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Adsorption Study of Ni (II) and Pb (II) onto Low-Cost Agricultural Biomasses Chemically Modified with TiO_2 Nanoparticles

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Abstract

Background: Heavy metal pollution in wastewater is a rapidly growing global concern and great effort has been made for developing efficient and low-cost alternatives to mitigate it. **Objectives:** This work attempts to evaluate the adsorption capacity of residual biomass from lemon, cassava and yam peels chemically modified with TiO_2 nanoparticles to remove Pb (II) and Ni (II) ions. **Methods/Analysis:** The TiO_2 nanoparticles were synthesized following a green procedure with leaf extract of lemon grass. After loading these nanoparticles to prepared biomass, chemical characterization was performed by FT-IR and EDX analysis in order to identify functional groups and elemental composition. **Findings:** The FT-IR analysis revealed that hydroxyl and carboxyl groups most contribute to adsorption process and the elements O, Ti and C were identified as main components of biosorbents. It was calculated a maximum adsorption capacity of136.3, 125.4 and 161.2 mg/g; and 181.5, 193.4 and 199.5 mg/g for Ni (II) and Pb (II) ions using modified CP, YP and LP, respectively. In addition, experimental data for Ni (II) ions uptake using YP-TiO_2, LP-TiO_2 and Pb (II) ions using YP-TiO_2biosorbent fitted to pseudo-second order. Meanwhile, Elovich model described accurately adsorption process overtime for Ni (II) using CP.TiO_2 and Pb (II) using LP-TiO_2 and CP-TiO_2biosorbent. The isotherm fitting revealed that Temkin and Freundlich best adjusted adsorption results for both heavy metal ions. **Novelty/Improvement:** These results suggested that modification with TiO_2 improves adsorption capacity of residual biomass from fruit and vegetable peels and the resulting biosorbents can be efficiently applied for lead and nickel removal.

Keywords: Agricultural Residues, Biosorption, Heavy Metals, Nanoparticles

1. Introduction

Heavy metals discharged through different industrial activities are one of the major causes of water pollution causing numerous diseases and disorders. Heavy metals can accumulate in the environment and steps must be taken to reduce their release and subsequent build-up[1]. Metals which are toxic pollutants include: mercury, cadmium, cobalt, nickel, and lead, among others. These metals show an extreme toxicity and high-level contamination in aquatic environments[2]. Exposure of humans to high levels of risk elements through their contact with contaminated waters, soils and the food chain can lead to serious chronic even carcinogenic disease[3]. In order to mitigate this problem, different methods have been developed by which such elements can be removed from aqueous solutions. Chemical procedures as reverse osmosis, coagulation, chemical precipitation, electro dialysis and ultra-filtration are widely employed in wastewater treatment[4]. However, all these methods are associated with discharge of toxic byproducts and are expensive[5]. Biosorption is regarded as one of the most suitable methods for removing heavy metals because of its promising advantages as low cost and high uptake efficiency[6,7].

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Abundant waste byproducts from industrial and agricultural activities may be potential inexpensive alternatives for heavy metals removal[8]. Fruit and vegetable peels are mainly composed of cellulose and pectin compounds which get ionized on alkaline treatment and generate negative charges which bind metal cations[5]. Being a renewable resource, agricultural waste peels are, therefore, a promising resource of biomass for preparing biosorbents[9]. In addition, agro-industrial sector generates a great amount of wastes annually worldwide and it is presently causing a serious disposal problem[10]. Alternatively, nanotechnology has been applied in wastewater treatment[11]. When nanomaterials are used as adsorbents mass transport resistance is greatly reduced due to their high surface area and adsorption capacity[12]. Titanium dioxide nanoparticles exhibit excellent chemical properties and nontoxicity, which make of it one of the most produced nanoparticles[13]. In this work, biomaterials from agricultural residues (lemon, cassava and yam peels) were modified with TiO_2 nanoparticles and used to carry out adsorption experiments for lead and nickel uptake.

