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Biosorption of Pb (II) Ions from Aqueous Solution using Economically Available Adsorbent: Adsorption

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ABSTRACT

The efficacy of the low-cost biosorbents Vigna Uguiculata Activated Carbon (VUAC) and *Oryza sativa* Activated Carbon (OSAC) for the removal of Pb(II) ions from synthetic waste water was investigated. Both adsorbents were carbonized and sieved to provide a wide range of adsorbent sizes. Batch adsorption experiments were carried out. To match the adsorption data, Lagergren, Bhattacharya Venkobachar, Weber-Morris, Langmuir, and Freundlich isothermal models were employed and the corresponding constants K_{Lager} , K_{Bhatt} , and K_{id} were determined. Concentration separation factor (R_L) and maximum adsorption capacity (Q) were determined. The E_a was also determined and taken into consideration. The thermodynamic parameters G^0 , H^0 , and S^0 were determined. Both adsorbents were characterized using FTIR spectroscopy and SEM. Spontaneity of the process is confirmed by the negative value of G^0 . Both intraparticle and pore diffusion occurred during the adsorption process.

Key words: Adsorption, Lead(II), Langmuir, Freundlich, Thermodynamic parameters, Isotherm

In general, industrial wastewater contains numerous hazardous metals, including lead, which possess serious health risks [1]. Manufacturing of lead acid storage batteries, printing, pigments, fuel additives, and photographic materials are all examples of industrial activities that pollute the environment with lead [2]. According to the World Health Organization, the acceptable maximum of lead (II) in drinking water is 3-10 $g L^{-1}$. Lead poisoning can cause nephropathy, mental retardation, convulsions, and anemia [3]. As a result, lead should be removed as much as possible from industrial wastes to avoid health and environmental risks associated with its industrial disposal. Several conventional techniques for removing pollutants from waste exist [4], including filtration [5], ozonization [6], flocculation [7], coagulation and adsorption [8]. Because of the presence of functional groups such as carboxyl, hydroxyl, and hydroxyl, biosorption is utilized to tackle control and sludge disposal concerns. Carbon stretching [9] is a term used to describe the process of removing carbon from Sour soup seeds [10], coconut shell [11], sago waste [12], and discarded tea leaves [13] have all been employed as efficient adsorbents for a variety of pollutants in recent years.

In terms of quantity, activated carbon from Vigna unguiculata (VUAC) and *Oryza sativa* activated carbon (OSAC) are both low-cost products. As a consequence, VU and

OS are used as adsorbent waste materials to remove Pb(II) ions from garbage in the study. Varied variables such as beginning concentration, dose adsorbents, adsorbent size, pH, and temperature have different impacts. The impacts of many variables such as initial concentration, dose adsorbents, adsorbent size, pH, and temperature have been studied. Biosorption equilibrium isotherms, kinetics, and thermodynamic parameters were also calculated.

MATERIALS AND METHODS

Adsorbent preparation and characterization

Both VU and OS were collected and broken into little pieces, then dried and cleaned with distilled water to remove dirt particles. The adsorbents were dried in a 100°C oven for 8 hours. The material was then carbonized in a Bunsen furnace and sieved to a particle size of 0-63 mesh. In the study, scanning electron microscopy and Fourier transform infrared (FTIR) spectroscopy were utilized (SEM).

Preparation of synthetic wastewater

The 1000ppm $Pb(NO_3)_2$ stock solution was prepared by dissolving 1.59g of $Pb(NO_3)_2$ in 1L of distilled water. This solution was kept as stock solution. Other required concentrations (100 - 1200ppm) were produced from the stocks solution. The volumetric analysis of Lead (II) concentration in synthetic wastewater was performed.

The batch biosorption equilibrium studies

The Batch Biosorption equilibrium experiments were conducted on Pb(II) adsorption on both VUAC and OSAC

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adsorbents. Contact time, initial concentration, adsorbent size, adsorbent dose, pH solution, and temperature variations were investigated. At various time intervals, the sample solution was removed from the thermostat mechanical shaker, and equilibrium was calculated [14].

