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Preparation of agriculture residue based adsorbents for heavy metal removal

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ABSTRACT

Guava seeds, a byproduct produced during guava juice processing, are currently of no economic value. In the present work two different types of adsorbents have been prepared from raw guava seeds, namely chemically activated guava seed carbon (AGSC) using zinc chloride and chemically modified guava seeds (MGS) through graft co-polymerization reaction. The adsorption capacity of both adsorbents towards Ni(II) has been investigated. It has been found that the equilibrium adsorption capacity is a function of initial pH, contact time, initial nickel(II) concentration, and adsorbent dosage. The optimum pH for both adsorbents was found to be 6. Both Langmuir and Freundlich models best describe the equilibrium experimental data. The maximum adsorption capacities for AGSC and MGS are 18.05 and 32.05 mg/g respectively. The kinetic experimental data were fitted well by the second-order model. The natures of the main functional groups which may be present on raw guava seeds and MGS have been investigated by infrared (IR) studies.

Keywords: Agriculture residues; Nickel ions removal; Adsorption; Chemically modified adsorbents; Activated carbon; Wastewater treatment

1. Introduction

The presence of low concentration of heavy metals within industrial effluents can lead to numerous environmental issues. Heavy metals are known to be highly toxic which can affect the aquatic life; beside they are non-biodegradable and can accumulate within plants and fish organism causing harmful effects on long term for both humans and aquatic life. Electroplating industry, metal finishing processes, batteries manufacture, printing and photographic industries and extractive hydrometallurgical processes discharge effluents containing a great deal of heavy metals [1]. Treatment processes for metal-contaminated waste stream include chemical precipitation [2], reverse osmosis [3], ion exchange [4], cementation [5], electrolysis [6] and adsorption. Adsorption appears to be the best choice for removal of heavy metals in low concentration in case that a low cost and efficient adsorbent is available. Activated carbon is the most popular and widely used adsorbent in industrial applications; however its high cost prohibits its wide use in wastewater treatment units [7]. The utilization of agricultural residues or agricultural by-products from industrial operations as adsorbents is increasingly becoming of vital concern because these residues and by-products represent unused recourses and in many cases represent a serious disposal problem [8]. A number of agricultural residue materials such as coir pith [9], peanut husks [10], almond husk [11] bagasse [12], apricot residue [13] silk cotton hull, coconut tree sawdust, sago waste, maize cob, banana pith [14] and rubber wood sawdust [15] have been used as a precursors for activated carbon

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preparation. Recently most of adsorption studies have been focused on chemical modification of agricultural residue materials. Chemical modification can enhance adsorption efficiency of the adsorbent towards heavy metals by introducing new functional groups on their surfaces [16]. These functional groups have ability to bind heavy metal ions by a certain chemical bond. The introduction of these functional groups into the surface of agricultural residue can be done either by chemical conversion of existing functional groups on the surface or by grafting certain monomers upon the surface by graft copolymerization [17]. Esterified rice straw [18], modified jute fibers [19] and succinic anhydride modified sugarcane bagasse [20] represent examples of chemical conversion of existing functional groups on surface of adsorbents used to remove heavy metal from stimulated wastewater. Polyacrylamide grafted banana stalk [21], polyacrylic acid grafted saw dust [22] and modified cellulose through graft copolymerization [23] are examples for improving adsorption towards heavy metal through graft co-polymerization. Grafting of functional group-containing chains onto the surface of adsorbents leads to large number of function groups compared to chemical conversion of existing groups on the surface.

The aim of the present work is to prepare graft copolymer of monomethylol thiourea on cellulose found in Guava seeds and investigates its adsorption capacity for Ni(II) ions removal from simulated wastewater under different conditions. The adsorption capacity of chemically modified guava seeds by graft copolymerization was compared to activated carbon prepared by chemical activation of raw guava seeds.

2. Methods

2.1. Preparation of raw guava seeds

The raw guava seeds were obtained from a juice processing factory. Table 1 shows a composition as mass percentage of raw guava seeds [24]. The raw material was rinsed with boiled water for several times until free from any guava residue, then three times with cold water. The raw material was dried in an oven at 105°C until constant weight. The seeds were then crushed to very fine powder, and divided into two portions for further processing.