2. Material and Methods

2.1 Preparation of Biomaterials

Agricultural wastes were selected as source of biomasses including lemon peels (*Citrus limonum*, LP), cassava peels (*Manhiotesculenta*, CP) and yam peels (*Dioscorearotundata*, YP), which were used to synthetize the biosorbents. These peels were cut and washed thoroughly to remove surface-adhered particles as reported by author in[14]. After drying for 24 hours at 80°C, the particle size of dried biomass was reduced to 0.5 mm by grounding and sieve-meshing[15].

2.2 Synthesis of TiO_2 Nanoparticles

The TiO_2 nanoparticles were synthesized by the green method pointed out by author in[16]. A leaf extract of lemon grass was used to reduce titanium (IV) isopropoxide. This extract was added to $Ti[OCH(CH_3)_2]_4$ solution and continuously stirred for 12 hours. The resulting nanoparticles were centrifuged in order to separate them from aqueous solution. To obtain powder, the TiO_2 nanoparticles were dried at room temperature and heated at 550°C for 3 hours.

2.3 Modification of Biomaterials with TiO2 Nanoparticles

In order to load TiO_2 nanoparticles onto biomaterials, Dimethyl Sulfoxide (DMSO) was used as organic solvent. In brief, 0.5 g of biomass was mixed with DMSO solution on a stirring plate for 24 hours at 120 rpm. The resulting suspension was stirred for 48 hours after adding 3 mL of Tetra Ethyl-O-Silicate (TEOS), which caused the hydrolysis and condensation of TEOS molecules. Then, 0.3 g of nanoparticles were added and centrifuged for 15 minutes at 3000 rpm. The synthetized biosorbents were washed with ethanol and dried[17,18].

2.4 Characterization Techniques

The Fourier Transform Infrared Spectroscopy (FT-IR) was carried out to identify functional groups in biosorbents (LP-TiO_2, CP-TiO_2 and YP-TiO_2) and TiO_2 nanoparticles. Energy Dispersive X-ray spectroscopy (EDX) on a JEOL JSM-6490 LV equipment was also used to identify elemental composition of these samples.

2.5 Batch Adsorption Experiments

Nickel sulfate ($NiSO_4$) and lead chloride ($PbCl_2$) were dissolved in deionized water to prepare stock solutions at 100 ppm. The initial solution pH was adjusted to 6 by adding NaOH and HCl solutions. The experiments were performed in a flask placed on a stirrer plate at 150 rpm and 25 °C. The pretreated biomass (YP, CP and LP) and the synthesized materials(LP-TiO_2, CP-TiO_2 and YP-TiO_2) were used as biosorbent and its concentration was fixed in 5 g/L and the remaining heavy metal concentration was determined by atomic absorption spectrophotometry analytical technique[19]. Equation (1) was used to calculate adsorption capacity:

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad (1)$$

Where (mg/L) is the initial concentration of nickel and lead, (mg/L) the remaining concentration of nickel and lead, is the sample volume (L) and the biosorbent amount (g).

2.6 Adsorption Isotherms and Kinetics

Aliquots of 5 mL were taken in a period of time and the remaining concentration was measured. These results were fitted to kinetic models (pseudo-first order, pseudo-second order, intraparticle diffusion and Elovich). The adsorption isotherms were calculated by varying initial heavy metal ions concentration in 25, 50 and 75 ppm and isotherm expressions purposed by Langmuir, Freundlich and Temkin were used as source of information related to adsorption mechanism and biosorbent surface[20]. The regression coefficient values were judged to find the applicability of these models to the adsorption data[21]. The application of experimental data on simple equations represents the fundamental interactions that happen between charged surface and nickel and lead ions[22]. The experiments were carried out in triplicate using chemically modified biosorbents and its arithmetic average was used to determine parameters of kinetic and isotherm models, whose mathematical expressions are presented in Tables 1,2.