The adsorbed concentration (q_t , mg g⁻¹) at(t) time was determined using equation (1)

$$q_t = \frac{(C_0 - C_t)V}{m} \dots\dots\dots (1)$$

Where, C_0 and C_t are the initial and final Pb(II) ion concentration (mg L⁻¹) correspondingly, V is volume of synthetic waste, m is mass of the adsorbent taken(g). The equilibrium biosorption at, q_e (mg g⁻¹), was estimated based on equation (2)

$$q_e = \frac{C_0 - C_e}{m} \dots\dots\dots (2)$$

Wherever, C_e is the equilibrium concentration Pb(II). The percentage of Pb(II) adsorbed was determined using the equation (3):

$$\text{Removal (\%)} = \frac{(C_0 - C_t) \times 100}{C_0} \dots\dots\dots (3)$$

Adsorption conditions

200 mg of VUAC was weighed and added with 50ml of 1000ppm Lead(II) solution at pH 7.0 in a 100 mL boron container. The thermostatic mechanical shaker was used to agitate the sample at 30°C with constant shaking speed for 150 minutes. After that, it was filtered. The concentration of lead(II) in the supernatant solution was also determined [15]. The influence of contact time (15, 30, 45, 60, 75, 90, 105, 120 minutes), biosorbent dosage (100-800mg), biosorbent size (0-63, 150-212, 250-300 and 420-600), pH (1-7), and temperature (30, 40, and 50°C) was calculated during the experiment. The varying parameter was calculated, while the other four parameters for VUAC and OSAC biosorbent remained unchanged.

RESULTS AND DISCUSSION

Biosorbent characterization

Activated adsorbents seems to have large number of pores which helps for greater adsorption [16]. Both VUAC and OSAC adsorbents are rich in functional groups and has been utilized for metal adsorption. According to the biosorbent characterization VUSA and OSAC are excellent adsorbents because they include many active sites. The picture depicts the FTIR spectra of the two adsorbents, the SEM picture were computed, while the other four values remained constant for VUAC and OSAC biosorbent.

Effect of contact time and initial concentration

Biosorption rates are solely determined by contact time and initial concentration. The initial metal ions concentration is an important adsorption parameter because it determines the adsorbent metal ion capacity for the concentration of metal ions [17]. The trend was increased with increase in contact time due to the proper residual time and higher driving force between the adsorbent and metal ions. The impact of contact time on the adsorption of lead (II) ions onto VUAC and OSAC is studied. The adsorbents increase with contact time until equilibrium is attained at 105 minutes and 120 minutes for VUAC and OSAC, respectively. Because of the enhanced obtainability of active required surface size on the adsorbent, biosorption was quick at first [18]. Similar study findings are available for the VUAC and OSAC, which had 92.5 percent and 73.6 percent elimination at equilibrium (Fig 1).

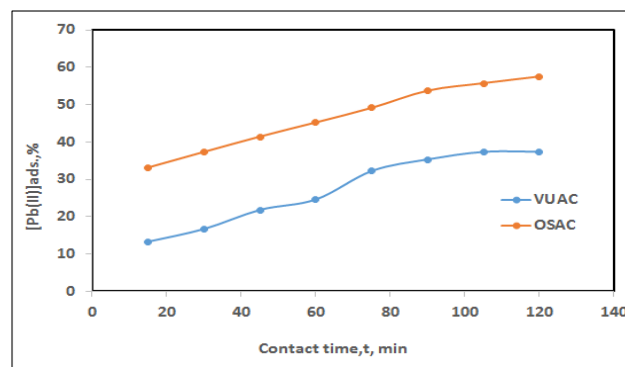


Fig 1 Influence of contact time on removal of lead (II) (VUAC) and (OSAC)

Influence of adsorbent dose

The adsorptive separation of toxic metals was raised gradually with rise in dose of the adsorbent [19]. The researchers were able to assess the influence of adsorbent dose on adsorption by increasing the dosage from 200 mg to 800 mg while keeping all other parameters constant. The percentage of adsorption rose from 12.6 percent to 92.5 percent when the adsorbent dosage was raised from 200 to 800 grams, but dropped by 24.8 percent for OSAC. The percentage of adsorption climbed from 12.6 percent to 92.5 percent when the adsorbent dosage was increased from 46.8% to 73.6 percent, and then fell to 41.2 percent for the relevant rate adsorbent's initial rise in active sizes [20].