2.2. Preparation of activated carbon from guava seeds

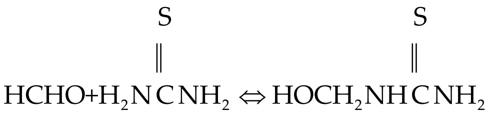
The crushed raw guava seeds were soaked in 50% $ZnCl_2$ solution for 48 h in a ratio of 1:2 by weight. The filtered material was dried then carbonized at 700°C for 1 h, after cooling; the excess $ZnCl_2$ present in the carbonized material was leached out using dilute HCl solution. The carbon was washed several times to get rid of $ZnCl_2$ and HCl and dried to be ready for adsorption experiments. This adsorbent was designated as activated guava seed carbon (AGSC).

Table 1
Composition as percentage of guava seeds [24]

Constituents	Mass %
Cellulose	31.4
Hemicelluloses	14.3
Lignin	40.2
Soluble	6.96
Moisture	6.51
Ash	~0.1

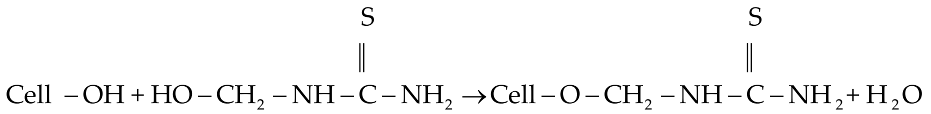
2.3. Preparation of chemically modified guava seeds

The modification was based on a procedure described by El Garf [25]. Monomethylol thiourea was prepared by the reaction of a 35% solution of formaldehyde with thiourea in the presence of magnesium oxide as a catalyst, at a temperature of 45°C with constant shaking for 4 h. Monomethylol thiourea was formed according to the following equation:

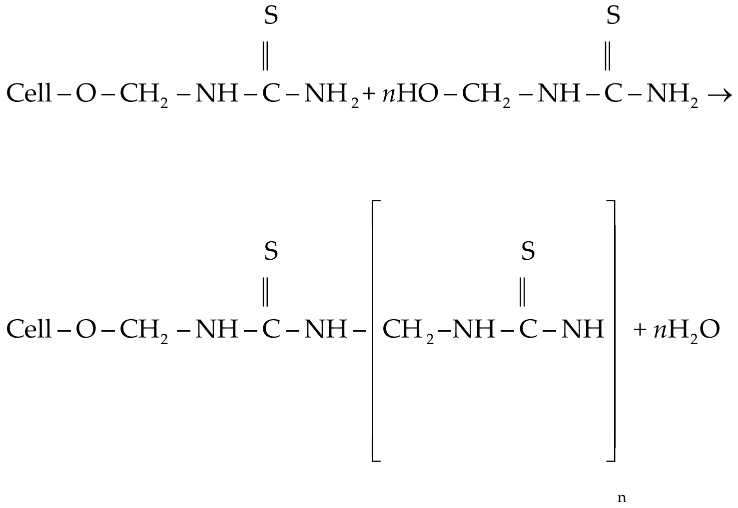


$$HCHO+H_2N\overset{\overset{S}{\|}}{C}NH_2 \Leftrightarrow HOCH_2NH\overset{\overset{S}{\|}}{C}NH_2 \quad (1)$$

The obtained crystals were used to prepare a 70% monomethylol thiourea, and 5% magnesium chloride was added. The second portion of raw guava seeds was soaked in the monomethylol thiourea solution for 15 min. The modified guava seeds were dried at 30°C for 20 min. Thermal treatment of the modified guava seeds took place at 130–140°C for 15 min. The modified guava seeds were washed several times with distilled water followed with boiling with distilled water for 1 h, then washed with methanol several times then dried and kept for adsorption experiments. This adsorbent was designated as modified guava seeds (MGS). The graft co-polymerization took place according to the following reactions:



$$Cell-OH+HO-CH_2-NH-\overset{\overset{S}{\|}}{C}-NH_2 \rightarrow Cell-O-CH_2-NH-\overset{\overset{S}{\|}}{C}-NH_2+H_2O \quad (2)$$



$$\mathrm{Cell-O-CH_2-NH-\overset{\overset{S}{\|}}{C}-NH_2} + n\mathrm{HO-CH_2-NH-\overset{\overset{S}{\|}}{C}-NH_2} \rightarrow \mathrm{Cell-O-CH_2-NH-\overset{\overset{S}{\|}}{C}-NH-}\left[\mathrm{CH_2-NH-\overset{\overset{S}{\|}}{C}-NH}\right]_n + n\mathrm{H_2O} \tag{3}$$

A stock solution of Ni(II) of 1000 mg/L was prepared by dissolving 4.47 g of ARG nickel sulphate [$NiSO_4.6H_2O$] in distilled water. Few mills of concentrated sulfuric acid were added to prevent hydrolysis.