Table 1. Mathematical expressions of kinetic models

Kinetic model	**Equation**	**Parameters**
Pseudo-1st-order	$q_t = q_e\left(1-e^{-kt}\right)$	q_e, Adsorption capacity at equilibrium (mg/g) k_1, pseudo-1st-order constant (min^{-1})
Pseudo-2nd-order	$q_t = \dfrac{t}{\left(\dfrac{1}{\left(k_2 q_e^2\right)}\right)+\left(\dfrac{t}{q_e}\right)}$	k_2 pseudo-2nd-order constant (g/mg.min) q_e, Adsorption capacity at equilibrium (mg/g)
Elovich equation	$q_t = \dfrac{1}{\beta}\ln(\alpha\beta)+\dfrac{1}{\beta}\ln t$	α, Elovich constant (mg/g min) β, Elovich exponent (g/mg)
Intraparticle diffusion	$q_t = k\sqrt{t}$	k, diffusion constant

Table 2. Parameters of isotherm models

Isotherm	**Equation**	**Parameters**
Freundlich	$q_e = K_F C_e^{1/n}$	K_F, indicator of the absorption capacity (mg/g) $1/n$, heterogeneity factor C_e, concentration of the metal (mg/L)
Langmuir	$q_e = \dfrac{q_{max} b C_e}{1+bC_e}$	q_{max}, maximum quantity of the metal/mass of biomass (mg/g) b, affinity of union sites C_e concentration of the metal (L/mg)
Temkin	$q_e = b_t \ln\left(K_t C_e\right)$	b_t, temkin isotherm constant (mg/g) K_t, equilibrium binding constant (L/mg)

3. Results and Discussion

3.1 Characterization of Biosorbent

Figure 1 shows FT-IR spectrum for all synthesized biosorbents. It was found characteristic peak around 1000 cm^{-1} attributed to carboxylate groups of cellulosic compounds[23]. The absorption band located between 3000-3500 cm^{-1} are assigned to -OH stretching vibrations[24]. The bands around 2300 and 1700 cm^{-1} correspond to aliphatic C-H groups and stretching vibrations of C=C and C=O, respectively[25]. The modification with TiO_2 nanoparticles is confirmed by the presence of Ti-O-Ti bond at 1457 cm^{-1} in YP-TiO_2 biosorbent spectrum[26]. The sharp peaks at 1456 cm^{-1} and 1507 cm^{-1} in CP-TiO_2 and LP-TiO_2 biosorbents spectrum were also attributed to Ti-O-N and Ti-O-C bonds[27].

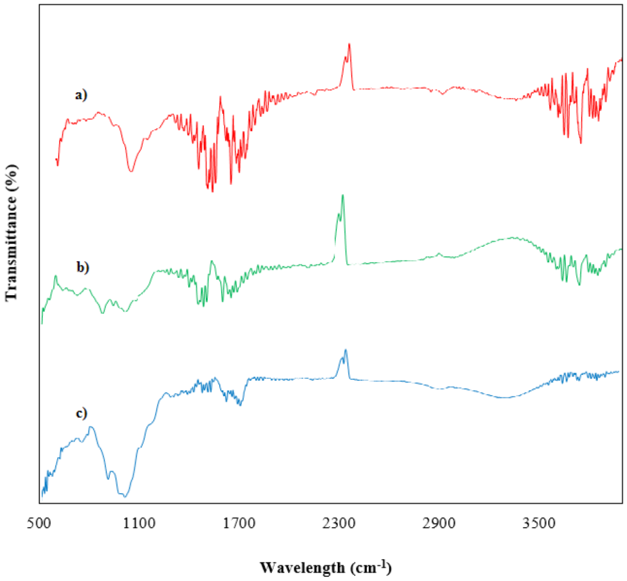

Figure 1. FT-IR spectrum for. **(a)** YP-TiO_2. **(b)** CP-TiO_2. **(c)** LP-TiO_2 biosorbents.