Influence of pH

The pH of metal ion solution affects the density of the surface charge and ionization degree of the adsorbents [21]. Change in pH make a vital role in adsorption rate process [22]. Adsorption was maximum for higher pH and utmost removal of lead Pb(II) happens in the of around 4.0 (VUAC) and the optimum adsorption was 93.5%. For OSAC, optimum pH was 1.01 and optimum adsorption was 67.4% (Fig 2).

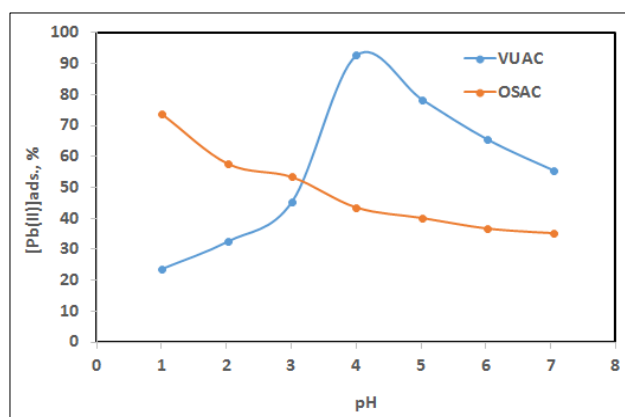


Fig 1 Influence of pH on removal of lead (II) (VUAC) and (OSAC)

Adsorption kinetics

Lagergren equation

The Lagergren equation suggests linearity for the plot of $\log_{10} (q_e - q)$ against contact time, t . the linearity shows that the Lagergren model fits for the system [23].

Bhattacharya –Venkobacher equation

The Bhattacharya-Venkobacher equation was employed to confirm the findings already achieved from the study of the Lagergren [24]. Bhattacharya Venkobachar equation K_{Bhatt} confirms the monomolecular layer formation of Lead(II) ions of the adsorbent surface.

Weber-Morris equation

The Weber-Morris equation was used to get the intra-particle transport rate constant (K_{id} was computed as a rate

constant) [25]. Pore diffusion of Lead (II) species within the adsorbent pores was confirmed by the linear part (Table 1).

Table 1 Effect of initial concentration of the lead(II) ion K_{Lager} , K_{Bhatt} , K_{id}

Name of adsorbent	K_{Lager}		K_{Bhatt}		K_{id}	
	R^2	K_{Lager}	R^2	K_{Bhatt}	R^2	K_{id}
VUAC	0.9586	1.1111	0.9589	1.1494	0.9930	11.18
OSAC	0.9338	1.0476	0.9438	1.1111	0.9840	10.00

Adsorption isotherms

The adsorption process of Lead (II) ions on to *Oryza sativa* activated carbon (OSAC) and *Vigna unguiculate* activated carbon were investigated using the three models of isotherm of Langmuir and Freundlich [26].

The Langmuir isotherm

The Langmuir isotherm model is based on the maximum adsorption relates to a saturated monolayer [27]. The Langmuir Isotherm equation can be calculated from the following linear form:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{max}} + \frac{1}{bQ_{max}} \dots \dots \dots (4)$$

Where, C_e = the equilibrium concentration of the Pb(II) (Mg/L)

q_e = the amount of Pb(II) weight of the adsorbent (Mg/L)

Q_m and b = Langmuir constants related to adsorption capacity.