The sorption of Ni(II) into MGS and AGSC was studied using batch adsorption techniques, in which a constant weight of the adsorbent (0.25 g) was allowed to contact with a 50 ml of a Ni(II) solution of known concentration in a 250-ml Pyrex glass flask at a fixed temperature in a shaker for a known period of time. The effect of pH, contact time, Ni(II) concentration, and adsorbents dosage were studied. After all the experiments the samples were filtered and diluted to 4 ppm to be suitable for analysis using atomic absorption spectroscopy. The pH of the solution was adjusted either by adding 30% NaOH or concentrated H_2SO_4 solutions. Blank experiments were carried out to reduce the errors which may results from adsorption by the wall of glass flasks.

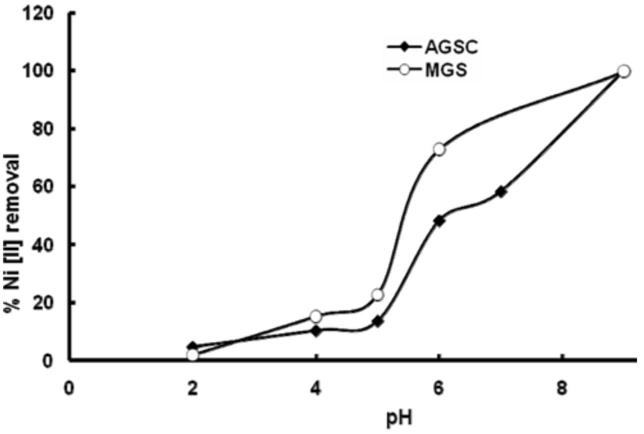


Fig. 1. Effect of initial pH on % of Ni(II) removal by adsorption (initial Ni(II) concentration = 50 ppm, sorbent dosage = 5 g/L, temperature = 25°C, contact time = 3 h, constant rotation speed).

3. Results and discussion

3.1. *Effect of pH*

Fig. 1 shows the effect of initial pH on the percentage of Ni(II) removal by both AGSC and MGS. As the pH increases the percentage of Ni(II) removal increases from 4.7% and 1.84% for AGSC and MGS respectively at pH = 2 to maximum removal of 99.8% and 99.7% at pH = 9 for AGSC and MGS respectively. The high percentage of Ni(II) removal at pH = 9 may be attributed to two mechanisms of adsorption and precipitation of Ni(II) in pores of the adsorbent which is in consistence with the results obtained by many other authors [26,27]. The low adsorption capacity obtained at acidic pH can be explained by the competition of protons with Ni(II) ions for the active sites on the adsorbents. It is worth mentioning that increasing pH beyond 9 would lead to decrease of % removal efficiency. The decrease of % removal beyond pH 9 may be attributed to that precipitation of Ni ions in pores of adsorbents which could results in decreasing the surface area for adsorption [28]. In order to avoid Ni(II) removal by precipitation the selected pH for further studies is pH = 6.

3.2. *Effect of contact time*

Figs. 2 and 3 show the effect of contact time on percentage of Ni(II) ions removal by both MGS and AGSC respectively. The percentage removal of Ni(II) increases rapidly up to 50 min and increases slowly until reaches a plateau at 60 min. According to these results an equilibrium time of 2 h is chosen for further experiments.

