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Equilibrium and kinetic studies of uptake of nickel in aqueous solution

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ABSTRACT

The uptake of Ni (II) ions from aqueous solution by biochar composed of may flower seed carbon (MFSC), produced by the thermal activation of may flower seed, under inert condition at 400°C for 1 h, was studied. The effect of pH, contact time and adsorption dose on the adsorption of Ni (II) ions by MFSC and the optimization of removal of Ni (II) ions from aqueous solution were investigated by batch adsorption studies. The results obtained gave a maximum adsorption capacity for Ni (II) ions at pH 6, exposure time of 40 min, and dosage of 200 mg/50 mL at 27°C. Analysis of kinetic data showed that the adsorption process of Ni (II) ions followed pseudo-second-order kinetics. Adsorption isotherms were used for determination of MFSC adsorption type and capacity and the Langmuir model was found to be well adapted to describe the adsorption of NI (II) ions, while poor fitting of the experimental data was observed with Freundlich and Temkin isotherm models. The extent of desorption of Ni (II) ions from MFSC under acidic condition was determined to be 45.16%. The results demonstrated the feasibility of using may flower seed carbon in the treatment of Ni (II) ions polluted electroplating industry effluent.

Keywords: Biochar; Adsorption; Desorption; Isotherm; May flower; Nickel

1. Introduction

Contamination of water bodies by heavy metals is a very serious concern, in terms of environmental safety, as well as harm to human health. This problem can only escalate further, due to increased toxic effect by accumulation through the food chain. Heavy metal contamination of water bodies occur primarily by discharge from various industries such as galvanization, smelting, mining, dyeing operations, batteries manufacturing, metal finishing making it unfit for human and animal consumption. Heavy metal ions are described as priority pollutants due to their mobility in natural water ecosystems in addition to their toxicity [1].Nickel is a non-biodegradable and toxic heavy metal which is used in silver refineries, electroplating, zinc base casting and storage battery industries [2]. Trace amounts of nickel are beneficial to human organism as an activator of some enzyme systems, but if it is beyond the scope of normal levels, exposure to nickel causes different type of diseases such as lung cancer, renal edema, skin dermatitis and gastro intestinal disorders [3]. According to Environmental Protection Agency, USA, the permissible limit of Ni (II) ions in wastewater is 1.0 mg L^{-1}. Therefore, it is necessary to ensure that the nickel concentration is below the prescribed limits before discharge. The conventional methods of Ni (II) ions removal from waste water include chemical oxidation or reduction, chemical precipitation, ion exchange, membrane separation, filtration, electrochemical treatment, electro-coagulation and adsorption etc. Electrocoagulation method was capable for the complete removal

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of arsenate from groundwater of Ballia district [4]. The choice of the treatment technique depends on many factors, including the nature of the metal, other constituent present in the effluent system, extent of removal desired, capital and operating cost and sludge generated and their disposal. Agro-based residues for heavy metal adsorption is an economical avenue, explored by many developing countries, as it kills two birds with one stone-tackle the processing of agro-waste and combats pollution. As an efficient method, adsorption onto surfaces of polymer of biological origin has been widely applied to remove heavy metal ions from waste water. This process offers flexibility in design and operation and in many cases will produce high-quality treated effluents. It is essential to explore the feasibility of the uses of several low cost, efficient adsorbents from agricultural wastes and natural materials [5–9].Adsorbents like, rice husk [10], neem bark [11], saw dust [12], tamarind nuts [13], cotton seed cakes [14], coconut oil cakes [15], wine lees biochars [16] and different low cost adsorbents [17–19], etc., for the elimination of heavy metals from wastewater have been investigated by various researchers.

May flower (*Delonix regia*) is an ornamental flowering tree belonging to Fabaceae. It is often cultivated for shade and soil preservation. It grows well in dry deciduous, tropical and subtropical regions and is well-adapted to the Indian sub-continent. The tree produces large quantities of seeds, which are encased in long (40–70 cm), strap-shaped and flattened pods, containing up to 50 seeds each. Each tree disperses a large quantity of pods which litter the environment. The waste products obtained from the tree (seed, leaves, flowers etc.,) have been used as natural low cost adsorbent for the removal of cobalt and lead [20]. However, utilization of biochar from may flower seeds for the removal of Ni ions from solution has not been explored so far. The main objective of the present work is to evaluate the adsorption capacity of may flower seed biochar for the removal of Ni (II) ions from aqueous solution using batch mode adsorption experiment. Also desorption analyses were carried out to ensure reusability and economic feasibility of the process.

