temperature should be kept at 45 ^{0}C for activated *AEA* and 15 ^{0}C for *AAO* biomass.

The biosorption capacity of Pb (II) ion onto *AEA* which is decreased with increase in reaction temperature may be due to rising metal desorption tendency from the interface to the solution. The experimental result showed that the adsorption capacity decreases with increase in the solution temperature. This indicates that the adsorption of metal ions on *AAO* is exothermic in nature. The decrease in the rate of adsorption with the increase in temperature may be attributed to the weakening of adsorptive forces between the active sites of the biosorbents and adsorbate species and also between the adjacent molecules of the adsorbed phases [41]. The variation in the extent of adsorption with respect to temperature has been explained on the basis of thermodynamic parameters. This effect proposed that a description of the biosorption mechanism [42, 43]. The biosorption of Pb(II) onto *AAO* biosorbent involves a physical process, in which biosorption arises from the electrostatic interaction, which is usually associated with low adsorption heat [43].

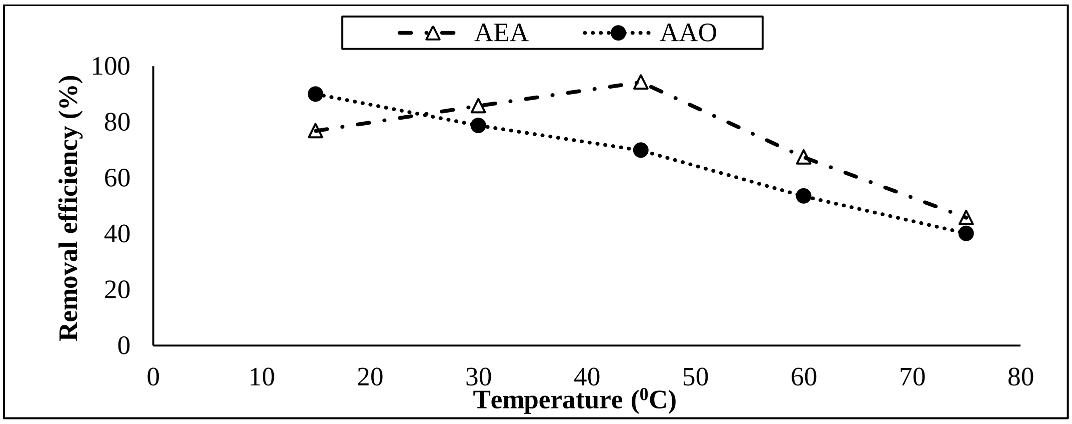

Figure 7 Effect of temperature on Pb (II) ion adsorption on to activated *AAO* and *AEA* biomass: (experimental condition: Initial metal ions concentration 10 mg/l; biosorbent dose 1gm/100 ml; contact time 30 min; pH 5; agitation speed 170 rpm)

3.2.2 Thermodynamic Study of Biosorption

At five different temperatures ranging from 288 to 348 K, the biosorption of lead ion onto AEA and AAO biomass as a biosorbent was examined. The initial concentration of Pb (II) ions was 10 mg/L. For adsorption of Pb(II) ion onto *AEA* and *AAO* biomass, the thermodynamic parameters enthalpy change (H^0), free energy change (G^0), and entropy change (S^0) describe the effect of temperature on the biosorption process. Whether the biosorption process is spontaneous or not, the variation in the process with regard to temperature has been described using thermodynamic factors. The Gibbs free energy change (G^0) is a measure of a chemical process' spontaneity, and it is affected by changes in enthalpy, entropy, and reaction temperature.

The ΔH° and ΔS° were obtained from the slope and intercept of the Van't Hoff plot of ln K_c versus 1/T. The value of ΔG^0, ΔS^0 and ΔH^0 are listed in Table 2.