The EDX analysis shown in Figure 2 revealed a strong signal in the titanium region. For TiO_2 nanoparticles, it was observed peaks for Ti and O elements and there are traces of other impurities, which differs to the results reported by author in[28]. Its elemental composition was: O (wt%) 69.38, Ti (wt%) 18.21, Si (wt%) 9.10 and P (wt%) 3.31. For chemically modified biomaterials more elements are identified including C, Mg, Ca, Cl, Al and S, which can be attributed to organic nature of biomasses. The main elements for CP-TiO_2 were: O (wt%) 50.81, C (wt%) 29.50 and Ti (wt%) 9.43; for YP-TiO_2: O (wt%) 45.10, C (wt%) 44.52 and Ti (wt%) 4.68; for LP-TiO_2: O (wt%) 48.11, C (wt%) 20.25 and Ti (wt%) 16.78. These results confirm the formation of TiO_2 nanoparticles and its loading onto biomasses.

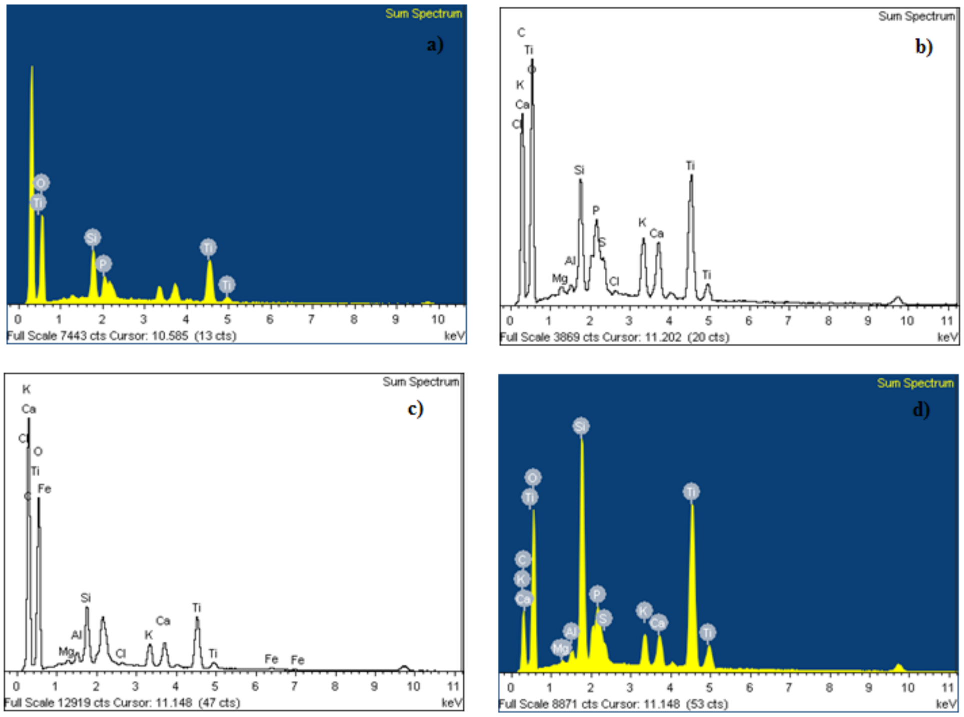

Figure 2. EDX analysis of. **(a)** TiO2 nanoparticles. **(b)** CP-TiO_2. **(c)** YP-TiO_2. **(d)** LP-TiO2 biosorbents.

