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Removal of Ni(II) and Pb(II) from aqueous solution using *Escherichia coli* immobilized in agarose gel

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ABSTRACT

The potential to remove Ni(II) and Pb(II) from aqueous solutions through biosorption using Escherichia coli immobilized in agarose was investigated. The effects of pH, contact time, initial concentration and temperature on the adsorption of Ni(II) and Pb(II) were studied. The optimum pH value was found to be 6 for Ni(II) and Pb(II) adsorption. The equilibrium experiment data were analyzed using Langmuir, Freundlich and Temkin isotherm models. The equilibrium data obeyed Langmuir isotherm with high correlation coefficient better than Freundlich and Temkin adsorption isotherms. From the Langmuir model, the maximum uptake capacities of Escherichia coli immobilized in agarose gel for Ni(II) were found to be 58.49 ±0.69 mg g^{-1} 63.28 ±3.41 mg g^{-1} and 69.69 ± 1.23 mg g^{-1} at 298K, 308K and 318K respectively. While for Pb(II) they were found to be 40.30 ±4.38 mg g^{-1}, 48.26 ±3.82 mg g^{-1} and 60.25 ±0.37 mg g^{-1} at 298K, 308K and 318K respectively. Increment in adsorption capacity with increasing temperature indicated that the adsorption process is endothermic in nature. Thermodynamic parameter ΔH^0_{ads} calculated for the two metals were found to be positive confirming the endothermic nature of the adsorption process. ΔG^0_{ads} were negative indicating the reaction is spontaneous and ΔS^0_{ads} obtained were positive indicating significant change in the internal structure of the adsorbent. The dependence of adsorption on time data were fitted with pseudo first order, pseudo-second-order and elovich kinetic models. The data fitted pseudo-second-order kinetic model with high correlation indicating that the adsorption processes were chemisorptions. The result indicated that Escherichia coli immobilized in agarose gel was suitable for biosorption of Ni(II) and Pb(II) from aqueous solution.

Key word: Biosorption, Lead, Nickel, Agarose and *Escherichia coli.*

INTRODUCTION

Toxic heavy metal release into the environment has been increasing continuously as a result of man's industrial activities and technological development. The release of these heavy metal posses a significant threat to the environment and public health because of their toxicity, bioaccumulation in the food chain and persistence in nature [1]. Lead provides no known biological benefit to human. it is associated with a continuum of health effects at both low levels of exposure resulting in damage to virtually all organs and organ systems, culminating ultimately in death at excessive levels of exposure. It also have effect on heam synthesis and other biochemical processes, impairment of psychological and neurobehavioral functions and a range of other effects [2]. Nickel is toxic to plant at concentration as low as 100 ugl^{-1}[3]. It adversely affects reproduction of fresh water crustacean at concentration as low as 0.995 mg l^{-1} [4]. In human (mammals) nickel acts to inhibit insulin release, depress growth and reduces cholesterol [5]. Nickel obtained from Ni-Fe storage batteries industries effluent cause's gastrointestinal irritation and lung cancer [6]

The conventional technologies for the removal of heavy metals from wastewater, which mainly include: chemical precipitation, ion exchange, adsorption, membrane processes and evaporation, requires high capital investment and running costs [7]. Therefore, there is an urgent need for development of innovative and low cost processes, where metal ions can be removed economically. The search for new treatment technologies has focused on biosorption [8]. Biosorption is a term that describes the removal of heavy metals by the passive binding to nonliving microorganisms (bacteria, fungi and algae) and other biomass (such as peat, rice hull, fruit peel, leave and bark of tree etc.) from an aqueous solution [9]. *Escherichia coli* a gram-negative, facultative anaerobic, non-sporulating and ovoid shaped microorganism stained red or pink by gram staining technique. The bacteria can be grown easily and its genetics are comparatively simple [10].

Commercial application of biomass as a biosorbent, however, has been hindered by problems associated with physical characteristics of these materials such as small particle size with low density, poor mechanical strength and rigidity, and solid/liquid separation [11]. Immobilization of the biomass within a suitable matrix can overcome these problems by offering ideal size, mechanical strength, rigidity, and porous characteristics to the biological material [12]. Many biopolymers such as calcium alginate, gluteraldehyde, agarose, and cellulose acetate are also known to absorb metals. These biopolymers are generally nontoxic, efficient, and inexpensive and thus highly competitive with conventional adsorbents. Biosorption technology based on the utilization biopolymers offers certain major advantages such as lack of toxicity constraints, non requirements of nutrients supply and recovery of bound metal species by an appropriate desorption method [13].

Agarose is a polysaccharide consisting of linear polymer of D-galactose and 3, 6-anhydro-L-galatose. Commercially, agarose is extracted from seaweed. Few works have been reported on the use of agarose to adsorb heavy metal from aqueous solution. It was reported that the maximum Cu(II) ions adsorbed by agarose gel was found to be 238 mg/g [14]. It was also reported that the maximum adsorption capacity onto agarose gel was 115 mg/ g for Pb (II) [15]. In this research, adsorption ability of *Escherichia coli* immobilized in agarose was investigated

for removal of Ni(II) and Pb(II) from aqueous solution. The effect of initial metal ion concentration, initial pH, temperature, and contact time were examined. Langmuir, Fruendlich and Temkin adsorption isotherms were applied to the equilibrium adsorption data. The pseudo first-order, pseudo second-order, and elovich kinetic models were used to study the dependence of adsorption on contact time.