Table 2: Thermodynamic parameters for adsorption of Pb (II) onto activated *AEA* and *AAO* biomass

Temperature (K)	***AEA***				***AAO***			
	ΔG^0 (kJ/mole)	**K_c**	**ΔH^0 (kJ/mole)**	**ΔS^0 (kJ/mole)**	**ΔG^0 (kJ/mole)**	**K_c**	**ΔH^0 (kJ/ mole)**	**ΔS^0 (kJ/mole)**
288	-7.97	3.33	+44.773	+0.157	-5.27	9.02	-35.47	-0.105
303	-15.22	6.04			-3.31	3.72		
318	-43.98	16.64			-2.23	2.32		
333	-5.75	2.08			-0.39	1.15		
348	-2.44	0.84			1.16	0.67		

The K_c values calculated for the adsorption of Pb (II) for activated *AEA* and *AAO* biomass are given in Table 2. As seen from the tables, the K_c values increase with increase in temperature which results in a shifting of equilibrium to the right i.e., adsorption lead ion is favored at higher temperatures. The low enthalpy values of ΔH° is 20 kJ/mole indicates that the physical sorption is involved in the process of adsorption [44]. The estimated values of ΔH° for the present system were greater than 20 kJ/mole and hence, the process may involve a spontaneous sorption mechanism as ion exchange where chemical bonds are not of strong energies. According to given data in activated *AEA* biosorbent the chemisorption takes place while in activated *AAO* biosorbent physical sorption takes place. The negative value of entropy change (ΔS°) corresponds to a decrease in degree of freedom of the adsorbed species and suggests the decrease in concentration of adsorbate in solid–solution interface indicating there by increase in adsorbate concentration onto the solid phase. This is the normal effect of the chemical adsorption phenomenon, which takes place through ion exchange interactions.

In Table 2, ΔG^0 values are -7.97, -15.22, -43.98, -5.75 and -2.44 kJ/mole at 288, 303, 318, 333 and 348 K for activated *AEA* biosorbent. It indicates that increase of spontaneity on rise in temperature till 45 ^{0}C. After 45 ^{0}C the free energy change became negative and decreases the spontaneity of biosorption process. The ΔG^0 values were found to be positive at temperature 288 K and became more negative at higher temperature 333K.

In Table 2, ΔG^0 values are -5.27, -3.31, -2.23, -0.39 and 1.16 kJ/mole at 288, 303, 318, 333 and 348 K respectively with activated *AAO* biosorbent. It indicates that the spontaneity decreases with rise in temperature. The ΔG^0 values were found to be high negative value at lower temperature 288 K and become more positive at higher temperature 348 K. The value of enthalpy change is -35.47 indicate that the reaction is exothermic in nature. The randomness decreases with rise in temperature.

The change in enthalpy ΔH^0, during biosorption of Pb (II) was found to be +44.77 and -37.47 kJ/mole for activated *AEA* and *AAO* biomass, respectively. The entropy change ΔS^0 for activated *AEA* biomass was +0.157 kJ/mole and that for the activated *AAO* biomass was -0.105 kJ/mole. The values of ΔH^0 obtained shows that the adsorption of Pb (II) onto both biosorbents was endothermic. The positive values of entropy may be due to some structural changes in the adsorbate and biosorbents during the adsorption process from aqueous solution onto the biosorbents. In addition to this, positive value of ΔS^0 indicates the increasing randomness at the solid–liquid interface during the adsorption of Pb (II) onto activated *AEA* biosorbents. The variation in the biosorption process with respect to temperature has been explained on the basis of thermodynamic parameters, whether the process is spontaneous or not. The Gibbs free energy change (ΔG^0) is an indication of spontaneity of a chemical process and depends on enthalpy change (ΔH^0) and entropy change (ΔS^0) [45].

In the biosorption of Pb (II) onto activated *AEA* biomass, the free energy range is -2 kJ/mole to -43.984 kJ/mole. It reveals that the physical adsorption takes place with rise in given temperature shown in Table 6.21. Generally for physical adsorption the free energy change (ΔG^0) ranges from (-20 to 0) kJ/mole and for chemical adsorption it ranges between (-80 and -400) kJ/mole [46]. At 318 K the ΔG^0 value is in range of -43.59 which indicates that the chemisorption at this temperature.