2. Materials and methods

2.1. Adsorbent preparation

May flower seeds were collected, washed with distilled water, dried, crushed and ground in a mixer grinder and then sieved to ≤ 0.1 mm size. The ground seed material was placed in a closed stainless steel vessel under inert conditions and heated in a muffle furnace at 400°C for 1 h. Biochar obtained was powdered using mortar and pestle and stored in airtight container for further use as adsorbent without any physical or chemical treatment. Characterization of the biochar was carried by measuring the parameters such as conductivity, moisture content, apparent density, specific gravity, porosity, matter soluble in water, matter soluble in acid, zero point charge and ash calculation. The surface morphology of loaded and unloaded MFSC was elucidated using scanning electron microscope (SEM-JSM, 840A, JEOL, Japan). The nature of the chemical bonding and functional groups of the Ni (II) ion-loaded and unloaded MFSC were observed by FTIR spectroscopy (PERKIN ELMER Spectrum One).

2.2. Adsorbate preparation

All reagents used are of analytical reagent grade. A stock solution of 1000 mg L^{-1} of Ni (II) ions was prepared by dissolving 4.4790 g of ultra-pure nickel sulphate [$NiSO_4 \cdot 6H_2O$] in double distilled water, acidified with nitric acid to prevent hydrolysis. Adsorption experiments were conducted to investigate the influence of adsorption parameters such as contact time, metal ion concentration, adsorbent dose and pH.

2.3. Batch mode adsorption studies

Batch mode experiments were carried out by taking 50 mL of Ni (II) ion solution of each concentration and a known amount of adsorbent in 250 mL Erlenmeyer flasks. The flasks were agitated in a mechanical shaker (125 rpm) at room temperature (27 ± 2°C). The adsorbent and adsorbate solutions were separated by centrifugation (6000 rpm; 15 min). The factors influencing the rate and extent of Ni (II) ion uptake by the adsorbent, agitation time, initial metal ion concentration, adsorbent dosage and pH were studied. The effect of contact time on the removal of Ni (II) ions from aqueous solution was studied using 50 mg of the adsorbent and 50 mL of Ni (II) ion aqueous solution, agitated for different durations of time. The effect of pH on adsorption was studied by adjusting the pH of Ni (II) ion solutions using 0.1 N HCl and NaOH solutions. The effect of initial metal ion concentration and adsorbent dosage were studied in 50 mL reactions, each consisting of initial Ni (II) ion concentrations (10–50 mg L^{-1}) and different adsorbent doses (50–250 mg) at equilibrium time. The amount of Ni (II) ions remaining in the solution was calculated by UV-Visible spectrophotometry at 445 nm by a standard dimethyl glyoxime (DMG) method [21]. The removal percentage was calculated as

$$R\% = \frac{(C_i - C_e)}{C_i} \times 100 \tag{1}$$

Where C_i and C_e are the initial and final concentrations of metal ion in the solution.

2.4. Desorption studies

After adsorption experiments with 50 mg L^{-1} solution of Ni (II) ions and 200 mg of carbon, the Ni (II) ion-laden carbon was separated out by centrifugation and the supernatant was discarded. The residual carbon was given a gentle wash with double distilled water to remove the unadsorbed metal ions and were agitated with 50 mL of various strengths (0.1–0.5 M) of HCl with four cycles. The desorbed Ni (II) ions was estimated as described in Section 2.3.