MATERIALS AND METHODS

Preparation of adsorbate solution

1000ppm stock Pb(II) solution was prepared by dissolving 1.5986 g of lead (II) trioxonitrate (V) ($Pb(NO_3)_2$)(BDH) in 200ml of distilled deionised water in a beaker. Then 1.5ml of conc. HNO_3(Sigma-Aldrich) was added. This was then quantitatively transferred into a 1- litre flask and diluted to the mark with distilled deionised water. Similarly,1000ppm stock Ni(II) solution was prepared by dissolving 4.9434g of nickel(II)trioxonitrate(V)hexahydrate ($Ni(NO_3)_2.6H_2O$)(BDH) in 200ml of distilled deionised water in a beaker. Then 1.5ml of conc. HNO_3(Sigma-Aldrich) was added. This was then quantitatively transferred into a 1- litre flask and diluted to the mark with distilled deionised water. Various working solution were prepared from the stock by serial dilution.

Generation of biomass

Pure strains of *Escherichia coli* was collected from the Microbiology department of Ahmadu Bello University, Zaria and maintain by monthly subculturing on plate count agar and kept at 4^0C. The biomass grown in a 250 ml corked conical flask containing 100ml Muller Hilton broth medium having the composition (g/l): beef infusion solid (2.0), casein peptone (2.0), starch (1.5), calcium (0.05 mg), magnesium (0.02 mg) at 35^{o}C, 120 rpm in a thermostated water bath for 24 hours. After 24hours, biomass was harvested by centrifugation at 4000 rpm for 15minute at room temperature (25 ± 2) and washed twice with sterile normal saline solution [16]. After washing, the required amount of wet biomass was used for immobilization.

Preparation of the adsorbent

4% agarose solution was prepared by dissolving 10g of agarose in 240 ml of autoclaved deionised distilled water. The solution was heated in a microwave oven until a clear homogenous solution is observed. The heating was such that the mixture was not allowed to boil over. The agarose solution was cooled to about 37^{o}C then 100ml of cell suspension corresponding to 10 McFarland nephelometer standard was thoroughly mixed with the agarose solution. The mixture was poured into petriplate and kept on ice. After solidification on the petriplate 3 by 3 mm^3 cubes were cut and wash with deionized distilled water. Agarose gel only was prepared to serve as the control.

Determination of pH point of zero charge of the adsorbent

The pH point of zero charge of the adsorbents were determine as described by Onyango *et al.*, 2004 [17].

Adsorption experiment

Adsorption experiments were conducted at varying pH, contact time and adsorbate concentration. The experiments were carried out by batch method using 100 mL corked conical

flask, 10 mg of the adsorbents and the total volume of the reaction mixtures was kept at 50 mL. The pH of solution was adjusted to the desired value by adding 0.1 M NaOH or 0.1M HCl. The flasks were shaken for the required time period in a thermostated water bath shaker (Gallenkamp BKS-300010 F model). The isotherm study was performed using various concentrations of Ni(II) and Pb(II) solutions ranging from 25 to 100 mg/L at 298K, 308K and 318K and pH 6. The kinetics study was carried out with 50 ml volumes of 100mg/l initial Ni(II) and Pb(II) ion concentration, 10 mg adsorbent adsorbent dose and pH 6. The mixture was agitated at 120 rpm and 25^{o}C for different contact time ranging from 10-180 min. At predetermined time, the flasks were withdrawn from the shaker and the reaction mixtures were filtered through Whatman 1 filter paper. The first 5ml of the filtrate was discarded. All experiments were performed in triplicates. The filtrate samples were analyzed by flame atomic absorption spectrophotometer (Bulk scientific 2000 model). The Ni(II) and Pb(II) concentration retained on the adsorbent phase was calculated according to the equation below:

$$q_e = \frac{V(C_O - C_e)}{M} \quad (1)$$

The metal percentage removal (%) was calculated using the following equation:

$$\text{Removal}(\%) = \frac{C_e - C_0}{C_o} \times 100 \quad (2)$$

Where q_e is the amount adsorbed in mg/g of the adsorbent at equilibrium, C_o and C_e were the initial and the equilibrium concentrations in mg/l, respectively, V is the volume in liters of the solution used during the experiment and M is the mass of the adsorbent in gram.

RESULTS AND DISCUSSION

pH Point of zero charge of the adsorbents

The pH point of zero charge (pHpzc) of the adsorbents were assessed from the plot of zeta potential (mV) versus initial pH presented in Figure1. The pHpzc of *Escherichia coli* immobilized in agarose gel was 5.30 and that of the Agarose gel only (i.e the control) was 5.53. pHpzc of *Escherichia coli* immobilized in agarose was lesser than that of agarose gel only due to more acidic group present in the cell walls of *Escherichia coli* [18]. At pH value less than that of pHpzc, the surface charge on the sorbent is a net positive charge, while at pH value greater than that of pHpzc the surface charge on the sorbent is a net negative charge [14]. This accounted for the favorable adsorption of Ni(II) and Pb(II) on at pH value higher than pHpzc.

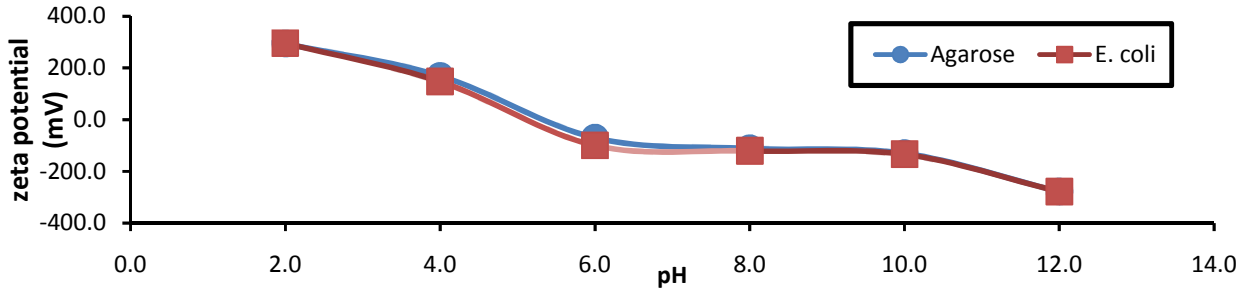

Fig.1 Zeta-potential against initial pH for the determination of pH_{pzc} of the adsorbents.