3.2.3 Adsorption Isotherm

An adsorption isotherm is characterized by certain constant values, which have to be investigated to understand the biosorption process. The surface properties and affinity of the biosorbent can also be used for the comparative study of the biosorbent for different pollutants [47]. Adsorption isotherm is important to describe how the adsorbate ions interact with the active site of biosorbent. The equilibrium data of biosorption of Pb (II) ion onto activated *AEA* and *AAO* biomass were subjected to Langmuir, Freundlich and Temkin isotherm models.

3.2.3.1 Langmuir Isotherm

According the Langmuir isotherm model the all-adsorption sites are homogeneous and does not dependent on the adjacent active sites are occupied or not, meaning monolayer. The Q_e and C_e correspond to the mg of metal adsorbed per g of activated *AEA* and *AAO* biomass and residual metal concentration in the solution when in equilibrium. K_L (L/mg) and Q_{max} are Langmuir constant and maximum capacity of adsorption (mg/g), respectively. Values of Langmuir parameters Q_{max} and K_L were calculated from the slope and intercept of linear plot of C_e/Q_e versus C_e and given in Figure 8(A). The values of Q_{max}, K_L and correlation coefficient R^2 are listed in Table 3.

The monolayer adsorption capacity Q_{max} is also calculated from Langmuir equation. The maximum biosorption capacity Q_{max} of Pb(II) ion was found to be 2.915 mg/g for *AEA* biosorbent and 3.002 mg/g for *AAO* biosorbent. High value of Q_{max} for *AAO* in comparison to *AEA* biosorbent was obtained.

3.2.3.2 Freundlich Isotherm

This model proposes heterogeneous distribution of active sites, accompanied by interaction between adsorbed molecules and based on the adsorption of metal ions on a heterogeneous surface of the biosorbent. The logarithmic values of Q_e and C_e for Pb(II) ion onto *AEA* and *AAO* leaf are given in the Table 3. K_F and 1/n can be determined from the linear plot of log Q_e versus log C_e. The linear plots log Q_e versus log C_e of Pb(II) ions on to *AEA* and *AAO* leaves are illustrated in the Figure 8(B).

Maximum adsorption capacity of Pb (II) ion was 1.16 and 0.96 mg/g with *AEA and AAO* biosorbent respectively. The regression coefficient R^2 values are recorded 0.993 and 0.9751 for *AEA* and *AAO* respectively. The values of 'n' at equilibrium are 3.878 and 2.365 for Pb (II) ion.