3. Results and discussion

3.1. Effect of contact time

Contact time of the solution and the adsorbent is an important parameter controlling the adsorption process. Fig. 1 indicates that the removal of Ni (II) ions increased with contact time and attained saturation after equilibrium time. The equilibrium time recorded was 40 min for all

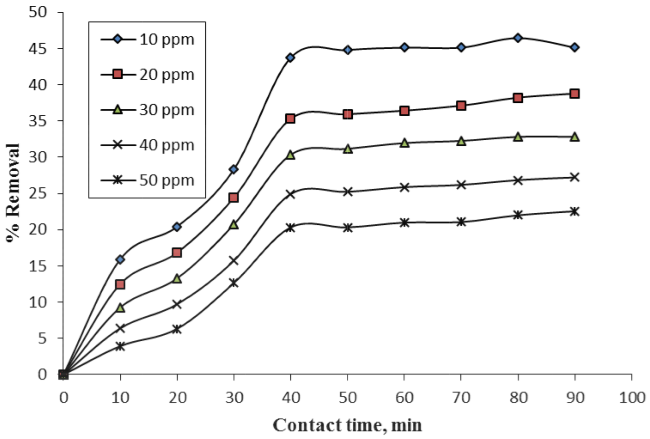

Fig. 1. Effect of contact time on adsorption of Ni (II) ions by MFSC (Adsorbent: 50 mg 50 mL^{-1}, Concentration: 10, 20, 30, 40 and 50 mg L^{-1}).

initial Ni (II) ion concentrations(10–50 mg L^{-1}). To ensure enough time to reach equilibrium, 40 min of contact was used throughout the batch experiments. Similar trend was observed by many researchers [22–24].

3.2. Effect of adsorbent dose

Effect of adsorbent dose was studied with five different dosages, viz 50, 100, 150, 200, 250 mg of may flower seed carbon. Fig. 2 indicated the effect of adsorbent dose on Ni (II) ion uptake on may flower seed carbon. The removal increased with increase in adsorbent dose and maximum adsorption was found to occur at 200 mg of adsorbent per 50 mL of the aqueous solution of Ni (II) ions. This is because of an increase in the number of available adsorption sites of the adsorbent which results in enhanced removal of Ni (II) ions. Erdogan et al., reported that adsorption increased with increase in adsorbent dose prepared from waste apricot [25].

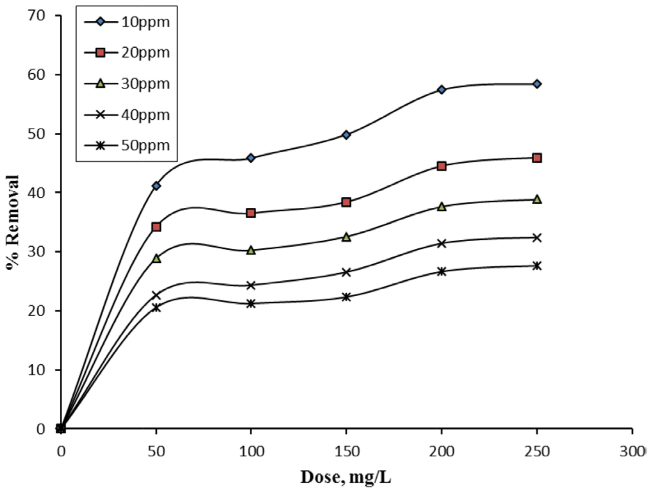

Fig. 2. Effect of adsorbent dose on adsorption of Ni (II) ions by MFSC (Equilibrium time: 40 min, Concentration: 10, 20, 30, 40 and 50 mg L^{-1}).

3.3. Effect of metal ion concentration

The effect of initial metal ion concentration on the removal of Ni (II) ions on MFSC was studied. The removal efficiency has decreased from 43.54% to 19.35% with increase in Ni (II) ions concentration from 10–50 mg L^{-1}. The dependence of the adsorption system at low initial metal ion concentration is explained by the availability of a number of sites of adsorption, However, at higher concentration, owing to the saturation of specific sites of adsorption, the available sites become fewer and hence the percentage removal of Ni (II) ions dependent upon the initial concentration [26].

