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Adsorption of heavy metal lead using *Citrus grandis* (Pomelo) leaves as low-cost adsorbent

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ABSTRACT

Among heavy metals, Pb(II) is considered to be very toxic, and hence its removal from contaminated water is of great significance in safeguarding the quality of the environment. Removal of Pb(II) by means of adsorption on *Citrus grandis* (Pomelo) leaves (PL) is determined to produce attractive results. Characterisation of the PL done using Scanning electron microscopic (SEM) images of PL before and after loaded of Pb(II) showed significant changes of surface morphology, clearly indicating the adsorption had taken place. Fourier transform infrared spectroscopy (FTIR) indicates the organic functional groups which might be involved in the adsorption of Pb(II). The Pb(II) - PL aqueous suspension reaches equilibrium at 2.5 h. Effect of equilibrium concentration of Pb(II) on its extent of adsorption at equilibrium follows the Sips adsorption isotherm model the best with maximum adsorption capacity (q_{max}) of 207.2 mg g^{-1}. The regeneration studies were carried out by different treatment methods such as treated with acid, base, distilled water, quick wash and control.

Keywords: Citrus grandis (Pomelo) leaf adsorbent; Heavy metal; Adsorption isotherm; Regeneration

1. Introduction

Pollution has become a major environmental concern encountered worldwide due to its adverse effects not only on human health, but also on the entire ecosystem. Ever expanding industrialization results in more and more toxic wastes and pollutants, such as dyes, phenols and heavy metals, being released to the environment [1,2]. Most of the toxic metals are often discharged from metal smelting and refining, electroplating, plastics, pigments, batteries storage, petroleum and mining industries. Of these, the main threats to human health are lead, chromium, cadmium, mercury and arsenic, to name a few [3–7]. Hence, their removal from wastewater is detrimental and attempts have been made using various methods to remove them [8–16].

The main sources of lead pollutant to the environment are in contaminated wastewater discharged from industries, such as batteries storage, petroleum, mining and smelting, paint, and metal plating. Lead is toxic to most living beings, specifically to human health. Lead can be absorbed into human bodies by inhalation, ingestion and dermal contact. Lead toxicity includes irreversible brain disorders, kidney failure and nervous system especially to babies when lead is transmitted through mother's placenta to the baby [17].

Hence, this research aimed to remove Pb(II) from simulated wastewater contaminated with Pb(II) using adsorption method, with pomelo (*Citrus grandis*) leaves (PL) as the adsorbent. To date, there have been many reports on the use of pomelo skin for the removal of heavy metals, such as cadmium, copper [18,19] and dyes [20–23]. However, utilizing its leaves as a natural low-cost adsorbent is scarce and literature revealed one report where PL was successfully used to adsorb methyl violet 2B dye [24]. No attempt on its use for the removal of heavy metals has ever been reported.

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Therefore, attention was focused on the adsorption characteristics of PL toward Pb(II) in order to provide insight on the suitability and application of PL as a potential low-cost adsorbent.

2. Materials and methods

2.1. Sample preparation

Pomelo leaves (PL) were collected and washed with distilled water to remove surface dirt prior to oven drying at 65°C. Upon obtaining a constant mass, the PL was blended and sieved to obtain particle size of <355 µm. This was then kept in a sealed bag and ready to be used in experiments.

2.2. Instrumentation

The NovAA® 300/400 fully automated flame atomic absorption spectrophotometer (AAS) was used for the determination of Pb(II) concentration in solutions at λ_{max} 283.3 nm. The Shimadzu Model IRPrestige-21 FTIR spectrophotometer was used to determine functional groups present in PL. The Tescan Vega XMU SEM was used to establish the surface morphology of PL. In addition, Stuart orbital shaker used for agitation of the solution was set at 250 rpm.