3.2 Adsorption Experiments

The effect of loading TiO_2 nanoparticles on the adsorption behavior of biomasses was evaluated by calculating the removal yieldsof both biomaterials and synthesized biosorbents by Equation (2). These results are shown in Figure 3.

$$\text{Removal yield}(\%) = \frac{(C_o - C_e)}{C_o} 100\% \qquad (2)$$

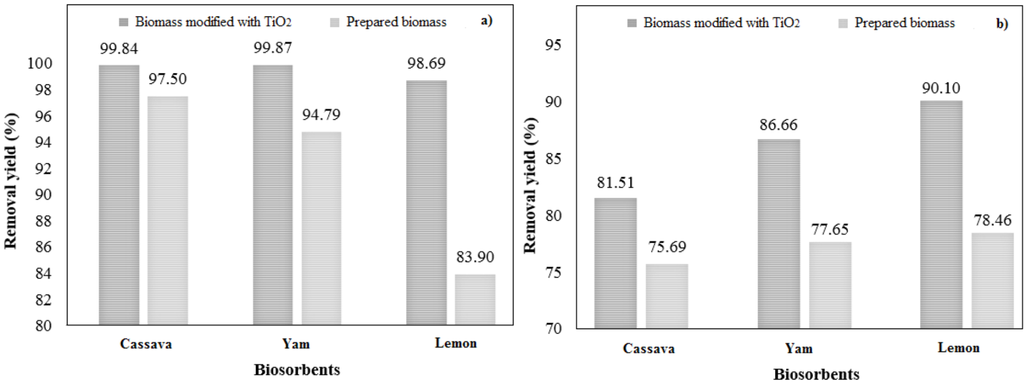

Figure 3. Removal yield of. (a) Pb (II). (b) Ni (II) using pretreated biomass and synthesized biosorbents.

The biomaterial schemically modified with TiO_2 nanoparticles exhibited the highest removal yield (99.87% using YP-TiO_2 and 90.10%using LP-TiO_2 for lead and nickel, respectively), which confirmed that loading these nanoparticles onto biomasses improves its adsorption capacity. As is shown in Figure 3, the removal yield increased in an approximated range of 2-15 % for synthesized biosorbents attributed to particle size homogeneity and crystalline form of nanoparticles[29]. In addition, it was observed that lead was more efficiently removed that nickel due to the affinity of this heavy metal with functional groups of biosorbents. Different authors have claimed that lignocellulosic biomasses from agricultural residues contain carboxyl and hydroxyl groups which can easily bind with metal ions to remove them from the solution[30,31]. Author in[32] reported removal yields for lead solutions between 40-70% using amorphous nano-aluminophosphates. Poursani showed removal yields above 90% using TiO_2 nanoparticles, which are similar to that obtained in this work[29].

3.3 Kinetic Study

To study the adsorption kinetics of biosorbents synthesized from TiO_2 nanoparticles and biomasses, different kinetic models were used to fit experimental results as pseudo-first order, pseudo-second order, and Elovich intraparticle diffusion. Among these models, intraparticle diffusion did not fit accurately the adsorption results over time showing significant deviations in Figures 4,5, which suggested that adsorption process takes place in heterogeneous surface-active sites instead of internal biomass porous[33,34]. The pseudo-second order model reported a better fit than the others for Ni (II) ions onto LP-TiO_2 and YP-TiO_2 and Pb (II) ions onto YP-TiO_2. Hence, the heavy metal ions are adsorbed onto two active sites obeying chemisorption, which involves chemical valence forces through ion exchange between lead/nickel ions and active sites, ion exchange reaction, complexation, coordination or quelation[14,35]. On the other hand, Elovich model best fitted experimental data for nickel ions onto CP-TiO_2 and lead ions onto LP-TiO_2 and CP-TiO_2. This model is based on interchanging of species in heterogeneous surface of solids assuming different isotopes interchange process[36,37].