3.4. Effect of pH

Zero point charge (pHzpc) of the adsorbent is an important parameter for adsorption of Ni (II) ions. The value of pHzpc of MFSC is found to be 8.0. Fig 3 shows the effect of pH change in the range 2–10 on the adsorption of Ni (II) ions on MFSC. The percentage removal increased with increase in pH and attains maximum of 92.52% removal at pH 6 and then decreased to 15.21% at pH 10 (Fig. 3). This trend was due to surface charge of the adsorbent and the H$^+$ ions present in the solution. At low pH, the metal cations compete with the H$^+$ ions in the solution for the active sites and therefore adsorption decreased. At high pH values surface of the adsorbent has a higher negative charge which results higher attraction of metal ions. Hence Ni (II) ions removal onto MFSC was optimum at pH 6.This pH is compared with pHzpc, since, at this pH, the adsorbent surface has a negative charge on it [27]. So, above pH 6.0, adsorption decreases but the total Ni (II) ion removal increases due to the formation of hydroxide of nickel which is precipitated.Mousavi and Seyedi [28] observed maximum adsorption of Ni and Cd on nettle ash at pH 6. It was observed that adsorption was decreased at higher pH because of precipitation of Ni (II) ions from solution. Similar results have also been reported by Ucar et al. [29].

3.5. Equilibrium modeling

Adsorption isotherm models are widely employed for fitting the data, of which the Langmuir, Freundlich and

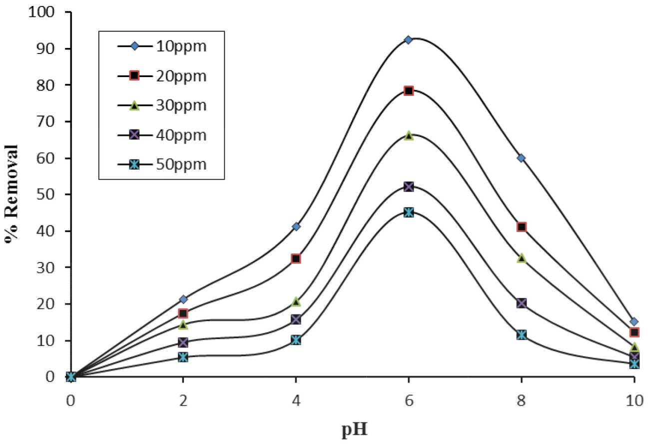

Fig. 3. Effect of pH on adsorption of Ni (II) ions by MFSC (Equilibrium time: 40 min, Adsorbent dose: 200 mg 50 mL^{-1}, Concentration: 10, 20, 30, 40 and 50 mg L^{-1}).

Temkin equations are most commonly employed. The Langmuir parameters [30] can be determined from a linearized form of equation,

$$C_e / q_e = 1/Qb + C_e/Q \tag{2}$$

where q_e is the metal ion sorbed (mg g^{-1}) at equilibrium, C_e the equilibrium concentration of metal ion solution, Q and b are Langmuir constants. The linear plot of C_e/q_e versus C_e showed that adsorption obeys the Langmuir model. Q and b (Table 1) were determined from the slope and intercept of the plot.

The essential characteristics of Langmuir isotherm model can be explained in terms of a dimensionless constant or equilibrium parameter R_L, which is defined by

$$R_L = 1/\left(1 + bC_0\right) \tag{3}$$

where C_o is the initial concentration of Ni (II) ions.

According to Mckay et al., [31], R_L values between 0 and 1 indicate favourable adsorption. Similar results (Table.1) were observed for Ni (II) ions—MFSC system indicating favourable adsorption.

The adsorption data obtained were then fitted to the Freundlich adsorption isotherm [32], which is expressed by the equation,

$$\log q_e = \log K_f + 1/n \log C_e \tag{4}$$

where K_f and n are constants represents adsorption capacity and intensity of adsorption respectively. The constants K_f and n were calculated from Eq. (4) using Freundlich plots as shown in Fig. 5. The values of n between 1 and 10 (i.e., $1/n$ less than 1) represent a favourable adsorption. The observed $1/n$ value was 0.4073 which represented a beneficial adsorption.

The Temkin isotherm[33] can be expressed by the following equation:

$$q_e = a + bt \ ln\ C \tag{5}$$

where C = concentration of adsorbate in solution at equilibrium (mg L^{-1}), q_e = Amount of metal adsorbed per unit weight of adsorbent (mg g^{-1}), a and bt are constants related to adsorption capacity and intensity of adsorption.

Fig. 6 indicated that the plots of q_e against ln C for Ni (II) ions adsorption, gives a straight line with slope bt and intercept a. Analysis of the data (Table 1) over a concentration range from 10 to 50 ppm of the metal ions, showed that the adsorption of Ni (II) ions onto may flower seed carbon was best described by the Langmuir isotherm.