Effect of solution pH on adsorption of the metal ions

Figs. 2 show the variation of sorption percentage of Ni(II) and Pb(II) ions by the adsorbents with pH of the solution respectively. The highest sorption percent removal by *Escherichia coli* occurred at pH of 6 for Ni(II) ions, while that of Pb(II) occurred at pH of 5.5. It was observed that Ni(II) percentage removal increased from 44.35% to 80.25% as pH increases from 2.0 to 6.0 and decreased to 69.32 % at pH 8.0 while for Pb(II) percentage removal increased from 40.10% to 65.85% as pH increases from 2.0 to 6.0 and decreased to 41.00% at pH 8.0.

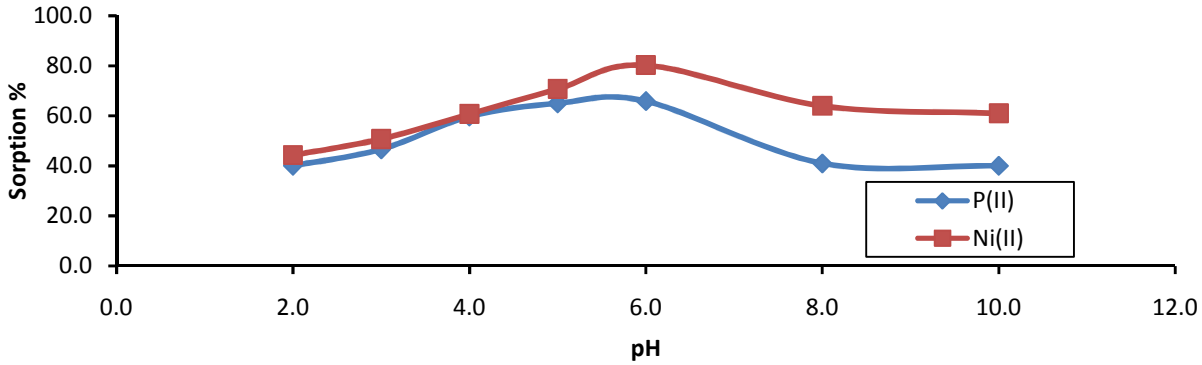

Fig.2. Sorption percentage against pH for the adsorption of Ni(II) and Pb(II) ion onto *Escherichia coli*.

At low pH values in aqueous medium, surfaces of adsorbents are closely associated with H_3^+O, this hinders the access of metal cations, by repulsive forces, to the surface functional groups and consequently decreasing the percentage metal removal [19]. Also the pH_{pzc} of the adsorbent used in this study is 5.30. These accounted for the reduction in percentage removal of Ni(II) and Pb(II) at lower pH and high percentage removal at pH 6. Furthermore, the decrease in percentage removal at pH value greater than 6 is attributed to the formation of insoluble metal hydroxides [20].

The effect of contact time and temperature

Figs.3 and 4 show the variation of adsorption percentage with time (minutes) for the adsorption Ni(II) and Pb(II) from aqueous solution onto *Escherichia coli* immobilized in agarose gel at different temperature.

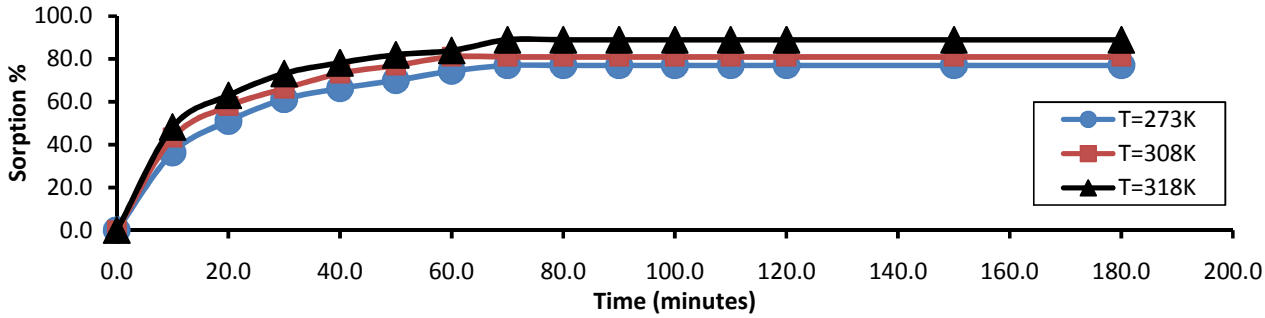

Fig.3 Variation of Sorption percentage with Time (minutes) for the adsorption of Ni(II) onto *Escherichia coli* at different temperature.

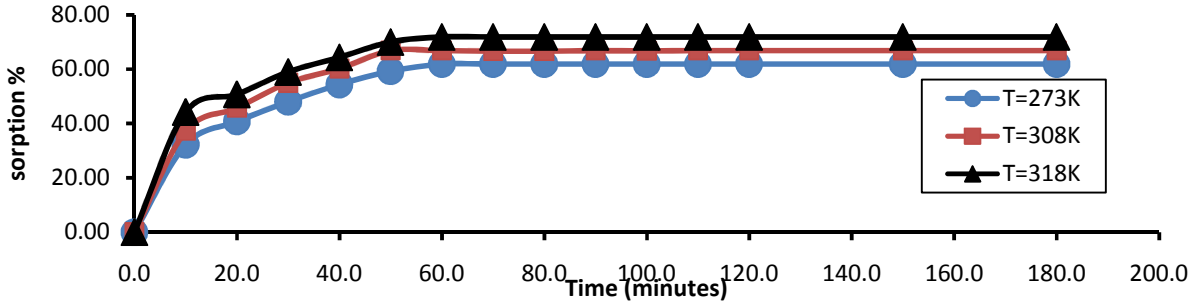

Fig. 4 Variation of Sorption percentage with Time (minutes) for the adsorption of Pb(II) onto *Escherichia coli* at different temperature.