2.3. Adsorption methodology

Lead chloride ($PbCl_2$) was purchased from Fluka Corporations and used without further purification. All the PL-Pb(II) mixture was kept at 1:500 (weight:-volume) ratio for all experiments, and experiments were done in duplicate at 250 rpm at room temperature and average values were reported, unless otherwise stated. The time taken to reach equilibrium was studied by varying the contact time up to 240 min and determining the extent of removal of Pb(II). Investigation of the effect of pH was carried out from pH 2.0 to 6.0 including the ambient (untreated) pH. The adjustment of pH to the desired value was done using 0.1 M HCl and/or 0.1 M NaOH. Four different salts namely, KCl, KNO_3, NaCl and $NaNO_3$ were used to study the effects of ionic strength on the adsorption of Pb(II) onto PL. Interference effects on the removal of Pb(II) in the presence of other heavy metals were investigated using 1:1 ratio of Pb(II):Metal(II). Batch adsorption experiments ranging from 0 to 1000 mg L^{-1} concentrations of Pb(II) were carried out for isotherm studies. Adsorption kinetics were done using 100 mg L^{-1} Pb(II) following the method as described by Lim et al. [25]. The re-usability of spent PL loaded with Pb(II) was also investigated using similar methods depicted by Lim et al. [24].

3. Results and discussion

3.1. Effect of shaking time

Contact time is one of the major important parameters in adsorption studies as it provides the estimated time required for an adsorption process to reach equilibrium. In this study, the time taken for the PL-Pb(II) suspension system to reach equilibrium was investigated by studying the extent of removal-contact time relationship. According to Fig. 1, a period of 150 min was sufficient for equilibrium to be reached. A rapid uptake of 100 mg L^{-1} Pb(II) within the first 30 min was observed, with 64% Pb(II) being adsorbed onto PL, which could be most likely due to the availability of vacant sites on the PL's surface allowing these sites to be filled by Pb(II) ions. Overtime as the sites are being gradually filled, the rate decreases and eventually reaches a plateau indicating the equilibrium of the adsorbent-adsorbate system. Henceforth, all other experiments, except for kinetics, were carried out using 150 min as the contact time. PL took a much longer time to reach equilibrium compared to adsorbents such as Amber lite IR-120 and multi wall carbon nanotubes, which required only 40 min and 50 min, respectively [26,27].

3.2. Effect of pH on adsorption of Pb(II) onto PL

Depending on what pollutants are present, the pH of wastewater would differ. It is therefore important to investigate how medium pH would affect the adsorption capacity of an adsorbent. It has been shown that some adsorbents are resilient to changes in pH. In this study, the effect of medium pH on the removal of Pb(II) from 100 mg L^{-1} solution by PL was limited to the pH range from 2.0 to 6.0, because the formation of lead hydroxide was observed at pH > 6. On the other hand, pH < 2.0 is not practically feasible. Fig. 2 shows that at the ambient pH of 5.41, the percentage removal

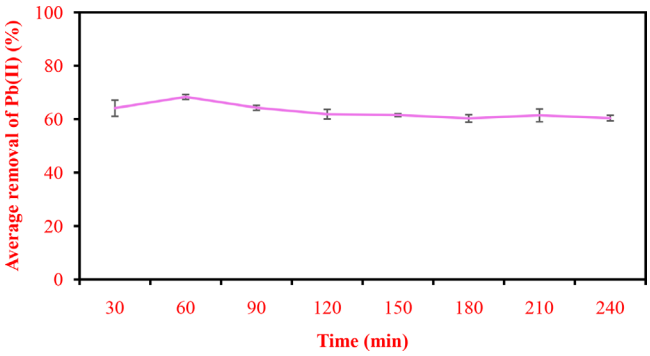

Fig. 1. Effect of contact time for the adsorption of Pb(II) onto PL [mass of adsorbent = 0.050 g; volume of Pb(II) = 25.0 mL, concentrations of Pb(II) = 100 mg L^{-1}].