3.3. *Adsorption isotherm studies*

Fig. 4 shows the sorption isotherm of Ni(II) removal by both MGS and AGSC. The isotherm equilibrium data

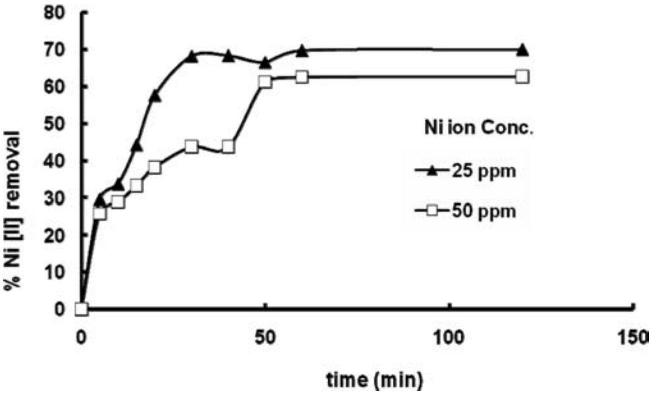


Fig. 2. Effect of contact time on % of Ni(II) removal by adsorption on modified guava seeds (MGS) (sorbent dosage = 2 g/L, pH = 6, temperature = 25°C, constant rotation speed).

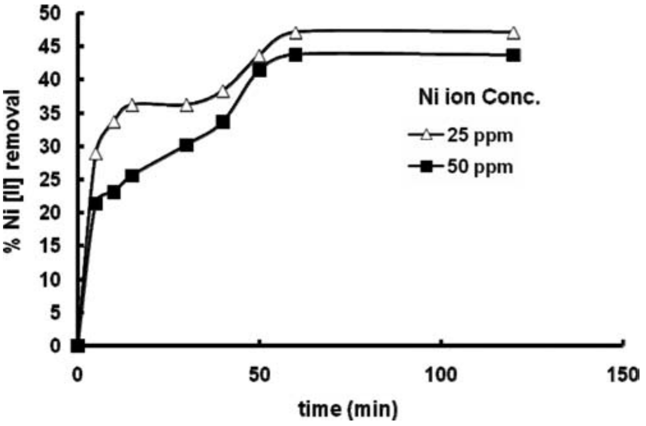


Fig. 3. Effect of contact time on % of Ni(II) removal by adsorption on activated guava seeds carbon (AGSC) (sorbent dosage = 2 g/L, pH = 6, temperature = 25°C, constant rotation speed).

were modeled by the standard Langmuir isotherm model and the Freundlich isotherm model [29]. The Langmuir assumes the uptake of the metal ions occur on a homogenous surface by monolayer adsorption without any interaction between the adsorbed ions. For adsorption from solution by solid adsorbents, the Langmuir adsorption isotherm is expressed as:

$$q = \frac{Q_{\max} b C_e}{1 + b C_e} \tag{4}$$

where q is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e — equilibrium concentration of the solute (mg/L), $Q_{\max}$ — maximum adsorption capacity (mg/g), b — Langmuir constant or the affinity constant.

For linearization of the data using Langmuir isotherm the following equation is used:

$$\frac{C_e}{q} = \frac{1}{bQ_{\max}} + \frac{C_e}{Q_{\max}} \tag{5}$$

Fig. 5 shows the Langmuir adsorption isotherm for both MGS and AGSC. Freundlich adsorption isotherm assumes that adsorption of metal ions occurs through multilayer adsorption on a heterogeneous surface. The Freundlich model is described by the following equation:

$$q = k_f C_e^{1/n} \tag{6}$$

where k_f is Freundlich constant related to adsorption capacity (mg/g) and $1/n$ represents the intensity of adsorption. Linearization of the model takes the form:

$$\log q = \log k_f + \frac{1}{n} \log C_e \tag{7}$$

Fig. 6 shows the Freundlich plot for both MGS and AGSC.

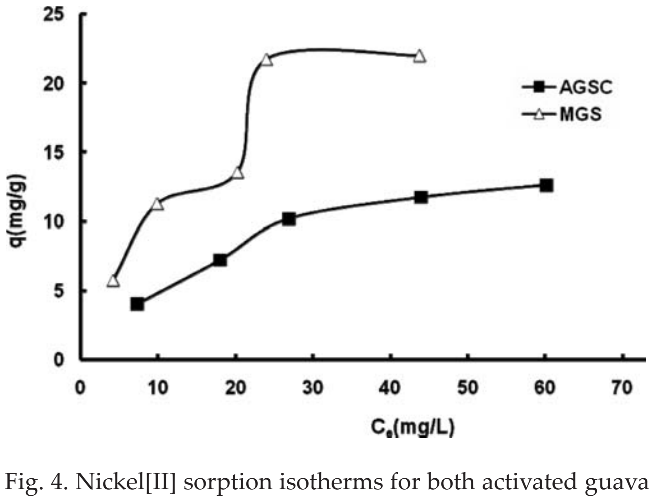


Fig. 4. Nickel[II] sorption isotherms for both activated guava seeds carbon (AGSC) and modified guava seeds (MGS) (contact time =2 h, pH = 6, sorbent dosage = 2 g/L, temperature = 25°C, constant rotation speed).