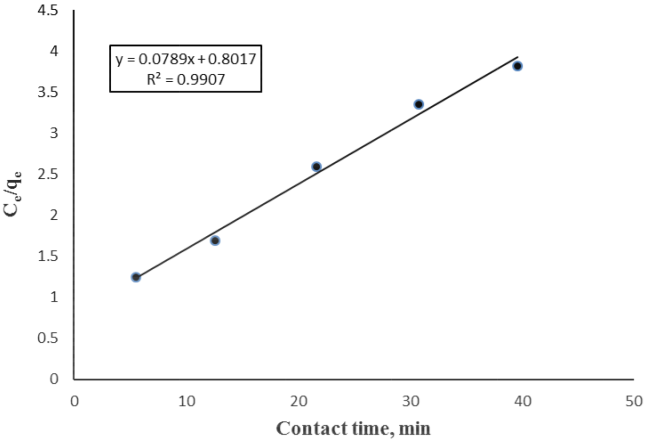

Fig. 4. Langmuir adsorption of Ni (II) ions by MFSC (Equilibrium time: 40 min, Adsorbent dose: 200 mg 50 mL^{-1}, Concentration: 10, 20, 30, 40 and 50 mg L^{-1}, pH: 6).

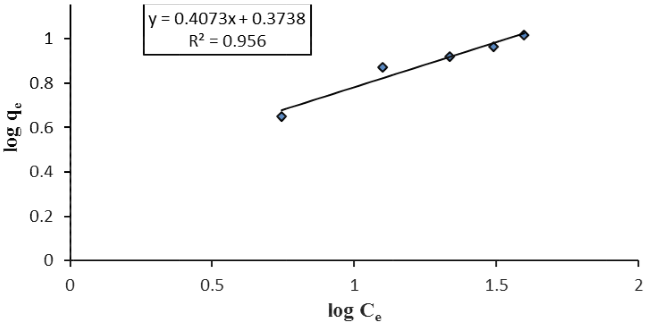

Fig. 5. Freundlich adsorption of Ni (II) ions by MFSC (Equilibrium time: 40 min, Adsorbent dose: 200 mg 50 mL^{-1}, Concentration: 10, 20, 30, 40 and 50 mg L^{-1}, pH: 6).

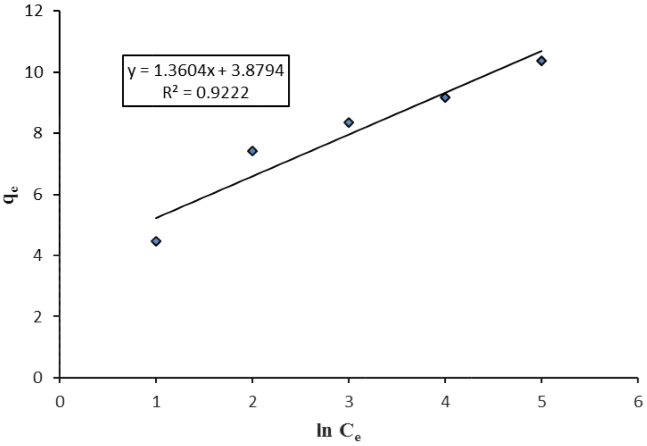

Fig. 6. Temkin plot for adsorption of Ni (II) ions by MFSC (Equilibrium time: 40 min, Adsorbent dose: 200 mg 50 mL^{-1}, Concentration: 10, 20, 30, 40 and 50 mg L^{-1}, pH: 6).

Table 1
Estimated isotherm constant values for Ni (II) ions

Metal ion	Langmuir constants			Freundlich constants			Temkin constants		
	Q_o	b	R^2	K_f	$1/n$	R^2	A	B	R^2
Nickel	12.674	0.984	0.991	2.365	0.407	0.956	3.880	1.360	0.981

3.6. Adsorption kinetics

In order to investigate the controlling mechanism, the pseudo-first-order, pseudo-second-order and intraparticle diffusion were applied to model the kinetics of Ni (II) ions adsorption onto MFSC. Lagergren proposed a pseudo-first-order kinetic model. The integral form of the model is [34]

$$\log\left(q_e - q_t\right) = \log q_e - \left(k_{ad} / 2.303\right) t \qquad (6)$$

where q_t is the amount of metal ion sorbed (mg/g) at time t (min), q_e is the amount of metal ion sorbed at equilibrium (mg g^{-1}), and k_{ad} is the equilibrium rate constant of pseudo-first-order adsorption (1 min^{-1}). This model was successfully applied to describe the kinetics of many adsorption systems.