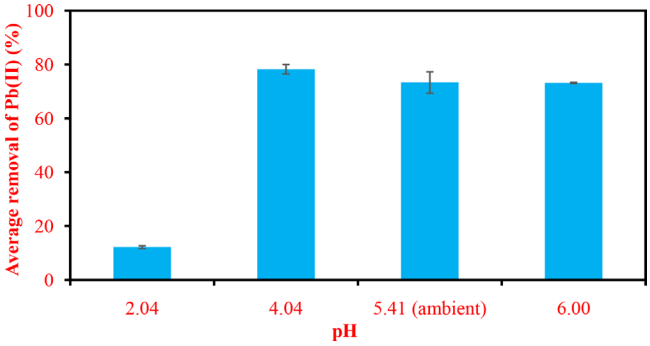

Fig. 2. Effect of pH on adsorption of Pb(II) onto PL in various medium pH [mass of adsorbent = 0.050 g; volume of Pb(II) = 25.0 mL; concentration of Pb(II) = 100 mg L^{-1}].

was approximately 73%. At pH of 2.0, only 12% of Pb(II) was adsorbed, because the high concentration of H^+ ions compete with Pb(II) ions for adsorption sites, suppressing Pb(II) adsorption on the PL's surface. The reverse is true for higher pH as can be seen by an increase of approximately 66% from pH 2.0 to 4.0. Thereafter, the adsorption did not deviate much. Since unadjusted medium pH gave comparable adsorption toward Pb(II), with only a slight difference of 5% compared to the highest adsorption at pH 4.0, no pH adjustment was done for all subsequent experiments.

3.3. Effect of ionic strength

Ionic strength of the medium is another important parameter in adsorption studies, because salts present in wastewater in different strengths could influence the adsorption ability of a given adsorbent toward an adsorbate. Fig. 3 shows that adsorption of Pb(II) on PL is greatly affected by the presence of salts, namely KCl, KNO_3, NaCl and $NaNO_3$, within the concentrations ranging from 0 to 1.0 M. As the salt concentration increases from 0 to 1.0 M, a decreased trend on the removal of Pb(II) is observed as expected. The order of ionic strength influence is NaCl > KCl > $NaNO_3$ ≈ KNO_3 with a reduction of 84%, 73%, 50% and 41%, respectively at 1.0 M salt concentration. This could be a result of electrostatic competition of K^+ and Na^+ metal ions with the Pb(II) ions because of the accumulation of K^+ and Na^+ on the surface of PL leads to the electrostatic repulsion with the Pb(II) ions. Slightly higher influence of Na^+ when compared to K^+ can be attributed to the size of the ion where smaller ions can occupy adsorption sites easily. Greater influence of Cl^- as compared to NO_3^- is also due to the size factor where cations surrounded by Cl^- ions would easily reach the adsorption site owing to its smaller size.

3.4. Interference effects

Fig. 4 shows the effect of five other divalent ions on the adsorption of Pb(II) from aqueous suspension. All four metal ions, namely Cd(II), Co(II), Ni(II) and Zn(II), exhibit a similar influence which can be attributed to the same charge as the target adsorbate, Pb(II). Nevertheless, Cu(II) despite having the same charge is found to preferentially adsorb on natural adsorbents, as reported, probably due to its stronger complexation ability with organic functional groups present in adsorbents [28,29].

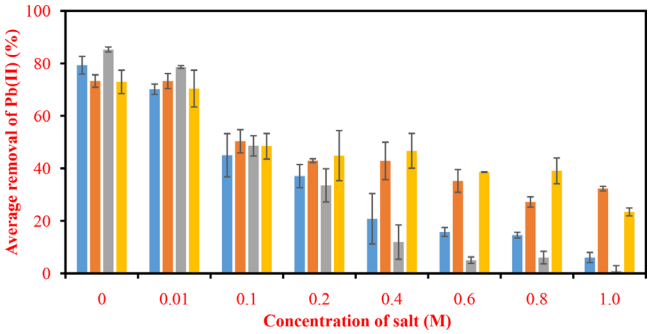

Fig. 3. Effect of ionic strength of KCl (■), KNO_3 (■), NaCl (■) and $NaNO_3$ (■) [mass of adsorbent = 0.050 g; volume of Pb(II) = 25.0 mL; concentration of Pb(II) = 100 mg L^{-1}].