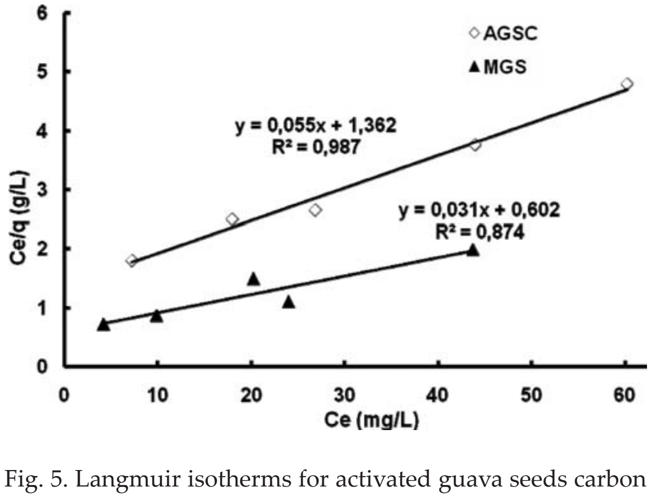


Fig. 5. Langmuir isotherms for activated guava seeds carbon (AGSC) and modified guava seeds (MGS) (contact time = 2 h, sorbent dosage = 2 g/L, pH = 6, temperature = 25°C, constant rotation speed).

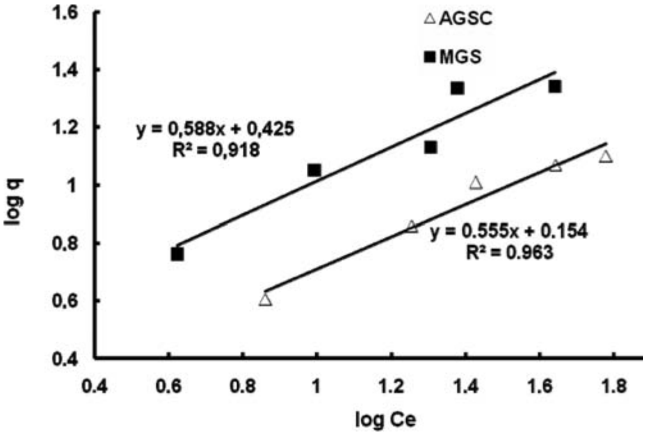


Fig. 6. Freundlich isotherm for both activated guava seeds carbon (AGSC) and modified guava seeds (MGS) (contact time = 2 h, sorbent dosage = 2 g/L, pH = 6, temperature =25°C, constant rotation speed).

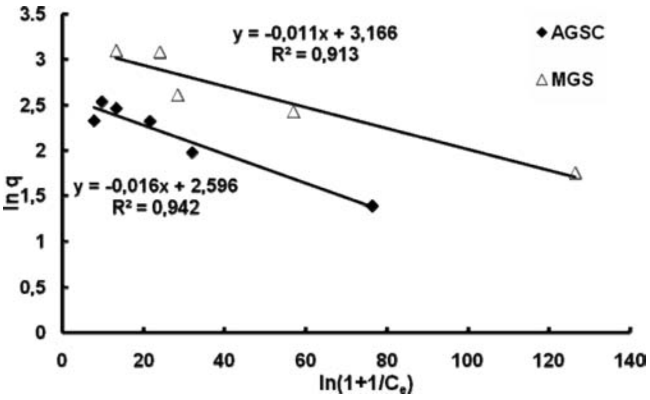


Fig. 7. Dubinin–Radushkevich isotherm model for both activated guava seeds carbon (AGSC) and modified guava seeds (MGS) (contact time = 2 h, sorbent dosage = 2 g/L, pH = 6, temperature = 25°C, constant rotation speed).