The adsorption kinetics may also be described by a pseudo-second-order reaction. The linearized integral form of the model is[35]:

$$t / q_t = 1 / k_2 q_e^{\,2} + t / q_e \qquad (7)$$

where k_2 is the pseudo-second-order rate constant of adsorption, q_t is the amount of metal ion sorbed (mg g^{-1}) at time t (min), q_e is the amount of metal ion sorbed at equilibrium (mg g^{-1}).The applicability of the above two models can be examined by each linear plot of log (q_e–q) versus t, and (t/q) versus t, respectively and are presented in Figs. 7, 8. The correlation coefficients calculated for two models are presented in Table 2. The results showed that the pseudo-second-order model, fits better the experimental data than the pseudo-first-order model.

To elucidate the diffusion mechanism, the intraparticle diffusion model [36] is expressed as:

$$q = K_{id} t^{0.5} + C \qquad (8)$$

where C is the intercept and K_{id} is the intraparticle diffusion rate constant (mg g^{-1} min$^{-1/2}$), which can be evaluated from the slope of the linear plot of qt versus $t^{(1/2)}$ as shown in Fig. 9 and Table 3. According to Eq. (8), the slopes of the linear portions of the plots of qt vs $t^{1/2}$ give the values of k_{id}. The intercept value C provide information about the thickness of the boundary layer. The resistance to the external mass transfer increases as the intercept increases. The constant C was found to increase from 3.54 to 13.26 with increase in Ni (II) ions concentration from 10 to 50 ppm onto MFSC. This indicates the increasing boundary layer thickness and decreases the chance of the external mass transfer and hence increases the chance of internal mass transfer.

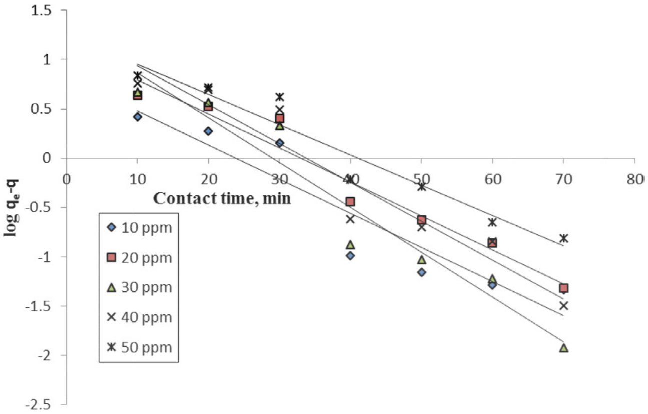

Fig. 7. Lagergren plot for the adsorption of Ni (II) ions by MFSC (Equilibrium time: 40 min, Adsorbent dose: 200 mg 50 mL^{-1}, Concentration: 10, 20, 30, 40 and 50 mg L^{-1}, pH: 6).

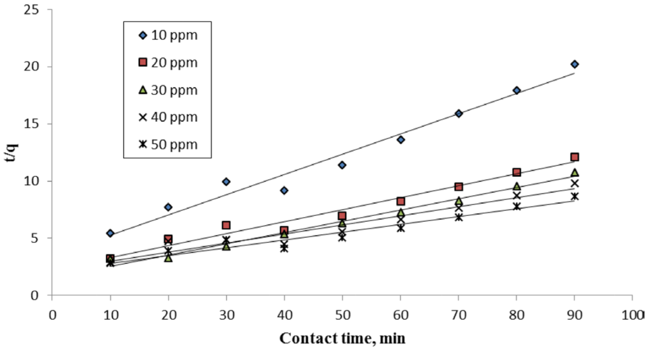

Fig. 8. Pseudo second-order adsorption of Ni (II) ions by MFSC (Equilibrium time: 40 min, Adsorbent dose: 200 mg 50 mL^{-1}, Concentration: 10, 20, 30, 40 and 50 mg L^{-1}, pH: 6).