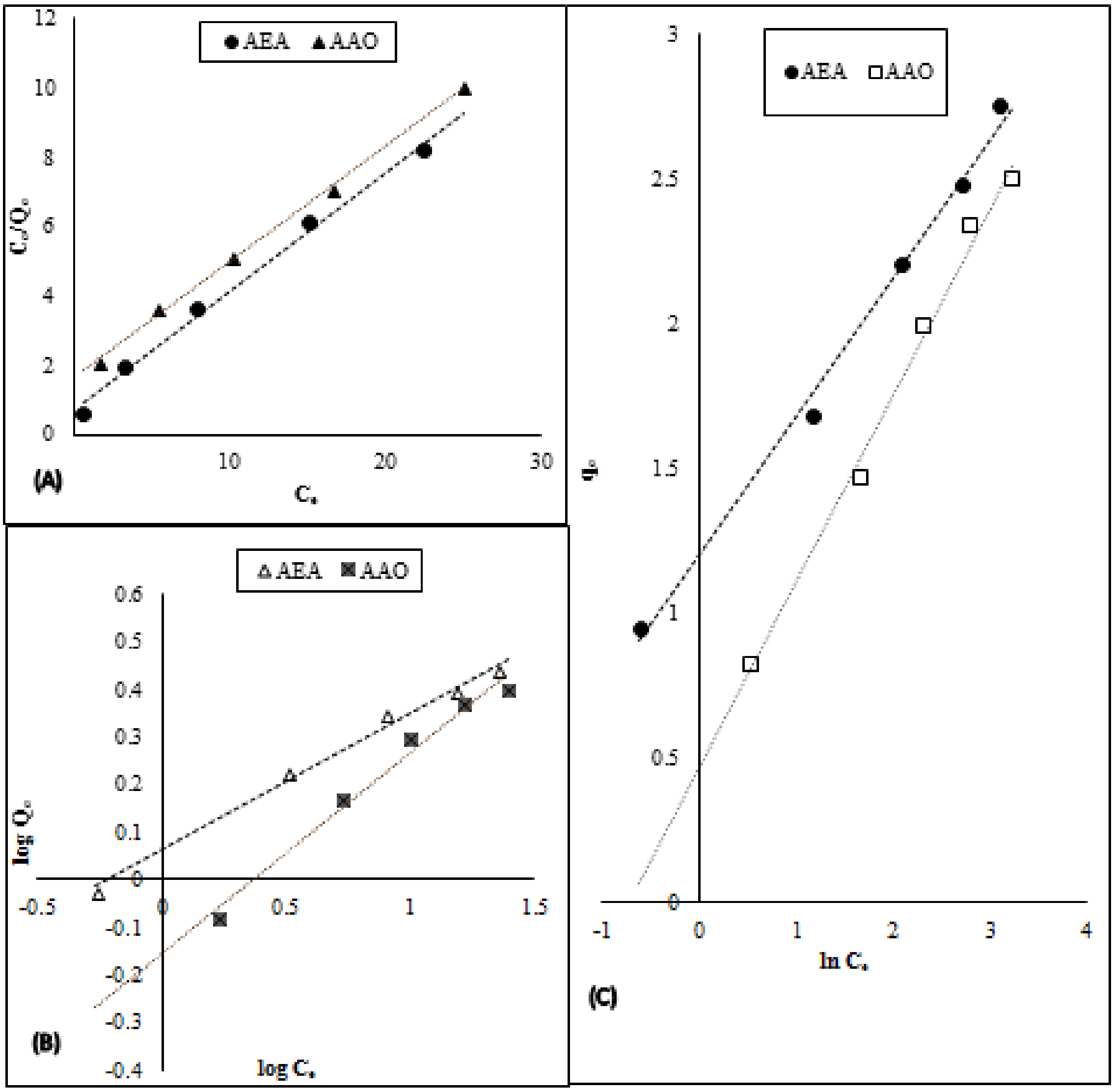

Figure 8: (A) Langmuir isotherm, **(B)** Freundlich isotherm, **(C)** Temkin isotherm, model for biosorption of Pb (II) onto activated *AEA* and *AAO* biomass

3.2.3.3 Temkin Isotherm

The Temkin isotherm model gives an idea of equal distribution of binding energies over a number of exchange sites on the surface. The equilibrium values of Q_e and ln C_e for Pb(II) ion onto *AEA* and *AAO* biosorbents are given in Table 6.24.

The constant A is related to the equilibrium binding constant (maximum binding energy), whereas constant B is related to the heat of adsorption, in this pattern *AAO* biosorbent shows more binding energy with lead ion as comparison with *AAO* biosorbent. The value of A and B are given in Table 6.2

The binding energy for the Pb(II) ion in terms of the Temkin isotherm model is 0.48 and 0.646 for activated *AEA* and *AAO* biosorbent respectively. High binding energy value for activated *AAO* biomass reveals that the activated *AAO* biomass has more binding energy for Lead in comparison activated *AAO* biosorbent. The regression coefficient R^2 values are recorded 0.994 and 0.993 for activated *AEA* and *AAO* biosorbent respectively.