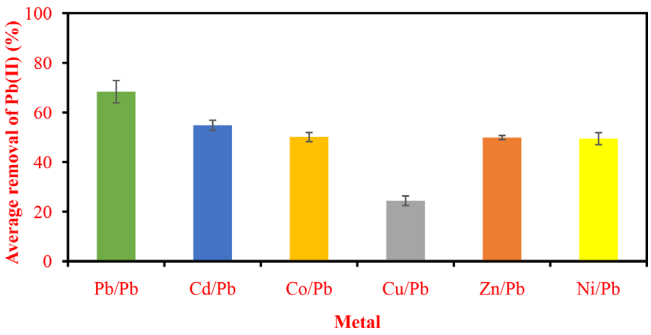

Fig. 4. Interference effect of other heavy metal ions on Pb(II) [mass of adsorbent = 0.050 g; volume = 25.0 mL].

3.5 Adsorption isotherm

Five isotherm models used in this study were the Langmuir, Freundlich, Temkin, Sips and Redlich-Peterson (R-P) models, whose equations are shown in Eqs. (1) to (5), respectively. The determination of the best fit isotherm model for adsorption of Pb(II) on PL is based on three criteria: (a) linear regression coefficients (R^2) determinant where isotherm model giving the higher R^2 is preferred (b) comparison between the simulation plots of the isotherm models with the experimental data and (c) error analyses using four error functions (Table 1), where the smaller error values indicate better fit of the isotherm model.

Langmuir isotherm model [30]:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{C_e}{q_{\max}} \tag{1}$$

Freundlich isotherm model [31]:

$$\log q_e = \frac{1}{n}\log C_e + \log K_F \tag{2}$$

Table 1
Four error functions and their equations

Error functions	Abbreviations	Equations
Average relative error	ARE	$\frac{100}{n}\sum_{i=1}^{n}\left\lvert\frac{q_{e,meas}-q_{e,calc}}{q_{e,meas}}\right\rvert_i$
Sum square error	SSE	$\sum_{i=1}^{n}\left(q_{e,calc}-q_{e,meas}\right)_i^2$
Sum of absolute error	EABS	$\sum_{i=1}^{n}\left\lvert q_{e,meas}-q_{e,calc}\right\rvert$
Non-linear chi-square test	χ2	$\sum_{i=1}^{n}\frac{(q_{e,meas}-q_{e,calc})^2}{q_{e,meas}}$

Temkin isotherm model [32]:

$$q_e = \left(\frac{RT}{b_T}\right)\ln K_T + \left(\frac{RT}{b_T}\right)\ln C_e \quad (3)$$

Redlich-Peterson isotherm model [33]:

$$\ln\left(\frac{K_R C_e}{q_e} - 1\right) = n\ln C_e + \ln a_R \quad (4)$$

Sips isotherm model [34]:

$$\ln\left(\frac{q_e}{q_{\max} - q_e}\right) = \frac{1}{n}\ln C_e + \ln K_s \quad (5)$$

where K_L is the Langmuir constant, K_F is the Freundlich constant indicative of adsorption capacity; n is related to the adsorption intensity, K_T is the Temkin constant; b_T is related to the heat of adsorption; R is the gas constant while T is the absolute temperature at 298 K, K_R and a_R the R-P constants and K_S is the Sips constant; n is the Sips exponent.

Briefly, the Langmuir adsorption isotherm is mainly based on the formation of monolayer of adsorbate molecules on the adsorbent's surface, which is in contrast to the Freundlich isotherm model where adsorption would take place in multi-layers onto the heterogeneous surface with non-uniform distribution of adsorption energy. The Temkin isotherm describes an indirect interaction of adsorbent-adsorbate with a linear decrease of heat of the adsorption with increasing coverage. The Redlich-Peterson model, which is a three-parameter isotherm model, combines the Langmuir and Freundlich isotherm models, and can be used for both homogenous and heterogeneous systems. It tends toward the Freundlich model when there is a high concentration of adsorbates and toward the Langmuir model at a low adsorbate concentration. Lastly, the three-parameter Sips model, otherwise known as the Langmuir-Freundlich model, is used for predicting the heterogeneous adsorption systems whereby at low adsorbate concentration, the Sips model reduces to the Freundlich isotherm model and follows the Langmuir model at high adsorbate concentration.