Langmuir isotherm can be expressed in terms of the dimension less constant and separation factor, R_L by the equation:

$$RL = \frac{1}{1+bC_o} \dots \dots \dots (5)$$

Where, C_o = is initial concentrating of the adsorbate (Mg/L)

B = Langmuir isotherm constant (L/Mg)

The Freundlich isotherm

The Freundlich isotherm model is represented by the equation in the linear form:

$$\log q_e = \log K_f + 1/n \log C_e \dots \dots \dots (6)$$

Where, q_e = amount of Pb(II) adsorbed per unit weight of the adsorbent (mg/l) [28].

K_f = adsorption capacity measured

$1/n$ = adsorption intensity

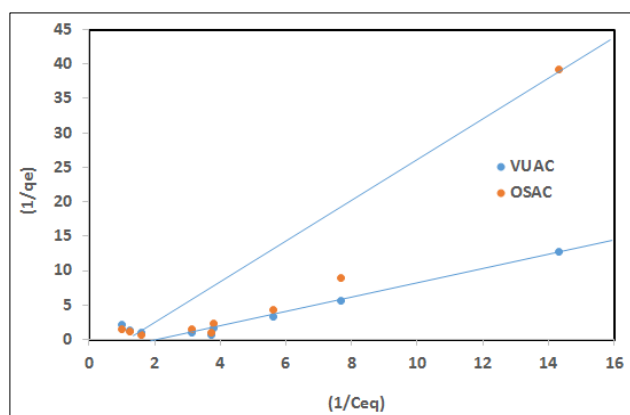


Fig 3 Data for Langmuir plot – VUAC and OSAC

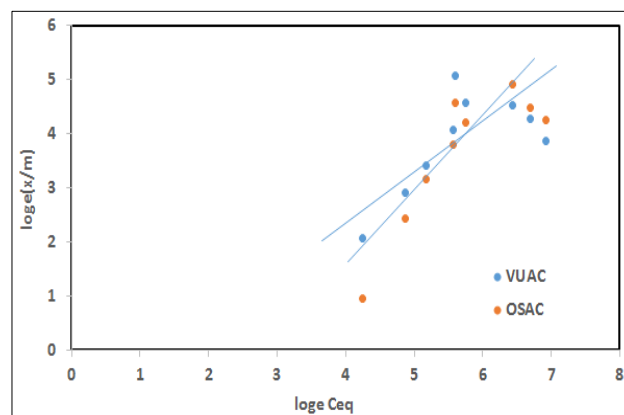


Fig 4 Data for Freundlich plot – VUAC and OSAC

Temkin isotherm

In the heat of sorption, Temkin adopts a linear rather than a logarithmic isotherm. It is based on the assumption that adsorption heat reduces linearly as adsorbent coverage rises and that adsorption heat decreases linearly as adsorbent coverage grows (OSAC). Pyzhev [29] was the created isotherm.

$$q_e = RT/bT \ln K_T + RT/bT \ln C_e \dots \dots \dots (7)$$

Where, b_T (KT/mol) is of sorption and K_T Temkin adsorption potential. The slope and intercept of the straight line K_T and b_T are evaluated.

Table 2 Effect of initial concentration of the lead(II) ion on Langmuir and Freundlich isotherm and Temkin isotherm

Name of the adsorbent	Langmuir Isotherm				Freundlich Isotherm			Temkin Isotherm		
	R^2	Q_m	B	R_L	R^2	$1/n$	K_f	K_T	b_T	R^2
VUAC	0.9471	0.6969	0.02	0.20	0.8751	0.8189	0.2041	0.01	38.88	0.9043
OSAC	0.408	0.6521	0.79	0.79	0.9803	0.9630	0.1674	0.03	23.80	0.9453

Thermodynamic parameters

The (ΔG°) standard free energy change, (ΔH°) standard enthalpy change and (ΔS°) standard entropy change were determined by the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \dots \dots \dots (8)$$

The thermodynamic adsorption Gibbs free energy change (ΔG°) adsorption method is possible and spontaneous.