Obviously, the rate of adsorption was rapid in the first 30minutes. Almost 60 percent removal of the metal ions by the adsorbents occurred at this time. There was an increase in the concentration of metal ion adsorbed, but at slower rate, until 60 minutes after which, there was no significant change in the adsorption percentage with further increase in contact time. This indicated that 60 minutes was the time required to achieve equilibrium and the uptake and unadsorbed metal ion concentration at the end of 60 minutes were given values q_e (mg/g) and C_e (mg/l) respectively. Such a fast adsorption rate before 30 minutes could be attributed to available functional group on the surface of the adsorbent [21]. The slower rate of adsorption in the latter stages may be attributed to great decrease of the binding site on the surface of the adsorbent [22]. A short contact time necessary to reach equilibrium in adsorption studies indicates that the predominant mechanism of reaction is chemical adsorption [23].

Considering the effect of temperature on the trend of adsorption, it was evident that the amount of metal ion adsorbed increases with increased in temperature. This indicate that the adsorption of the metal ions support the mechanism of chemical adsorption. For a chemical adsorption mechanism, the extent of adsorption is expected to increase with increase in temperature as observed in this study [24]. With increase in temperature, the attractive forces between adsorbents' surfaces and metal ions became stronger and these usually resulted in increase in extent of adsorption [25]. This behavior is typical for the adsorption of most metal ions from their solution onto natural materials [26]. It was reported that adsoption of Ni(II) on *Syzygium aromaticus* attained equilibrium within 40 minutes [23]. Similar rapid metal uptake has been reported for the biosorption of Pb(II) using *Ecklonia radiate* wherein the system reached over 50-60% of the equilibrium uptake capacity in 10 min [27].

Effect of initial metal ion concentration

Fig. 5 show the effect of initial metal ion concentration on the adsorption of Ni(II) and Pb(II) by *Escherichia coli* immobilized in agarose gel at 298 K. The increase in initial metal ion concentration decreased the percentage removal and increased the amount of metal ion uptake per unit mass of the adsorbent (mg/g). The figures revealed that for Ni(II) ions percentage removal decreased from 70.50% (8.82 mg/g) to 55.00 % (34.38 mg/g) while for Pb(II) ions it decreased from 64.96 % (8.12 mg/g) to 50.95 % (33.05 mg/g) by increasing the concentrations from 25 to 125 mg/L.

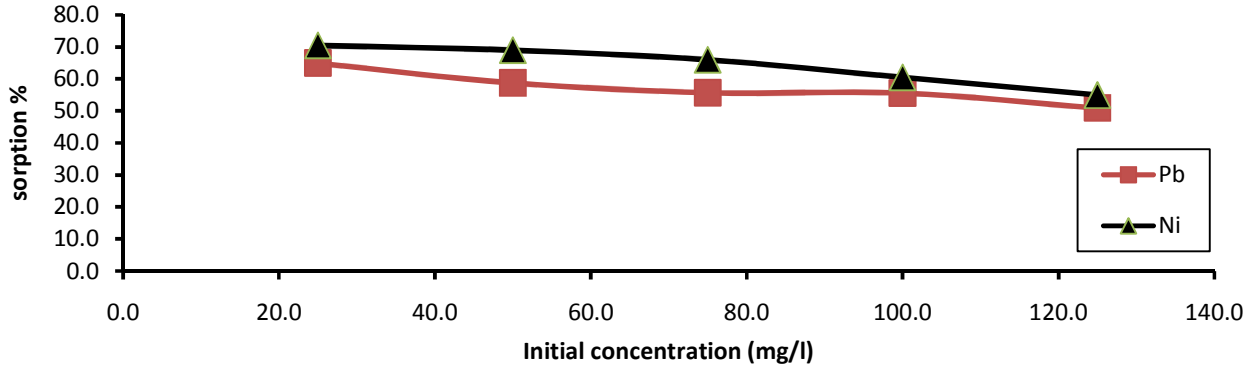

Fig.5 Variation of Sorption percentage with Initial concentration for the adsorption of Ni(II) and Pb(II) onto *Escherichia coli* immobilized in agarose.

The increase in the amount of metal ion uptake per unit mass of the adsorbent (mg/g) observed as initial concentration is increased was as a result of increase in concentration gradient, the driving force for adsorption. Though an increase in metal uptake (mg/g) was observed, the decrease in percentage adsorption may be attributed to lack of sufficient surface area to accommodate more metal ion available in the solution as the concentration increases. At lower concentrations, all metal ions present in solution could interact with the functional group and binding sites on the surface of the adsorbent and thus the percentage adsorption was higher than those at higher metal ion concentrations. At higher concentrations, lower adsorption yield is due to the saturation of adsorption sites. Thus, purification yield can be increased by diluting the wastewaters containing high metal ion concentrations.

ADSORPTION ISOTHERM

Adsorption isotherms are empirical equations essential for adsorption data interpretation and prediction. They are important for the description of how adsorbates will interact with an adsorbent and are critical in optimizing the use of adsorbent [28]. Langmuir, Freundlich and Temkin isotherms were employed for interpretation of adsorption data obtained in this work. Equations 3 to 5 represent the Langmuir, freundlish and the temkin adsorption isotherm.