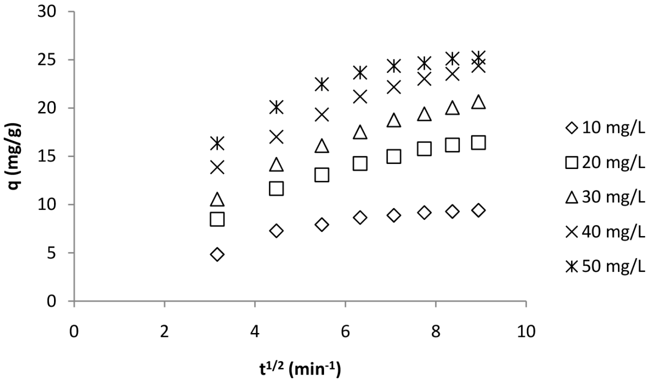

Fig. 9. Intraparticle diffusion Plots for Ni (II) ions adsorption on MFSC (Equilibrium time: 40 min, Adsorbent dose: 200 mg 50 mL^{-1}, Concentration: 10, 20, 30, 40 and 50 mg L^{-1}, pH: 6).

Table 2
Estimated kinetic parameters in adsorption of Ni (II) ions

Metal ion	Pseudo first order kinetic model				Pseudo second order kinetic model		
	q_e (exp)	K_{ad}	q_e (cal)	R^2	K_2	q_e (cal)	R^2
Nickel	4.123	7.968 x 10^{-2}	6.687	0.876	11.05 x 10^{-2}	5.663	0.971

Table 3
Intraparticle diffusion model rate constants and experimental *qe* values

Concentration	K_{id}	C	R^2	q_e	q_e(exp) (mg g^{-1})
10	0.718	3.549	0.865	9.971	9.97
20	1.328	5.294	0.950	17.172	17.17
30	1.691	6.258	0.965	21.383	21.38
40	1.793	9.012	0.972	25.049	25.05
50	1.471	13.26	0.892	26.417	26.42

3.7. Adsorbent characterization

FT-IR spectrum for MFSC before and after adsorption of Ni (II) ions showed the complex nature of MFSC (Fig. 10). The sharp band at 3418.21 cm^{-1} showed the presence of the –OH groups. The small peaks in the range of 2858.16–2922.35 cm^{-1} were associated with the methylene (–CH$_2$–) bridges of the MFSC. The band observed at about 1000–2000 cm^{-1} may be attributed to the presence of C–O groups. The peak at 1600–1700 cm^{-1} was indicative of C=O groups. The peaks at 1587 cm^{-1} and 1429 cm^{-1} are characteristic of the elongation of the aromatic –C–H– bonds. The peaks at 1051 cm^{-1} was due to C–O stretching and C–H deformation [37]; –OH stretching band shift from 3418.21 to 3422.97 cm^{-1} confirms the presence of –OH groups. Shifting of peaks from 1051.18 to 1060.45 cm^{-1} was due to binding of Ni (II) ions at phenol and alcoholic groups respectively. The functional groups observed in FTIR studies could participate in the adsorption process.

A scanning microscope (SEM) was used to examine the surface of the may flower seed carbon. Fig. 11 showed a highly porous morphology of adsorbent with pores of different sizes and shapes. The porous surface will be more favorable for adsorption. The physico-chemical characterization of MFSC was given in Table 4.

