Utilization Properties of Jatropha De-Oiled Cake for Removal of Nickel (II) from Aqueous Solutions

Garima Mahajan,[a,]* Umesh Garg,[b] Dhiraj Sud,[a] and Vinod Garg [c]

In the present study, jatropha oil cake (JOC), a waste produced from processing jatropha seeds for biodiesel production, has been investigated for the removal of nickel (II) from aqueous solutions. Jatropha oil cake contains different functional groups that can participate in the metal ion complexation. Jatropha oil cake is used in its natural form (JOCN) as well as in its immobilized form (JOCB). Batch experiments were performed for adsorption of Ni (II) by JOCN and JOCB. Parameters affecting the adsorption, such as the effect of adsorbent dose, pH, the initial concentration of metal ion, agitation speed, and contact time, were studied for the maximum removal efficiency. Removal efficiency was found to be 62% and 63% for Ni (II) at pH 6.2 in its natural and immobilized forms, respectively. Maximum adsorption occurred within an hour for Ni (II) with JOCN and 90 min for JOCB. The equilibrium data was analyzed using Langmuir and Freundlich isotherms.

Key words: Jatropha oil cake (JOC); Biosorption; Heavy metal remediation; Immobilization

Contact Information: a: Department of Chemistry, Sant Longowal Institute of Engineering and Technology, Longowal 148106; b: Department of Applied Sciences, Adesh Institute of Engineering and Technology, Faridkot 151203; c: Department of Environmental Science and Engineering, Guru Jambeshwar University of Science and Technology, Hisar 125001, India;
** Corresponding author: garima8mahajan@hotmail.com*

INTRODUCTION

Heavy metals are essential in trace amounts for the normal growth and development of animals and plants, but they become toxic if released in higher concentrations. These metals are of special concern due to their recalcitrant and persistent nature. Heavy metals are generally introduced into the environment through natural phenomena and various human activities (Friedman and Waiss 1972; Kjellstrom *et al.* 1977; Pastircakova 2004).

The increased use of heavy metals has resulted in an increased concentration of the metallic substances in different environmental segments. Ni (II) is extensively used in a number of industries, *e.g.*, electroplating, battery manufacturing, mining, metal finishing, and forging; thus, the release of nickel into the environment is an issue of great concern. Ni (II) concentration in wastewater from mine drainage, tableware plating, metal finishing, and forging has been reported to be up to 130 mg L^{-1} (Patterson 1985; Nuhoglu *et al.* 2002), and the maximum contaminant limit for nickel in potable water has been fixed as 50 µg/L by the European Economic Community (EEC). A higher concentration of Ni (II) in ingested water may cause severe lung and kidney damage, gastrointestinal distress, nausea, vomiting, diarrhea, pulmonary fibrosis, renal edema, and skin dermatitis (Akhtar *et al.* 2004).

The disposal of wastewater containing such toxic heavy metals is always a challenging issue for environmentalists. There are various conventional treatment processes for nickel and other heavy metal ions from wastewater that include precipitation with hydroxide, carbonate, and sulphide, ion exchange, electrowinning, electrocoagulation, cementation, and reverse osmosis (Ahluwalia and Goyal 2005a; Christensen and Delwiche 1982). Some of these processes are based on physical displacement or chemical replacement, generating yet another problem in the form of toxic sludge. Thus, the techno-economic feasibility of the treatment process is affected (Ahluwalia and Goyal 2005b; Sandau *et al*. 1996; Mahmood *et al.* 2010). Adsorption, compared with other methods, appears to be an attractive process due to its efficiency and the ease with which it can be applied in the treatment of heavy metal-containing wastewater.

Agricultural waste materials are economic and ecofriendly due to their unique chemical composition, availability in abundance, renewability, low cost, and increased efficiency, and they seem to be a viable option for heavy metal ion remediation (Hubbe 2008). This process of biosorption involves a solid phase (sorbent) and a liquid phase (solvent) containing a dissolved species to be sorbed. Due to the high affinity of the sorbent for the metal ion species, the latter is attracted and bound by a rather complex process affected by several mechanisms, involving chemisorption, complexation, adsorption on the surface and pores, ion exchange, chelation, adsorption by physical forces, and entrapment in the inter and intra-fibrillar capillaries and spaces of the structural polysaccharide network as a result of the concentration gradient and diffusion through the cell wall and membrane (Sud *et al.* 2008).

Several investigations have been undertaken for the removal of nickel ions from wastewater using different low-cost agricultural waste materials (Sud *et al*. 2008), such as hazelnut activated carbon (Volesky and Holan 1995), *Cassia fistula* biomass (Demirbas *et al*. 2002), sugarcane bagasse (Hanif *et al*. 2007), waste tea leaves, wheat straw (Ahluwalia and Goyal 2005b; Garg *et al.* 2009), black gram husk (Malkoc and Nuhoglu 2005), coir fibres (Saeed *et al.* 2005), jute fibers (Sukla and Pie 2005), and sawdust from oak and black locust (Sciban *et al*. 2006). These agricultural wastes mainly consist of lignin, cellulose, hemicellulose, carbohydrates, and some proteins that make them effective adsorbents for heavy metal ions (Hubbe and Lucia 2007, Hubbe and Rojas 2008).