Langmuir equation

$$\frac{C_e}{q_e} = \frac{1}{K_L Q^o} + \frac{C_e}{Q^0} \quad \text{----------(3)}$$

Where K_L (L/g) is a constant related to the adsorption/ desorption energy and Q^0 (mg/g) is the maximum sorption upon complete saturation of the adsorbent (biosorbent) surface (Horshfall *et*

al., 2004). The experimental data were fitted into the equation (3) by plotting of $\frac{C_e}{q_e}$ againstC_e . K_L (L/g) (Figures 6 to 9) and Q^0 (mg/g) were calculated from the slope and the intercept of the plots respectively.

Freundlich equation

$$Inq_e = InK_l + \left(\frac{1}{n}\right) InC_e \text{ ----------(4)}$$

where q_e (mg/g) is the adsorption density, C_e is the concentration of metal ion in solution at equilibrium (mg/l), K_f and n are the Freundlich constants which determines the curvature and steepness of the isotherm [29]. The experimental data were fitted into the equation (4) by plotting InC_e against Inq_e (Figure not shown).The value of $\frac{1}{n}$ and InK_l were determined from the slope and intercept of the plots respectively.

Temkin

$$q_e = \frac{RT}{b_T} \text{InA}_T + \frac{RT}{b_T} \text{InC}_e \text{ ----------(5)}$$

where $\frac{RT}{b}$ = B, q_e is the amount adsorbed at equilibrium and C_e is the residual equilibrium concentration, T is the absolute temperature (K) and R is the gas constant (8.314 J mol^{-1} K^{-1}). The experimental data were fitted into equation (5) by plotting plots of q_e against log C_e (Figure not shown) and the constant A_T (L/g) and b_T were determined from the slope and intercept of the plots respectively.

The adsorption data generally fitted Langmiur adsorption isotherm with hiigher correlation coefficients. Figures 6 display the Langmuir isotherms at various temperatures for the adsorption of Ni(II) onto *Escherichia coli* immobilized in agarose . Similar plots was obtained for Pb(II) and the adsorption of the metal ions agarose only i.e control (figures not shown). Adsorption isotherms are characterized by certain parameters (constants or coefficients), the values of which express the surface properties and affinity of the adsorbent towards the adsorbate and can also be used to find the maximum adsorption capacity of the adsorbents. Tables1 summarized the constants of the isotherms and their corresponding correlation coefficient (R^2) at different temperature for the adsorption of Ni(II) and Pb(II).

Table.1 Langmuir, Temkin and Freundlich isotherms constants and correlation coefficients for Ni(II) and Pb(II) adsorption *Escherichia coli* immobilized in agarose

	Nickel(II)						Lead(II)					
	Escherichia coli			Agarose			*Escherichia coli*			Agarose		
Temp.	298K	308K	318K	298K	308K	318K	298K	308K	318K	298K	308K	318K
langmuir												
$q_m(mgq^{-1})$	58.49± 0.69	63.28± 3.41	69.69± 1.23	24.18± 1.86	27.71± 0.54	32.42± 2.92	40.30± 3.82	48.26± 3.82	60.25± 0.37	21.99± 1.87	25.25± 2.15	28.07± 2.75
$K_L(Lmg^{-1})$	0.028± 0.01	0.030± 0.01	0.040± 0.01	0.017± 0.01	0.024± 0.01	0.027± 0.01	0.019± 0.01	0.023± 0.01	0.023± 0.01	0.009± 0.00	0.010± 0.00	0.011± 0.00
R^2	0.989± 0.00	0.957± 0.01	0.954± 0.04	0.963± 0.01	0.978± 0.01	0.989± 0.01	0.972± 0.03	0.976± 0.00	0.979± 0.01	0.982± 0.01	0.981± 0.01	0.993± 0.00
Temkin												
$A_T(L/g)$	0.272± 0.02	0.330± 0.02	0.473± 0.01	0.093± 0.00	0.100± 0.01	0.106± 0.02	0.174± 0.01	0.209± 0.01	0.250± 0.04	0.124± 0.02	0.165± 0.03	0.200± 0.04
B_T	11.83± 0.14	11.81± 0.27	11.62± 0.27	7.935± 0.57	7.499± 0.54	6.733± 0.24	11.81± 1.62	12.56± 1.29	13.42± 0.36	4.094± 0.68	3.999± 0.57	4.113± 0.34
R^2	0.918± 0.01	0.908± 0.03	0.895± 0.02	0.906± 0.00	0.906± 0.06	0.911± 0.01	0.909± 0.01	0.918± 0.00	0.914± 0.02	0.869± 0.03	0.916± 0.01	0.913± 0.01
Freundlich												
$K_F(mg/g)$	2.527± 0.07	3.680± 0.01	6.360± 0.80	0.387± 0.02	0.583± 0.02	1.146± 0.08	1.550± 0.02	2.256± 0.23	2.947± 0.58	0.373± 0.02	0.577± 0.10	0.737± 0.01
1/n	0.634± 0.04	0.573± 0.02	0.533± 0.05	0.819± 0.01	0.773± 0.01	0.759± 0.01	0.732± 0.02	0.691± 0.05	0.706± 0.08	0.737± 0.01	0.682± 0.05	0.682± 0.05
R^2	0.897± 0.02	0.892± 0.01	0.892± 0.01	0.895± 0.02	0.903± 0.01	0.913± 0.00	0.893± 0.01	0.875± 0.03	0.884± 0.02	0.896± 0.03	0.906± 0.02	0.924± 0.00