According to the experimental data obtained from the adsorption of Pb(II), as shown in Table 2, the best fit isotherm model in decreasing order of R^2 is Redlich-Peterson > Langmuir > Sips > Temkin > Freundlich whereas, from the error functions analyses the Sips model has the lower errors as compared to R-P and the other isotherm models which are shown in Table 2. However, based on the simulation plots as shown in Fig. 5, both the Sips and R-P isotherm models have a closer fit to the experimental isotherm data, compared to the Langmuir model. Hence, based on the Sips isotherm model, the maximum adsorption capacity (q_{max}) value was 207.2 mg g^{-1}.

Furthermore, Table 3 displays the q_{max} values of PL and some reported adsorbents for the removal of Pb(II). It is clear that PL shows a higher q_{max} value as compared to that of the reported adsorbents, especially, coconut activated carbon and seed hull of the palm tree activated carbon having much lower q_{max} values. A high adsorption capacity of 909.1 mg g^{-1} of the *Citrus grandis* (Pomelo) peel was reported as compared to the PL.

Table 2
The adsorption isotherm constants and error values of different isotherm models

Isotherm model	Value	ARE	SSE	EABS	χ^2
Langmuir		14.78	0.03	0.52	0.18
q_{max} (mmol g^{-1})	0.633				
K_L (L mmol^{-1})	0.014				
R^2	0.9813				
Freundlich		13.98	0.01	0.31	0.13
K_F (mmol g^{-1} (L mmol^{-1})$^{1/n}$)	0.046				
n	2.523				
R^2	0.9669				
Temkin		11.52	0.02	0.41	0.11
K_T (L mmol^{-1})	0.246				
b_T (kJ mol^{-1})	22.734				
R^2	0.9674				
Redlich Peterson		16.69	0.01	0.31	0.12
K_R (L g^{-1})	1.000				
α	0.638				
a_R (L mmol^{-1})	17.731				
R^2	0.9924				
Sips		13.34	0.01	0.32	0.10
q_{max} (mmol g^{-1})	1.000				
K_S (L mmol^{-1})	0.034				
n	1.765				
R^2	0.9769				

3.6. The investigation of adsorption kinetics of Pb(II) onto PL

Adsorption kinetics is important because it provides a better understanding to the mechanism involved and with this information one can then work on designing a more effective adsorption system in real application of wastewater treatment. The Lagergren pseudo first order model [56]

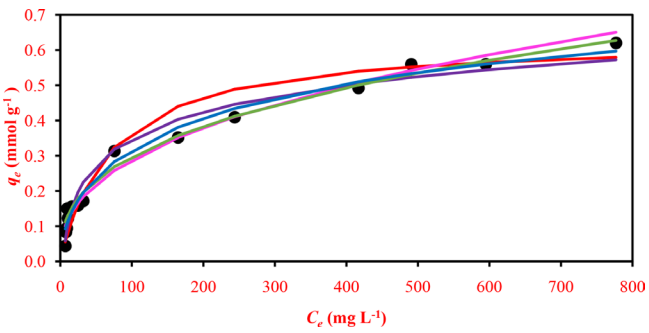

Fig. 5. Comparison of the simulation plots of isotherm models of Langmuir (——), Freundlich (——), Temkin (——), R-P (——) and Sips (——) with experimental data (•) [mass of adsorbent = 0.050 g; volume of Pb(II) = 25.0 mL; concentration of Pb(II) = 0 to 1000 mg L^{-1}].

Table 3
Comparison of the adsorption capacity (q_{max}) of PL with reported adsorbents on the removal of Pb(II)

Adsorbent	q_{max} (mg g^{-1})	Reference
Citrus grandis (Pomelo) leaf	207.2 (Sips)	This study
Citrus grandis (Pomelo) peel	909.1	[17]
Mango peel	99.1	[35]
Nanchem skin	57.0	[25]
$ZnCl_2$-modified pomelo peel	950.0	[36]
Modified pomelo peel cellulose – cell 5	142.9	[37]
Modified pomelo peel cellulose – cell 6	181.8	[37]
Averrhoa bilimbi leaves	1598	[38]
Modified *Tephrosia purpuria* leaf	100.0	[39]
Artocarpus odoratissimus leaves	75.1	[40]
Terminalia catappa L. (Indian almond) leaf	41.9	[41]
Ficus carcia leaf	34.4	[42]
Melocanna baccifera Roxburgh (bamboo) activated charcoal	53.8	[43]
Pine cone activated carbon	27.5	[44]
Coconut activated carbon	4.4	[45]
Seed hull of the palm tree activated carbon	3.8	[45]
Magnetic biochar from coconut shell	162.8	[46]
Polyethylenimine-grafted gelatin sponge	80.6	[47]
Palm kernel fibre,	49.9	[48]
Peanut shells	39.0	[49]
Coconut tree sawdust	25.0	[50]
Peat	15.0	[51]
Fig sawdust activated carbon	80.6	[52]
Ash	588.2	[53]
SDS acrylamide Zr(IV) selenite	18.4	[54]
Ti(IV) iodovanadate cation exchanger	18.8	[55]