ΔH° is negative value of the exothermic process. If the ΔG° value was available from 0 to -20 KJ mol⁻¹, then physisorption favours [30]. In this research work, the ΔG° values were in this range, confirms the process of physical adsorption. There was a possibility solid-liquid interface during the adsorption of (VUAC) and (OSAC) on to Pb(II) if the entropy (ΔS°) value positive. Activated energy E_a for the Pb(II) adsorption on to (VUAC) the (OSAC) were obtained using the equation.

$$\ln K_2 = \ln A - E_a/RT \dots\dots\dots (9)$$

Where, A- is the Arrhenius constant, K_2 is the biosorption

constant, E_a is the activated energy can be E_a slope and linear plot is presented (Table 3).

Table 3 Thermodynamic parameters and E_a value

Temperature K	VUAC			OSAC			Ea- Value	
	ΔG°	ΔS°	ΔH°	ΔG°	ΔS°	ΔH°	VUAC	OSAC
303	-16,640.2	54.90		-18,712.6	60.76			
313	-17,703.7	56.54	-6.36	-17,642.4	61.99	-3.20	20.46	26.60
323	-19,956.4	61.77		-20,260.7	62.71			

SEM image

The (Fig 5ab and Fig 6ab) represent SEM Photographs of both VUAC and OSAC before and after adsorption.

Morphology surface area pore size for the SEM photograph is shown below:

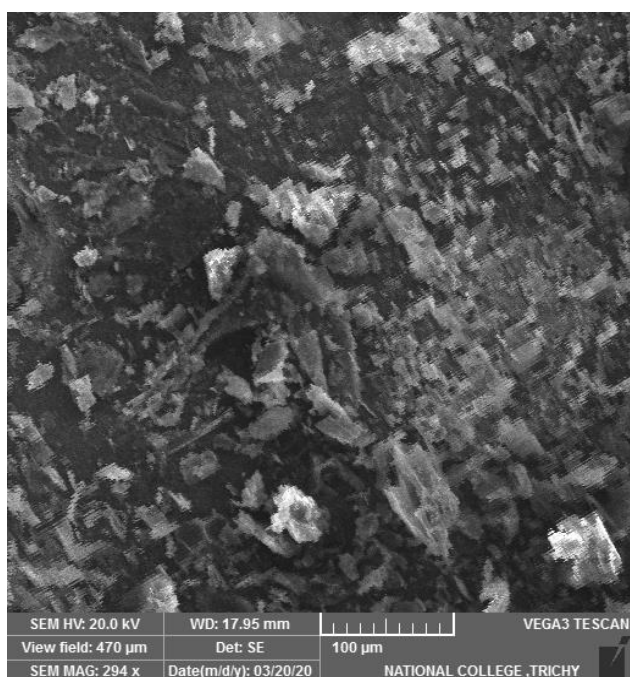


Fig 5 Before adsorption(a) VUAC

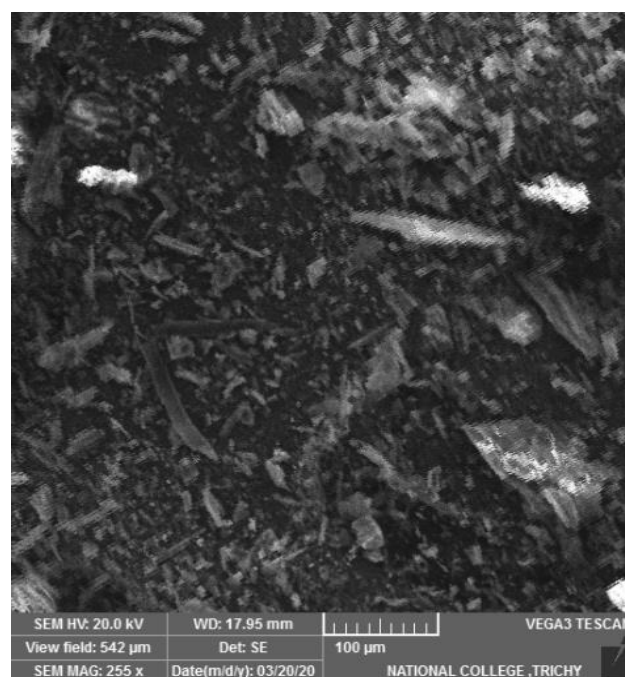


Fig 5 Before adsorption (b) OSAC

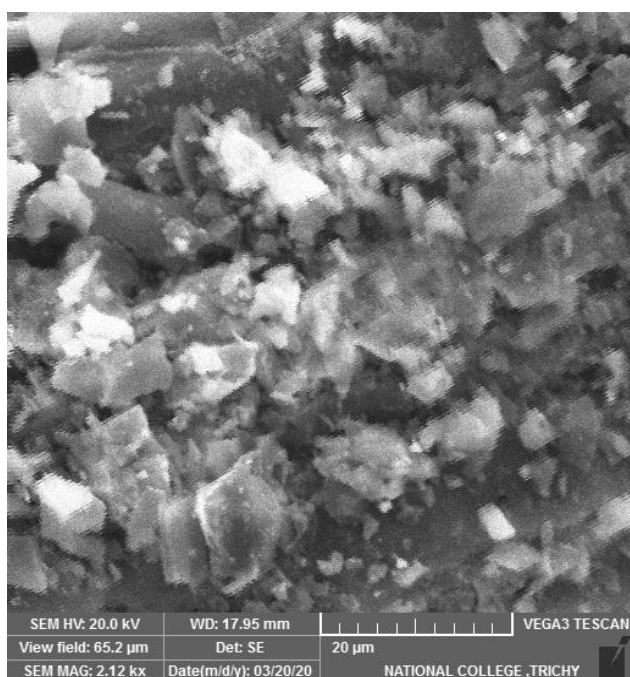


Fig 6 After adsorption (a) VUAC

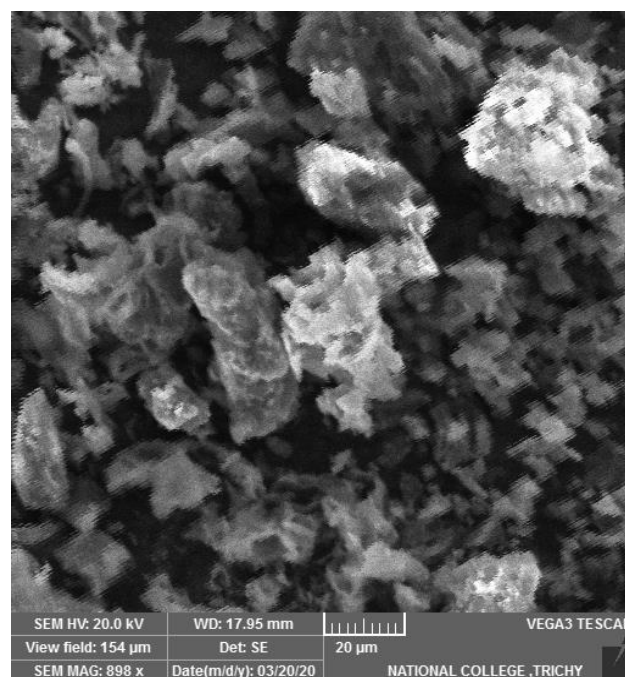


Fig 6 After adsorption (b) OSAC

FTIR spectra

The (Fig 7ab and Fig 8ab) show FTIR Photographs of VUAC and OSAC before and after adsorption. Effect of

activated carbon (VUAC) and (OSAC) on the elimination of certain functional groups is improved. The presence of the surface before functional groups indicates the adsorbent metal

binding ability. (VUAC) following functional groups after 1087- C-O-C- stretch strong, 1597- NO_2 strong, 576-C-Br and (OSAC) following functional groups after 1576- NO_2 strong,

1379- CH_3 -bend medium, 1073- C-O-C-stretch, 562-C-Br-strong.