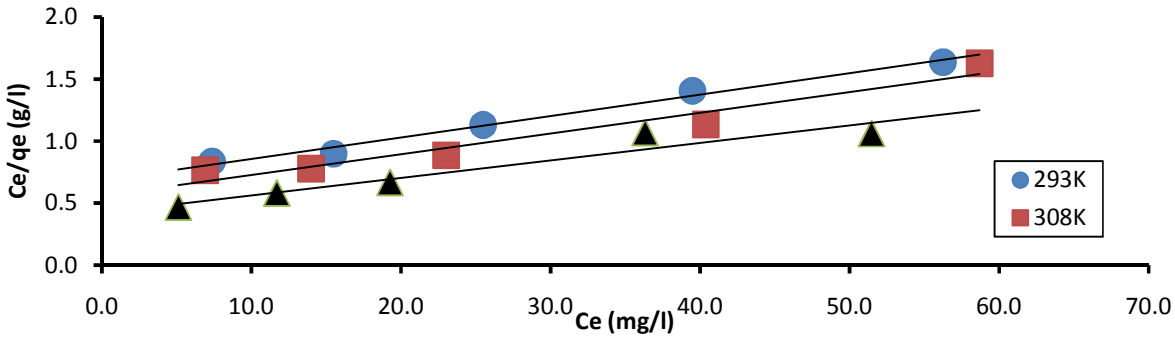

Fig.6 Langmuir isotherm at different temperature for Ni(II) ion adsorption on *Escherichia coli* immobilized in agarose.

Table 2 Thermodynamic parameters for the adsorption of Ni(II) and Pb(II) onto *Escherichia coli* immobilized in agarose

	Nickel(II)			Lead(II)		
	Escherichia coli			*Esherichia coli*		
Temperature	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1} K^{-1})	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1} K^{-1})
298 K	-18.34 ± 0.26			-20.35 ± 0.95		
308 K	-19.15 ± 0.43	9.80 ± 0.27	0.09 ± 0.00	-21.45 ± 1.29	10.27 ± 1.58	0.10 ± 0.00
318 K	-20.53 ± 0.49			-22.05 ± 1.69		
	Agarose only			Agarose only		
298 K	-16.84 ± 1.45			-18.72 ± 0.22		
308 K	-18.49 ± 0.68	9.06 ± 0.59	0.08 ± 0.01	-19.55 ± 0.17	6.54 ± 1.32	0.09 ± 0.00
318 K	-19.46 ± 0.63			-20.41 ± 0.28		

Examination of the correlation coefficients reported in Table 1 showed that the Langmuir model was more applicable to the adsorption of Ni(II) and Pb(II) by the adsorbents used than Tempkin and Freundlich models. This implied that a monolayer adsorption occurred over a surface containing a finite number of adsorption sites and the adsorbed ions cannot migrate across the surface or interact with neighboring molecules [30]. The Langmuir constants K_L and q_m which are related to the affinity between the adsorbent and adsorbate and adsorption capacity were found to increase with increasing temperature for all the adsordate on the adsorbents used. This indicated that the adsorption processes involved more heat of adsorption and increased adsorption capacity for the adsorbent with increasing temperature [31].Thus, the process is endothermic [32].

As could be seen, there was improvement in the adsorption capacity of agarose gel as a result of immobilization of microorganism. This was due to increased number of function group at the surface of agarose as a result of cell immobilization because microorganism cell walls are made up of peptidoglycan layers. Peptidoglycan contains functional groups like carboxyl groups (R-COOH), phosphomonoesters (R-OPO_3H_2), phosphodiesters $(RO)_2$, –$P(OH)_2$), amines (R-NH_3^+), and hydroxyls (R-OH) that could react with metal ions [33].

The Langmuir based adsorption capacity (q_m) of several adsorbents was reported in mg/g, for Novel saw dust (24.44 mg/g)[34], *Tamarindus indica* (25.34 mg/g) [35], resting cells of *Aspergillus sp* (34.8 mg/g) [36],Activated sludge (30 mg/g) [33] Algae, Nile water (37.43 mg/g), *Fucus spiralis* (64 mg/g), marine-algae dead biomass (80 mg/g) [37]. These values were in agreement with the data reported in Table 1. This implies that *Esherichia coli* immobilized in

agarose gel is an effective potential adsorbents for the removal of Ni(II) and Pb(II), from aqueous solution.

Adsorption thermodynamic

The thermodynamic parameters, change in enthalpy (ΔH^0_{abs}), free energy (ΔG^0_{ads}), and entropy (ΔS^0_{ads}) of adsorption were calculated to evaluate the thermodynamic feasibility of the process and to confirm the nature of the adsorption process. ΔG^0_{abs} for the adsorption processes was calculated using equation (6), ΔH^0_{abs} and ΔS^0_{ads} were obtained from the slope and intercept of the plot In K_o versus 1/T (Figure not shown) using the Vant Hoff equation (7). The results obtained were reported in Table 2.

$$\Delta G^0_{ads} = -RT\ In\ K_0 \text{----------(6)}$$

Where K_0 is the equilibrium constant (m^3mol^{-1}) determined from the Langmuir constant K_L[38,39]. ΔS^0_{ads} and ΔH^0_{ads} was determined using the Vant Hoff equation [40,41].

$$InK_0 = \frac{\Delta S^0_{ads}}{R} - \frac{\Delta H^0_{ads}}{RT} \text{----------(7)}$$

Where T is the absolute temperature (K) and R is the gas constant, (8.314 J mol-1 K^{-1}). The plot of InK_0 as a function of 1/T should give a linear relationship with slope of ΔH^0_{ads}/R and an intercept of ΔS^0_{ads}/R.