Isotherm studies reveal that Langmuir isotherm model best describes the adsorption of Ni(II) on AGSC. However the Frenudlich isotherm model best describes the adsorption of Ni(II) on MGS.

The apparent energy of adsorption has been evaluated by using Dubinin–Radushkevich isotherm model [1]. The model is represented by:

$$q = q_D \exp\left\{-B_D\left[RT\ln\left(1+1/C_e\right)^2\right]\right\} \tag{8}$$

where B_D is related to the free energy of sorption per mole of the sorbate as it migrates to the surface of the adsorbent from infinite distance in the solution. q_D is the Dubinin–Radushkevich isotherm constant related to the degree of adsorbate sorption by the surface of adsorbent.

The linear form of the equation is given by:

$$\ln q = \ln q_D - 2B_D RT\ln\left(1+1/C_e\right) \tag{9}$$

A plot of ln q against RT ln (1 + 1/C_e) yields a straight line and confirms the model. Fig. 7 shows Dubinin–Radushkevich isotherm model for both AGSC and MGS. The results fit well with a high correlation coefficient. The apparent energy of adsorption can be computed using the relationship:

$$E = 1/\left(2B_D\right)^{1/2} \tag{10}$$

Table 2 shows the Langmuir, Freundlich and Dubinin–Radushkevich isotherm parameters for both MGS and AGSC. The apparent energies of adsorption for both AGSC and MGS are higher than 84 Kcal/mole (20 KJ/mole) that means that the adsorption is chemical adsorption. The adsorption of nickel ions over MGS may be attributed to the chelating effect of the new functional groups that have been introduced to the surface of guava seeds by graft copolymerization such as –NH and C=S.

3.4. Kinetic studies

Kinetic studies are important for selecting the optimum operating conditions for large industrial scale adsorption units. There are many models to describe the kinetic of the uptake rate of the adsorbate on the adsorbent. In the present work pseudo-second-order model was used to describe the kinetic data obtained from the

Table 2
Langmuir, Freundlich and Dubinin–Radushkevich isotherm constants for both AGSC and MGS

	AGSC			MGS		
Langmiur constants	Q_{max} (mg/g)	b (L/mg)	R^2	Q_{max} (mg/g)	b (L/mg)	R^2
Freundlich constants	18.05	0.0406	0.987	32.05	0.0518	0.874
	k_f (mg/g)	$1/n$	R^2	k_f	$1/n$	R^2
	1.427	0.555	0.963	2.66	0.588	0.918
Dubinin–Radushkevich	E (Kcal/gmole)	q_D (mg/g)	R^2	E (Kcal/gmole)	q_D (mg/g)	R^2
	250	13.41	0.942	293	23.72	0.914

uptake of Ni(II) on both MGS and AGSC surfaces. The obtained kinetics from batch experiments has been analyzed using the pseudo-second order model proposed by Ho et al. [30]. The differential equation that describes the model is the following:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \tag{11}$$

where q_t is the amount of metal adsorbed at any time t (mg/g), q_e is the amount of metal adsorbed at equilibrium (mg/g), k is second-order rate constant (g/mg.min).

Separating the variables and integrating for the initial condition $t = 0.0$ and $q_o = 0.0$ yields:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \tag{12}$$

Figs. 8 and 9 show a plot of t/q_t against t for both AGSC and MGS respectively. Results reveal a straight line in both cases with a high correlation coefficient indicating that chemisorption kinetics prevails. Kinetic results also show that k decreases with increasing the initial ion concentration which is in consistence with the other work [31].

Table 3 shows the second-order rate constant and the correlation coefficient for both AGSC and MGS. The kinetic data of removal of many heavy metals on different adsorbents were best described by pseudo-second order kinetics [31–35].

3.5. IR studies

Due to the complex structure of guava seeds and the presence of many compounds, the IR gives no useful information as a result of the interference of many functional groups.

3.6. Effect of adsorbent dosage

Fig. 10 indicates that as the adsorbent dosage increases the percentage of Ni(II) removal increases by both adsorbents. The percentage of Ni(II) removal reaches 95.3 and 83.1 for MGS and AGSC respectively. The increase of the adsorption capacity with the increasing adsorbent dosage is attributed to the increase of the available active sites for adsorption.