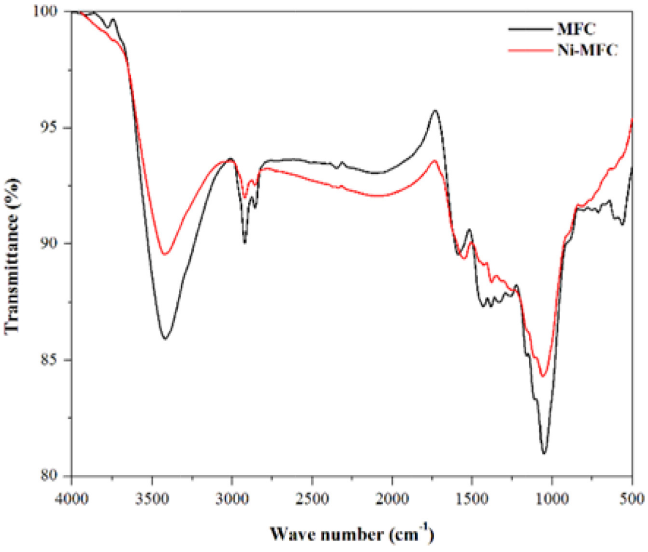

Fig. 10. FTIR Spectrum of nickel loaded and unloaded may flower seed carbon.

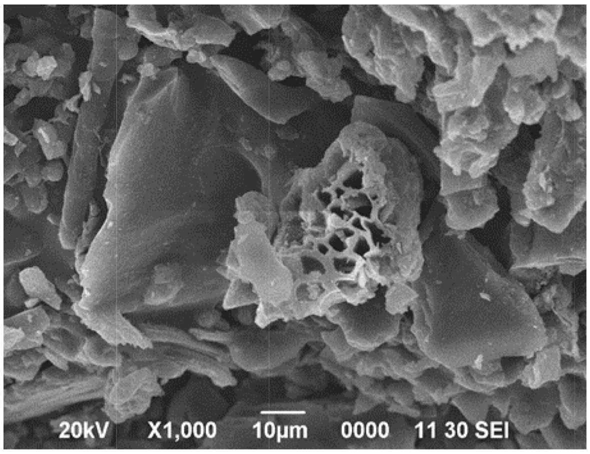

Fig. 11. Sem image of nickel loaded May flower seed carbon.

3.8. Desorption

Desorption was done to reduce the cost of adsorption process and it was carried out using different HCl concentration solutions (0.1 M–0.5 M). Maximum of 45.16% desorption occurred at 0.2 M HCl solution due to competition between H$^+$ ions and metal ion on the active sites. At low pH value, the complexation between the adsorbent and Ni (II) ions was destroyed [38]. Binding capacity of the adsorbent doesn’t vary with acid treatment and the active site of the adsorbent may not be altered.

3.9. Comparison of adsorption capacity with different adsorbents reported in literature

A comparative study for the adsorption capacities of different adsorbents for the removal of Ni (II) ions was presented in Table 5. It is clear from this table that MFSC, used in the present study has significant adsorption capacity in comparison with other adsorbents, and it can be a better alternative for the Ni (II) ions adsorption.

Table 4
Characteristics of biochar prepared from may flower seeds

Parameter	Value
Conductivity	0.7
Apparent density (g mL^{-1})	0.67
Specific gravity	1.376
Moisture (%)	5.2
Porosity (%)	51.31
pHzpc	8.0
Mater soluble in water (%)	1.98
Mater soluble in acid (%)	5.86
Ash (%)	0.767

Table 5
Comparison of adsorption capacities of the adsorbents for the removal of Ni (II)ions with those other adsorbents.

S. No	Adsorbents	Adsorption capacities, mg g^{-1} Ni (II) ions	Reference
1	Cashew nut shell	18.868	[39]
2.	Acacia nilotica seed pods	10.417	[40]
3.	Activated olive stone	8.42	[41]
4.	Bacillus laterosporus	44.44	[42]
5.	May flower seed	12.67	Present work

4. Conclusions

The present work demonstrates that MFSC has good Ni (II) ions adsorption potential when compared to other reported adsorbents. Isotherm studies indicated that among the Langmuir, Freundlich and Temkin isotherm models, Langmuir model fits well with Ni (II) ions adsorption by MFSC. The Freundlich constant ($1/n$) of 0.4073 denoted that the adsorption process on to MFSC was favorable. The kinetic studies showed that pseudo–second order rate equation was able to provide a realistic description of adsorption kinetics of nickel. The nickel was desorbed to a maximum of 45.16% in 0.2 M HCl. This adsorbent is of low cost, its utility will be economical and can be viewed as a part of a feasible waste management strategy. The results will be useful for the fabrication and designing of waste water treatment plants for the removal of heavy metals particularly for Ni (II) ions.

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