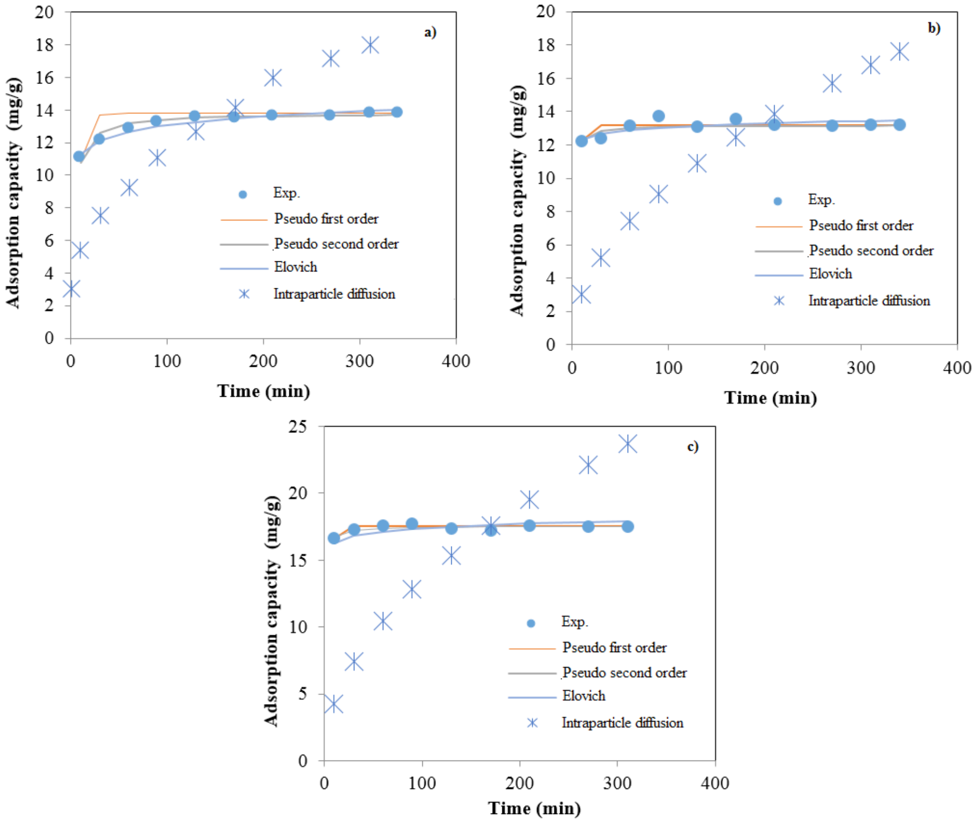

Figure 4. Kinetic models for Ni (II) ions onto. **(a)** CP-TiO_2. **(b)** YP-TiO_2. **(c)** LP-TiO_2 biosorbents.

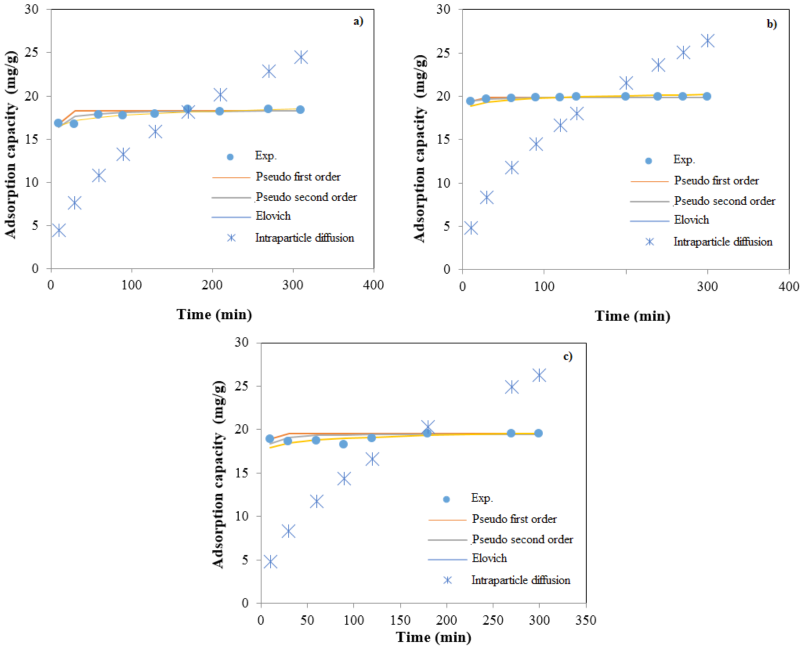

Figure 5. Kinetic models for Pb (II) ions onto. **(a)** CP-TiO$_2$. **(b)** YP-TiO$_2$. **(c)** LP-TiO$_2$ biosorbents.