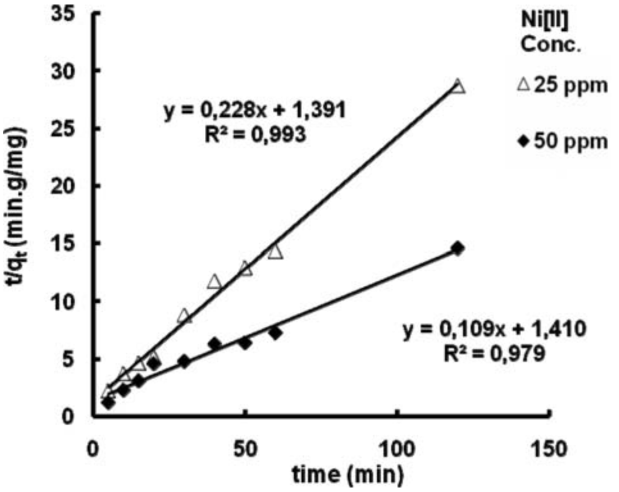


Fig. 8. Plot of second order kinetic model for activated guava seeds carbon (AGSC) (sorbent dosage = 2 g/L, pH = 6, temperature = 25°C, constant rotation speed).

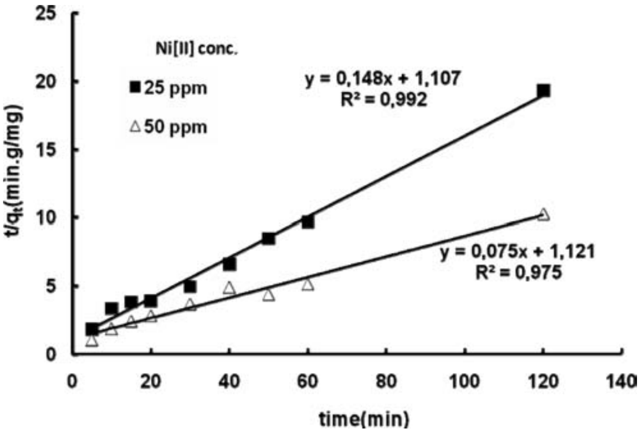


Fig. 9. Plot of second order kinetic model for modified guava seeds (MGS) (sorbent dosage = 2 g/L, pH = 6, temperature = 25°C, constant rotation speed).

3.7. Adsorption mechanism

The most commonly used technique for identifying the rate determining step is fitting the kinetic data by the intraparticle diffusion model. According to Weber and Morris [34], an intraparticle diffusion coefficient is given by the equation:

Table 3
Second order constant parameters for both AGSC and MGS

	25 ppm			50 ppm		
	k (g/mg.min)	q_e (mg/g)	R^2	k (g/mg.min)	q_e (mg/g)	R^2
AGSC	0.0376	4.37	0.9939	0.00844	9.166	0.9793
MGS	0.01997	6.725	0.9926	0.005043	13.297	0.975

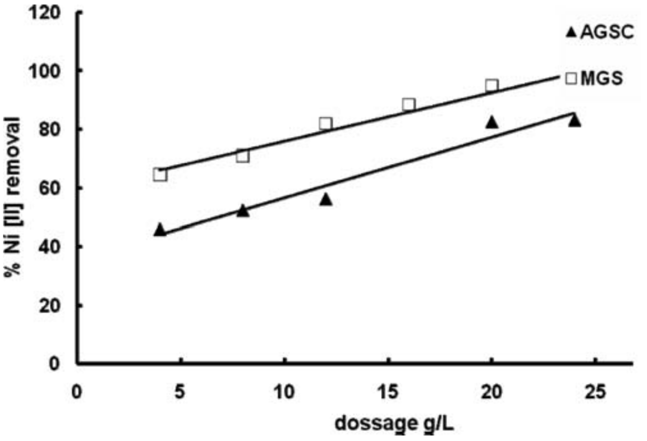


Fig. 10. Effect of adsorbent dosage on the % removal of Ni(II) using modified guava seeds (MGS) and activated guava seeds carbon(AGSC) (initial Ni(II) conc. = 100 ppm, contact time = 2 h, pH = 6 , constant rotation speed).