and the pseudo second order model [57], whose equations are presented in Table 4, are two of the most commonly used models to describe adsorption kinetics [58,59] and these were used in the present study to predict the adsorption of Pb(II) onto PL. The former model depicts the binding of Pb(II) to one adsorption site on PL's surface with the rate being proportional to the number of unoccupied adsorption sites. The latter model describes chemisorption of adsorbate with the adsorbent's surface giving rise to strong bonding. Results of kinetics studies are clear cut, as seen from Table 5 and Fig. 6. The pseudo second order kinetic model has a higher R^2 close to unity and lower errors as compared with

Table 4
The linear equations of kinetics models

Kinetics model	Linear equation	Plot
Pseudo first order	$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t$	log ($q_e - q_t$) vs. t
Pseudo second order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t$	t/q_t vs. t

the pseudo first order model with $R^2 < 0.14$. In addition, it can be further confirmed with the $q_{e,calc}$ and $q_{e,expt}$ for each kinetics models. The $q_{e,calc}$ and $q_{e,expt}$ for pseudo second order are 0.1553 mmol g^{-1} and 0.1718 mmol g^{-1}, respectively. However the $q_{e,calc}$ for pseudo first order was 0.012 mmol g^{-1}, a far deviation from the experimental value. Hence it is valid to said that the pseudo second order is the best fit model for the adsorption of Pb(II) onto PL. This implies that the adsorption process is most likely dependent on the amount of Pb(II) as well as the vacant sites of the PL's surface and that the binding could be chemisorption in nature.

3.7. The cycle of regeneration

In this study, three desorbing agents such as HCl, NaOH, distilled water, and a control were used for the investigation of PL's reusability in removing Pb(II) for four consecutive cycles. The results obtained are as shown in Fig. 7. Untreated spent adsorbent and spent PL which was either washed or quick rinse with distilled water all showed drastic reduction in adsorption toward Pb(II) and could only be regenerated and reused up to 3 cycles. With HCl, adsorption capacity was reduced by almost 50% in the fourth cycle. The best method of regenerating PL was with NaOH. Not only did it give the highest percentage removal, there was also an enhancement in the adsorption capacity which was retained throughout the four cycles. This could be the result of exposure of surface functional groups since base can remove surface wax and fats. Further, deprotonation of these functional groups increases electrostatic attraction between the negative surface of PL and Pb(II) ions.

3.8 Characterization of PL

The SEM surface morphologies of the PL before and after adsorption with Pb(II) are shown in Fig. 8. PL exhibits a very rough and undulating surface with highly irregular shaped pores and cavities. Upon adsorption of Pb(II), very distinct changes of the surface were observed whereby the roughness was replaced by a much smoother surface. Generally, increase in surface roughness increases the surface area of PL, thereby providing more active sites for Pb(II) to be adsorbed. This is in line with the high q_{max} obtained for PL as compared to many other adsorbents.