The result presented in Table 2 revealed that ΔH^0_{abs} of the processes have positive values which range from 6.54 ± 1.32 kJ mol^{-1} to 10.27 ± 1.58 kJ mol^{-1} . This confirms that the adsorption processes is endothermic in nature and there was a strong interaction between the adsorbents and the metal ions. The negative values of ΔG^0_{abs} , which range from -16.84 ± 1.45 (kJ mol^{-1}) to -22.05 ± 1.69 (kJ mol^{-1}), indicated that the processes were feasible and spontaneous. The positive values of ΔS^0_{ads} ranged from 0.08 ± 0.01 (kJ mol^{-1} K^{-1}) to 0.10 ± 0.00 (kJ mol^{-1} k^{-1}), this reflect the affinity of the adsorbents for the metal ions and also suggest some structural changes in the adsorbents [42,43]. As reported in Table1 the value of q_e (mg g^{-1}) increased with increasing temperature, this was because ΔG^0_{abs} decreases with increasing temperature of the solution [44]. This explains why the negative values of ΔG^0_{abs} increase with increasing temperature as presented in Table 2.

Adsorption kinetics

Kinetics of adsorption in terms of solute uptake rate, which governs the residence time, is one of the important characteristics defining the efficiency of adsorption processes. Kinetic parameters as a function of temperature were determined to predict the adsorption behaviour of Ni(II) and Pb(II) onto *Escherichia coli* immobilized in agarose gel. Pseudo-second order, pseudo-first-order (Lagergren), and elovich kinetic models were used to fit the experimental data obtained at different temperature.

Pseudo-first order kinetic equation

The integrated form of Pseudo-first order kinetic equation can be written as:

$$Log\ (q_e - q_t) = Log\ q_e - \frac{k_1}{2.303}t \quad \text{----------} \quad (8)$$

Where q_e(mg g^{-1}) and qt(mg l^{-1}) are the adsorption capacities at equilibrium and at time t, k_1(l min^{-1}) is the rate constant of pseudo-first-order adsorption . k_1(l min^{-1}) and q_e(mg g^{-1})can then be determine from the slope and the intercept of the plot of $log\ (q_e - q_t)$ against "t"

Pseudo-second order kinetic equation

The integrated form of pseudo-second order kinetic equation is express as [45]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{----------} \quad (9)$$

Where q_e(mg g^{-1}) and qt(mg l^{-1}) are the adsorption capacities at equilibrium and at time "t" respectively, k_2 (g mg^{-1} min^{-1}) is the rate constant of pseudo-second-order equation. The plot of t/q_t against "t" would give a linear relationship from which q_e and k_2 can be determined from the slope and intercept, respectively.

Elovich kinetic equation

The integrated form of elovich kinetic model is express as [46]

$$q_t = \frac{1}{\beta}\ In(\alpha\beta) + \frac{1}{\beta}\ In(t) \quad \text{----------} \quad (3.25)$$

where α is the initial adsorption rate (mg/gmin); β is the desorption constant (g/mg) during any one experiment.Thus the plot of q_t against $In(t)$, should give a straight line if Elovich equation gives a good model.

The result obtained showed that the kinetic plots of t/q_t versus t (i.e pseudo-second order) gave a better linear relationship compare to that of pseudo-first order and elovich kinetic models (figures not shown). Figure 7 and 8 represent the pseudo-second order kinetic plot for the adsorption of Ni(II) and Pb(II) at the temperatures of study.

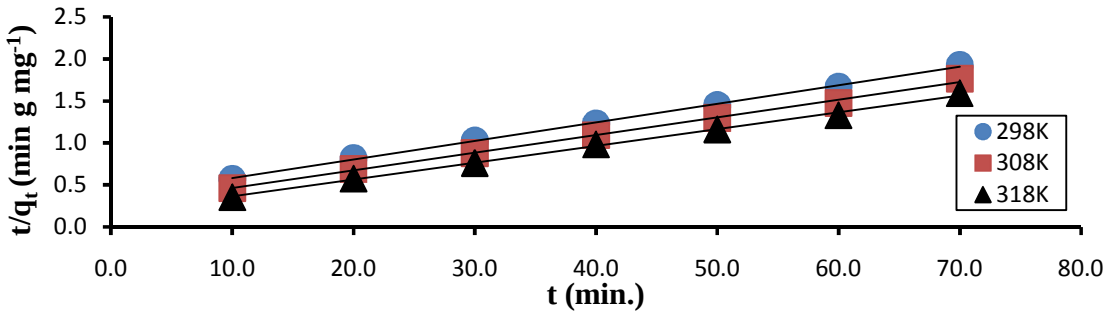

Fig. 7 Pseudo-second order kinetic plot at different temperature for the adsorption of Ni(II) onto *Escherichia coli* immobilized in agarose.

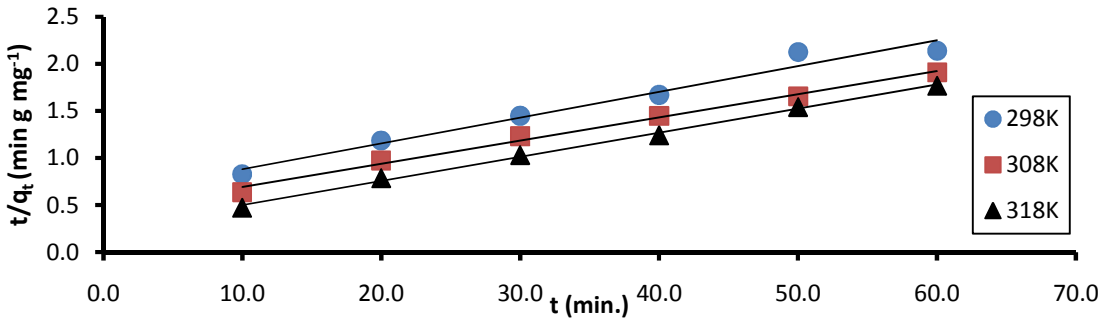

Fig. 8 Pseudo-second order kinetic plot at different temperature for the adsorption of Ni(II) onto *Escherichia coli* immobilized in agarose.