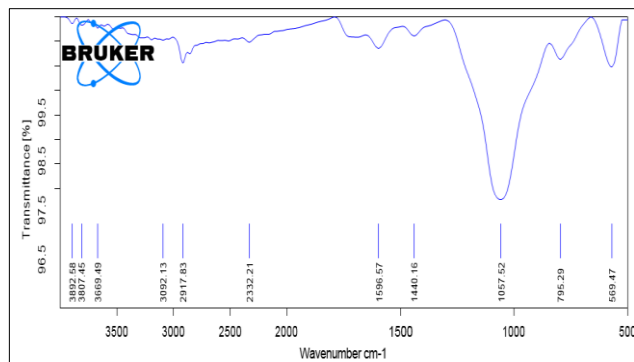


Fig 7 Before adsorption (a) VUAC-FTIR

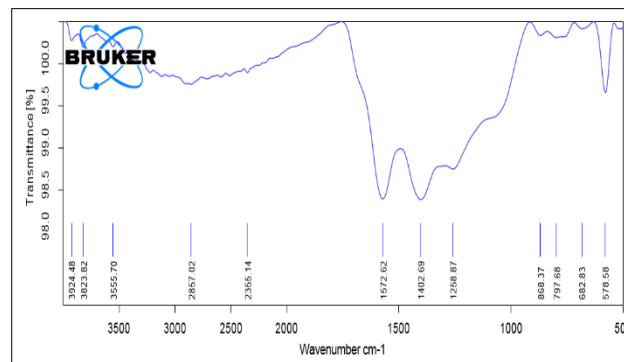


Fig 7 Before adsorption (b) OSAC-FTIR

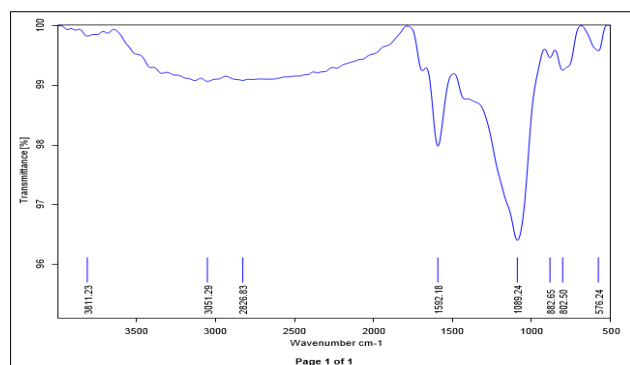


Fig 8 After adsorption (a) VUAC-FTIR

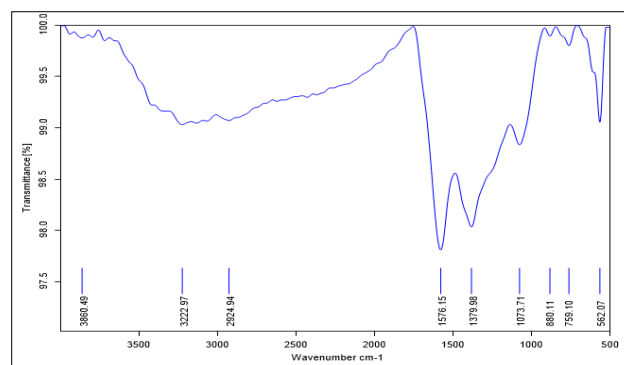


Fig 8 After adsorption (b) OSAC-FTIR

CONCLUSION

The elimination of Lead (II) ions on the surface of both VUAC and OSAC has been studied. The optimal conditions like contact time, dose, size, pH and temperature were determined. Lagergren, Bhattacharya-Venkobacher, and Weber-Morris were also put to the test. The activation parameter, E_a , has been identified. The thermodynamic constants for the exothermic adsorption process have been calculated. The negative G^0 indicates that this adsorption is unintentional. Functional groups present on the surface as well

as pore adsorbent have made it an effective adsorbent. SEM and FTIR confirms the adsorption process.

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