The presence functional groups of PL treated with Pb(II) and untreated PL are shown in Fig. 9. It can be noted that the presence of hydroxyl (-OH) or amino (-NH) groups were slightly shifted from 3416 to 3588 and 3337 cm^{-1}, followed by the shifting of methyl (CH) group from 2926 to

Table 5
Kinetics parameters and error values for the adsorption of 100 mg L^{-1} Pb(II) onto PL

Kinetics model	Parameter	ARE	SSE	EABS	χ^2
Pseudo first order		101.53	0.48	2.76	2.81
k_1 (min^{-1})	–0.01				
R^2	0.1392				
q_{calc} (mmol g^{-1})	0.0118				
Pseudo second order		35.34	0.26	0.94	1.59
k_2 (g $mmol^{-1}$ min^{-1})	–2.70				
R^2	0.9982				
q_{calc} (mmol g^{-1})	0.1553				
q_{expt} (mmol g^{-1})	0.1718				

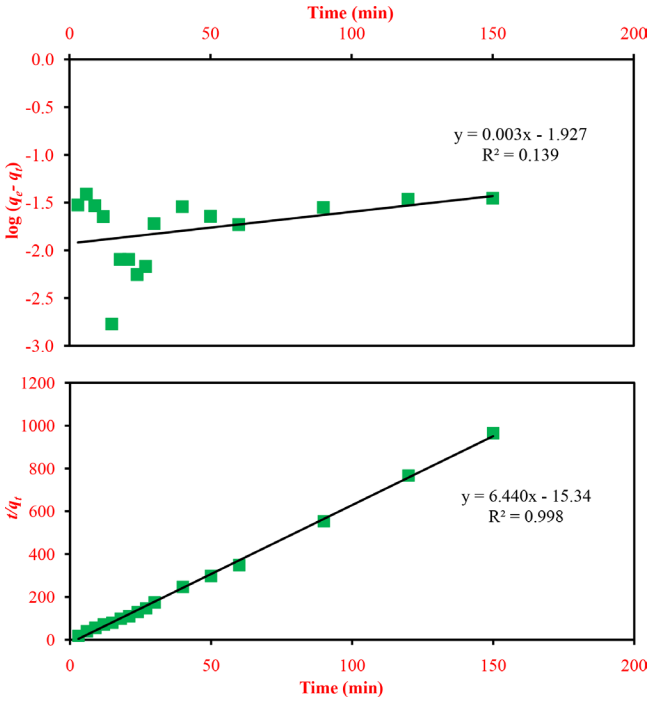

Fig. 6. Linear plots of (top) Lagergren pseudo first order and (bottom) pseudo second order models for the adsorption of Pb(II) onto PL [mass of adsorbent = 0.050 g; volume of Pb(II) = 25.0 mL; concentration of Pb(II) = 100 mg L^{-1}].

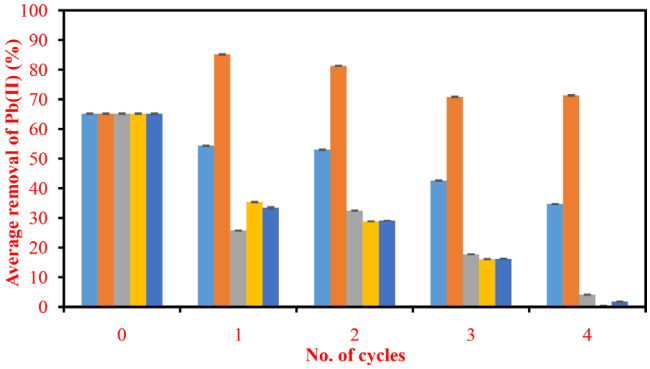

Fig. 7. Illustrating the regeneration of PL for 5 consecutive cycles by treating with different methods: HCl (■), NaOH (■), H_2O (■), quick wash (■) and control (■) [mass of adsorbent = 0.050 g; concentration of Pb(II) = 100 mg L^{-1}].

2942 cm^{-1}. At 1737 to 1745 cm^{-1}, the carbonyl (C=O) groups was identified to be one of the functional groups presence on the sample's surface. Shifting of band was observed at 1639 to 1626 cm^{-1} which represents the alkene (C=C) group.