Table 3: Biosorption isotherm constants for sorption of Pb (II) onto activated *AEA* and *AAO* biomass

Biosorbent	**Langmuir isotherm**			**Freundlich isotherm**			**Temkin isotherm**		
	Q_{max} (mg/g)	**K_L (L/mg)**	**R^2**	**K_F (mg/g)(L/mg)$^{1/n}$**	**N**	**R^2**	**b_T (mg/g)**	**A**	**R^2**
AEA	2.915	2.024	0.99	0.651	7.55	0.992	0.48	12.134	0.994
AAO	3.001	9.96	0.99	0.124	7.83	0.93	0.646	2.046	0.993

The isotherm constants and correlation coefficient R^2 of Langmuir, Freundlich and Temkin isotherm models are listed in Table 6.25. The correlation coefficients for Langmuir isotherm are highest in comparison to the value obtained for Freundlich and Temkin isotherms. Therefore, the Langmuir isotherm is followed in biosorption of Pb (II) ion onto *AEA* and *AAO* biomass. Q_{max} is the monolayer saturation at equilibrium. K_L which corresponds to the concentration at which the amount of Pb (II) ion bound to the *AEA* and *AAO* biomass is equal to 2.024 L/mg and 9.96 L/mg respectively. The affinity of Pb (II) ion with *AEA* and *AAO* biomass is very high. Show higher monolayer adsorption capacity. K_F and 1/n indicate the adsorption capacity and adsorption intensity, respectively. The higher value of 1/n indicates that the higher affinity and heterogeneity of the adsorption sites. The linear plots for Temkin adsorption isotherm (Figure 6.15), which consider chemisorption of adsorbate onto the biosorbent, fit quite well with correlation coefficients ($R^2 > 0.99$).

3.2.3.4 R_L Values at Different Initial Metal Ion Concentrations

R_L values can be used to predict whether an adsorption system is favourable or unfavourable [48]. The essential feature of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L[48]. C_0 is initial concentration of metal ions (mg/L) and K_L is Langmuir constant (L/mg).

Table 4: The R_L value for *AEA* and *AAO* biomass

Biosorbent	**R_L Value**				
	10 mg/L	**20 mg/L**	**30 mg/L**	**40 mg/L**	**50 mg/L**
AEA	0.047	0.024	0.016	0.012	0.01
AAO	0.02	0.01	0.007	0.005	0.004

The parameter, R_L indicates the adsorption nature to be either irreversible if ($R_L=0$), favourable if ($0<R_L<1$), linear if ($R_L=1$) and unfavourable if ($R_L>1$) [48]. In this study, the values of R_L obtained for Pb (II) ions onto *AEA* and *AAO* biomass at 293K are given in Table 6.26 and are greater than 0 and less than 1. This indicates that the adsorption of metal ions onto *AEA* and *AAO* biomass is favourable. In this study, all R_L values fall between zero and one as shown in Table 4.

IV. CONCLUSION

The findings of biosorption of Pb(II) ions onto *AEA* and *AAO* biomass make it clear that the biosorbent is quite effective for the removal of metal ions from synthetic waste water. It is observed that the removal efficiency (%) increases with increase in biosorbent dose and adsorption capacity (q_e) decreases with increase in biosorbent dose. Removal percent of Pb (II) ion onto *AEA* and *AAO* biomass decreases with the increase of the metal ion concentration while metal biosorption capacity (mg/g) increases with increasing metal ion concentration. The maximum removal is achieved at pH 5. The adsorption increases with increase in biosorbent dose and adsorption capacity decreases with increase in biosorbent dose. The thermodynamic parameters ΔH^0, ΔG^0 and ΔS^0 give information about spontaneity of adsorption process. The results indicated that Pb (II) biosorption onto *AEA* was spontaneous, endothermic and irreversible and for *AAO* biosorbent biosorption process was spontaneous, exothermic, reversible chemisorption process. Langmuir, Freundlich, and Temkin adsorption models were used to represent the experimental data. The Langmuir adsorption isotherm was best correlation coefficient for biosorption of Pb (II) ions onto activated *AEA* and *AAO* biomass, this indicating that the applicability of monolayer coverage of Pb (II) on activated *AEA* and *AAO* biomass surface. The biosorption capacity of *AAO* is greater than *AEA* biomass. The equilibrium data are also well described by the Temkin equation further supporting Pb (II) biosorption onto *AAO* as a chemisorption process.

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