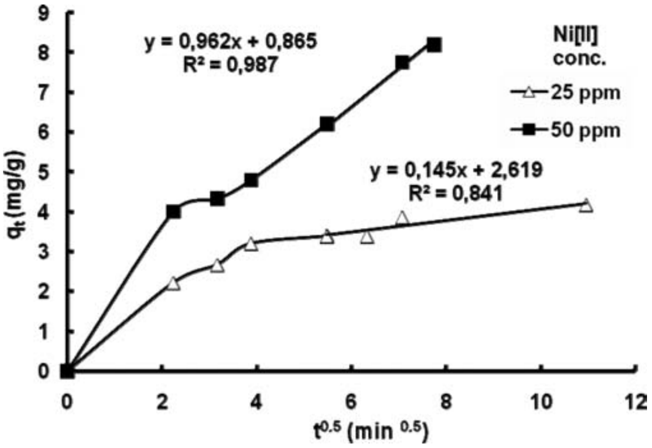


Fig. 11. Plot of intraparticle diffusion model for Ni(II) adsorption on activated guava seeds carbon (AGSC).

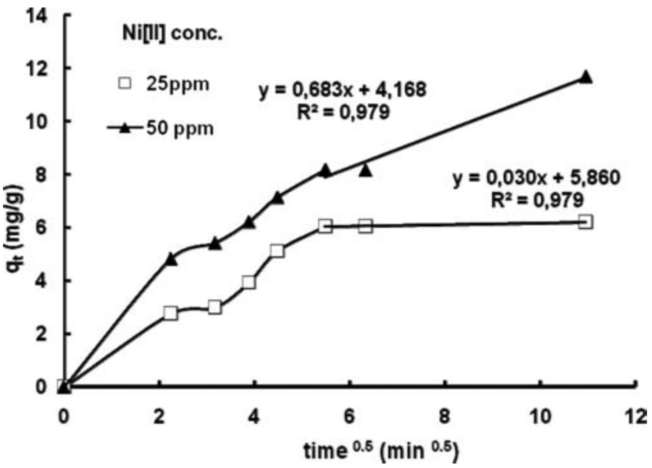


Fig. 12. Plot of intraparticle diffusion model for Ni(II) adsorption on modified guava seeds (MGS).

$$q_t = k_p t^{0.5} \tag{13}$$

where k_p is the intraparticle diffusion coefficient. The plot of q_t vs. t0.5 is shown in Figs. 11 and 12 for both AGSC and MGS. The initial curved portion relates to the boundary layer diffusion (film diffusion) and the later linear portion represents the intraparticle diffusion. From both figures it is obvious that both film diffusion and intraparticle diffusion contribute to the adsorption mechanism. In low concentration however the effect of film diffusion predominates over intraparticle diffusion. The slope of the second portion of the figures represents the intraparticle diffusion coefficient. The calculated values of intraparticle diffusion coefficient for different concentration are listed in Table 4.

4. Conclusions

The performance of two types of adsorbents prepared from guava seeds, namely AGSC and MGS has been investigated for the removal of Ni(II) ions from simulated industrial wastewater. Adsorption capacity of both types has been found to be as a function of pH, contact time, initial Ni(II) ions concentration and adsorbent dosage. An optimum pH value of 6 was selected for the both types of adsorbents.

Adsorption isotherms studies revealed that Langmuir isotherm best fit equilibrium data for AGSC. However isotherm data for MGS best fitted by Frendlich isotherm.

Pseudo-second order model was best fit kinetics data for both types of adsorbents.

Results have shown that MGS adsorbent is a more efficient adsorbent for Ni(II) removal than AGSC. Chemical modification can enhance the adsorption capacity towards heavy metals by i) improving the ion-exchange properties, ii) increasing the number of active binding sites or by iii) formation of new functional groups. Although MGS can enhance the adsorption of Ni(II) ions, the economical consideration have to be taken into account for fair comparison.

Table 4
Intraparticle diffusion coefficient for both AGSC and MGS

	AGSC		MGS	
	25 ppm	50 ppm	25 ppm	50 ppm
k_p (mg/g.min$^{0.5}$)	0.1456	0.9629	0.0308	0.6434
R^2	0.842	0.987	0.979	0.979

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