3.9. Mechanistic aspects of interaction of Pb(II) with PL

Adsorption, in general, includes all mass transfer processes from the solution phase to the surface of the solid adsorbent. This is a complex issue with regard to natural

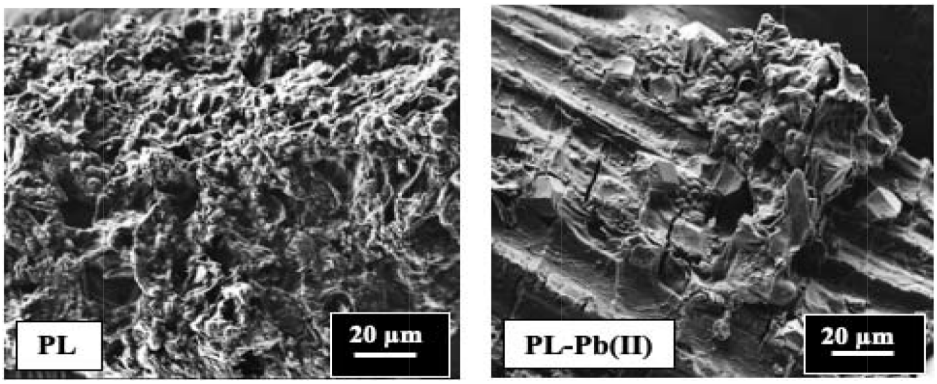

Fig. 8. The SEM surface morphology of PL and PL-Pb(II) at 800× magnification.

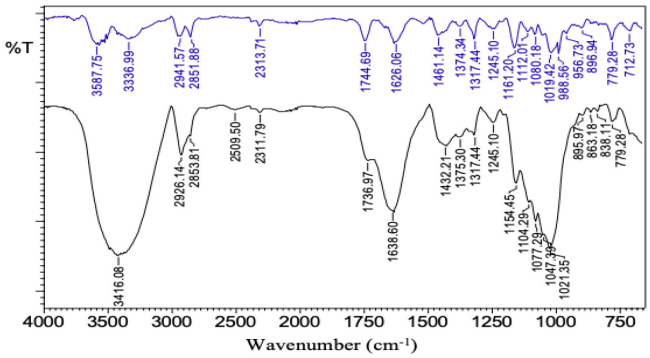

Fig. 9. The FTIR spectra of PL (black) and PL with Pb(II) (blue).

adsorbents. Based on the results of ionic strength and interference studies, it can be argued that ion-exchange contributes to the mass transfer, and on the other hand, changes on the absorption peaks locations of the FTIR spectrum in the presence of Pb(II) solutions is a clear indication of complexation of the adsorbate with organic functional groups present in PL. Therefore, ion-exchange and complexation would be possible modes of mass transfer leading to adsorption of Pb(II) from solution. The other important aspect is that, although the Sips and R-P isotherm models show the validity for the adsorption system under investigation, these findings were based on the results of solution analysis. At high concentrations of Pb(II) in solution, the extent of removal of Pb(II) from solution is equivalent to more than a monolayer. Nevertheless, it is argued that adsorption of Pb(II) on the surface of Pb(II) would not be uniform as the adsorbent's surface is not properly ordered in contrast to synthetic adsorbents, and thus covering a surface of PL by a single layer of Pb(II) through ion-exchange of complexation, and subsequent transfer of Pb(II) into the bulk of the adsorbent into mesopores and micro pores, and further intra-particle diffusion would be possible. Such mass transfer effects would decrease the concentration of Pb(II) in solution equivalent to more than a monolayer, showing the validity of the Sips and R-P isotherm models. The validity of the pseudo second order model further supports the complexation of Pb(II) where two different types of organic moieties on the PL's surface would interact with Pb(II). The linearity of the above kinetics model even at initial time period of adsorption indicates that the number of adsorption sites can be used to fulfill the pseudo order condition.

4. Conclusion

Pomelo leaves (PL) was successfully utilized as a potentially low-cost adsorbent for the removal of heavy metal lead (Pb(II)) from the aqueous solution. Kinetics studies indicate that the adsorption of Pb(II) on PL follows the pseudo-second order due to its $q_{e,}$ calculated value being closer to the q_e experimental value and with the higher R^2. The studies of SEM supported this through the observed surface morphology on PL's surface before and after adsorption with Pb(II). There were shifting of bands in FTIR spectrum of PL treated with Pb(II), confirming the adsorbates [Pb(II)] being adsorbed on PL. Further, PL can be effectively regenerated and reused using 0.1 M NaOH where the adsorption capacity increases throughout the cycles.

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