Kinetic parameters obtained from the plots and their correlation coefficients (R^2) are presented in Table 3. It was observed, as presented in Table 3, that the correlation coefficients obtained for pseudo second order kinetic model ranged from 0.944 to 0.997 and it is higher compared to those of pseudo-first order and elovich kinetic models. This confirmed that the adsorption data fitted pseudo second order very well. This indicated that the adsorption process can be described as chemisorptions [26]. At the equilibrium time, for each of the adsorbent used, the amount of metal ion adsorbed per unit gram of the adsorbent (q_e mg g^{-1}) increased with increase in temperature, indicating the chemisorptive nature of the adsorption processes [24].

Table3 Kinetic parameters for the adsorption of Ni(II) and Pb(II) onto *Escherichia coli* immobilized in agarose

	Nickel(II)				Lead(II)			
				Second order				
Temp.	q_e(mg g^{-1})	k_2x10^{-3} ($gmin^{-1}mg^{-1}$)	R^2	Ea ($kJmol^{-1}$)	q_e(mg g^{-1})	k_2 x 10^{-3} ($gmin^{-1}mg^{-1}$)	R^2	Ea ($kJmol^{-1}$)
298 K	40.47 ± 2.32	1.140 ± 0.02	0.955±0.01		34.82±1.52	1.277 ± 0.06	0.984±0.01	
308 K	47.39 ± 0.69	1.685 ± 0.05	0.989±0.01	31.58±6.87	38.10± 1.61	1.294 ± 0.06	0.986±0.01	22.02±0.91
318 K	49.65 ± 0.66	2.493 ± 0.09	0.986±0.01		40.23± 0.27	2.589 ± 0.06	0.983±0.01	
				First order				
	q_e(mg g^{-1})	K_1x10^{-2} (min^{-1})	R^2		q_e(mg g^{-1})	K_1x10^{-2} (min^{-1})	R^2	
298 K	24.25 ± 2.00	58.65 ± 0.11	0.868 ± 0.05		22.59± 0.52	43.86 ± 0.57	0.906 ± 0.01	
308 K	35.89 ± 0.82	60.29 ± 0.07	0.872 ± 0.08		28.57± 0.53	44.59 ± 0.72	0.905 ± 0.03	
318 K	44.05 ± 3.22	63.57 ± 0.05	0.846 ± 0.08		38.56± 1.39	48.44 ± 1.00	0.890 ± 0.01	
				Elovich kinetic				
	α (mg g^{-1})	β ×10^{-2} (mgg^{-1} min^{-1})	R^2		α (mg g^{-1})	β ×10^{-2} ($mgg^{-1}min^{-1}$)	R^2	
298 K	5.31 ± 0.56	8.69 ± 0.59	0.854±0.06		4.11 ± 0.31	11.19 ± 0.06	0.916 ± 0.01	
308 K	13.48 ± 1.74	10.37 ± 0.07	0.906±0.07		7.83 ± 1.15	11.45 ± 0.06	0.901 ± 0.06	
318 K	23.73 ± 2.43	15.47 ± 0.68	0.806±0.07		14.17± 1.05	11.83 ± 0.06	0.918 ± 0.02	

Also the values of the rate constant k_2 increased with increase in temperature. The increase in rate of adsorption with increasing temperature is described by the Arrhenius equation:

$$Ink_2 = InA_0 - \frac{E_a}{RT} \quad \text{----------(8)}$$

Where, Ao is the temperature independent factor called frequency factor, k_2 is the rate constant and Ea is the activation energy. A linear relationship was obtained between ln k_2 and 1/T because the correlation coefficient obtained from the plots of ln k_2 against 1/T were greater than 0.9. The

activation energies Ea was calculated from the slope of the plots (figures not shown) and the values obtained were presented in Table 3. The values of activation energies calculated were found to range from 19.63 ± 1.33 kJ mol^{-1} to 44.84 ± 1.59 kJ mol^{-1}. These values of activation energy obtained indicated the adsorption processes is chemisorptions [44].

CONCLUSION

The results of this study revealed that *Escherichia coli* immobilized in agarose gel could be used as an effective adsorbents material for the removal of Ni(II) and Pb(II) from water solution. The adsorption of the metal ions onto adsorbents used was found to be time, concentration, pH and temperature dependent. Maximum percentage removal occurs between the pH range of 5.0 to 7.0 for Ni(II) and Pb(II).The milligrams of metal ion adsorbed per gram of the adsorbent (q_e) were found to increase with increasing temperature, indicating endothermic and chemisorptive nature of the adsorption processes. The adsorption equilibrium data fitted Langmuir model better than Temkin and Freundlich models.

The positive values of ΔH^0_{ads} that ranged from 6.54 ± 1.32 (kJ mol^{-1}) to 10.27 ± 1.58 (kJ mol^{-1}) confirmed the endothermic nature of the adsorption processes and that strong interaction existed between the adsorbate and the adsorbents used. The positive values of ΔS^0_{ads} that ranged from 0.08 ± 0.01(kJ mol^{-1} k^{-1}) to 0.10 ± 0.00 (kJ mol^{-1} k^{-1}) reflected that significant changes occurred in the internal structure of adsorbents used. The negative values of ΔG^0_{abs} , which range from -16.84 ± 1.45 (kJ mol^{-1}) to -20.53 ± 0.49 (kJ mol^{-1}), indicated that the processes were feasible and spontaneous. Time dependent data indicate the applicability of pseudo-second order kinetics with correlation coefficient (R^2) ranging from 0.955 ± 0.01 to 0.989 ± 0.01 and the calculated activation energy (Ea) for the adsorption processes which were 22.62 ± 0.91 (kJ mol^{-1}) for Pb(II) and 31.58 ± 6.87 (kJ mol^{-1}) confirmed that the adsorption processes were chemisorptions and had low potential energy barrier.

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