3.4 Adsorption Isotherms

Adsorption isotherms are widely used to describe the adsorption characteristics of adsorbents providing information about adsorbent surface properties[38]. Tables 3,4 summarize parameter of isotherm models for nickel and lead, respectively. The results revealed that Temkin model best describes adsorption process of Ni (II) ions using CP-TiO$_2$ and YP-TiO$_2$biosorbentsand Pb (II) ions using CP-TiO$_2$, YP-TiO$_2$ and LP-TiO$_2$ biosorbents. The adsorption of nickel onto LP-TiO$_2$biosorbent obeyed Freundlich model. The maximum adsorption capacity corresponds to 136.3, 125.4 and 161.2mg/g for Ni (II) ions removal using CP-TiO$_2$, YP-TiO$_2$ and LP-TiO$_2$biosorbents, respectively. For Pb (II) ions, the maximum adsorption capacities were 181.5, 193.4 y 199.5mg/g using the previously mentioned biosorbents.

Table 3. Fitting data of the nickel adsorption onto biosorbents according to Langmuir, Freundlich and Temkin models

Model	**Parameter**	**CP- TiO$_2$**	**YP- TiO$_2$**	**LP- TiO$_2$**
Langmuir	q_{max}(mmol/g)	1073.36151	35579.9685	116.308065
	(L/mg)	0.0004123	9.8136E-06	0.01307292
	SSE	3.56	11.81	6.34
Freundlich	(mg/g)	0.26633036	0.08761077	1.64762062
	1/*n*	0.86588074	0.70670138	1.09954012
	SSE	2.61635423	8.02	6.22
Temkin	K(L/mg)	0.13104266	0.09555859	0.5155867
	B_t(mg/g)	0.25549676	0.23423656	0.29330272
	SSE	0.87129866	7.58564566	7.77940648

Table 4. Fitting data of the lead adsorption onto biosorbents according to Langmuir, Freundlich and Temkin models

Model	Parameter	CP- TiO_2	YP- TiO_2	LP- TiO_2
Langmuir	q_{max}(mmol/g)	14596.9363	35514.581	78595.222
	(L/mg)	0.00013937	0.00095617	7.177E-05
	SSE	10.81	11.50	86.25
Freundlich	(mg/g)	0.8876557	34.072352	0.14134529
	$1/n$	0.6974323	0.99507288	0.17983056
	SSE	2.45355312	11.50	8.70
Temkin	K(L/mg)	0.36824434	8.23363248	0.53753166
	B_t (mg/g)	0.15496514	0.20194981	0.03379395
	SSE	0.56847401	12.1145784	1.77215775

4. Conclusion

The removal of nickel and lead by adsorption technology using biomaterials chemically modified with TiO_2 nanoparticles was studied in this work. The presence of titanium dioxide in biomasses was confirmed by elemental composition analysis. FT-IR spectra revealed carboxyl and hydroxyl groups in biosorbents, which can easily bind with metal ions to remove them from aqueous solution. All biomasses exhibited higher removal yields after loading TiO_2 nanoparticles reaching values above 98% and 80% for Pb (II) and Ni (II), respectively. It was found that pseudo-second order and Elovichbest fitted experimental results for both heavy metal ions. The adsorption process obeyed Temkin and Freundlich isotherms suggesting a heterogeneous surface for lead and nickel uptake.

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