Jatropha crops are gaining momentum for their property of eco-restoration of degraded waste lands and production of biodiesel (Niveta *et al.* 2008). Jatropha oil cake (JOC) is a waste byproduct of the industrial processing of jatropha seeds for biodiesel production. Our previous experimental studies that focused on using biomass of natural JOC for the removal of Cr (VI) proved the potential of JOC as a good biosorbent for Cr (VI) ions (Garg *et al.* 2007).

Biomass in its natural form may lead to the release of soluble organic materials. Furthermore, it is not mechanically strong and has a wide size distribution, which can lead to problems in reactor operations by blocking flow lines and clogging filters. Also, separation of biomass and effluent can be difficult and expensive, whereas immobilization of biomass in a polymeric matrix can yield beads or granules with an optimum size, mechanical strength, rigidity, and porosity characteristics. Thus, the objective of the present study was to investigate the binding of nickel ions by natural JOC and immobilized JOC biomass beads from aqueous solutions and to study the various factors affecting the efficiency of the process.

EXPERIMENTAL

Preparation of Adsorbent

Jatropha oil cake was collected from a jatropha biodiesel processing plant. A hot water treatment was given to the JOC for one hour to remove the soluble organic components and sugars; it was then dried at 120 °C in a hot air oven for 24 h, ground, and sieved (150 MICS). Beads of JOC were prepared by mixing sodium alginate (polymer) and JOC at different ratios. JOC:polymer rations were, 1:1, 1:3, 1:5, 1:7, 1:9, and 1:11, in a pre-calculated amount of deionized water and dropping the mixture into a 2% solution of calcium chloride using a micropipette. The prepared beads were stirred in the $CaC1_2.2H_2O$ solution for 24 h to harden. The beads were then washed three times with deionized water and maintained in a 2% $CaC1_2$ solution at 4 °C (Tsezos 1990; Sekha *et al.* 2003; Taty-Costodes *et al.* 2003). To explore the number and positions of the functional groups available for the binding of nickel to the JOC, FT-IR spectra of native and nickel-loaded adsorbent were acquired using a Perkin-Elmer-RX FT-IR system.

Preparation of Adsorbate

A stock solution of Ni (II) was prepared (1000 mg L^{-1}) by dissolving 4.95 g of nickel nitrate in 1 L of deionized water. The stock solution was diluted with deionized water to obtain the desired concentration range of the Ni (II) solution. The concentration in the test solution was determined spectrophotometrically using a Double Array UVVIS Spectrophotometer (Agilent 8453) at a wavelength corresponding to the maximum absorbance (470 nm) for Ni (II) (DMG method, APHA, 1995). The solutions' pH was adjusted using 0.1 m mol L^{-1} HCl or NaOH using the Orion 420A pH meter. All chemicals used were of analytical grade. Batch sorption experiments were performed on simulated as well as real industrial effluents. The composition of the industrial wastewater is given in Table 1.

Table 1. Characterization of Industrial Effluents

Parameters	Amount in Effluent
pH	4.33
Temperature	22.8 ^oC
Electric Conductivity	65.5 mS/cm
Salinity	43.4%
Total Solids	76000 mg L^{-1}
Total dissolved solids	63000 mg L^{-1}
BOD	290 mg L^{-1}
COD	312.6 mg L^{-1}
Sulphide	1.35 mg L^{-1}
TKN	210.14 mg L^{-1}
Cr (Total)	1500 mg L^{-1}
Cr (VI)	BDL
Ca	152 mg L^{-1}
Cu	0.1 mg L^{-1}
Cd	0.012 mg L^{-1}
Ni	1.152 mg L^{-1}
Pb	15.26 mg L^{-1}
Zn	0.793 mg L^{-1}

Adsorption Experiments

Adsorption experiments were carried out using 100 mL of nickel solutions of varying concentrations (5 to 500 mg L^{-1}) at varying initial pHs (1 to 7, as after pH 7, precipitation of the sample was observed) with different agitation speeds (50 to 300 rpm), different contact times (5 to 120 min), and different adsorbent doses (50 to 2500 mg) in a 250-mL Erlenmeyer flask at 25±1 °C (ambient temperature). Samples were separated by centrifugation at 4000 rpm for 10 min. All experiments were repeated in triplicate, and an average was taken. The removal percentage (R%), defined as the ratio of the difference in metal concentration before and after adsorption (C_i – C_e) to the initial concentration of nickel in the aqueous solution (C_i), was calculated using Eq. 1:

$$\mathrm{R\%} = \left(\frac{C_\mathrm{i} - C_\mathrm{e}}{C_\mathrm{i}}\right) \mathrm{x}\ 100 \tag{1}$$

RESULTS AND DISCUSSION

It was found that structurally, JOC contains crude fat (38%), carbohydrates (17%), crude protein (18%), fiber (15.5%), and ash (5.3%). FT-IR analysis of the adsorbent before and after sorption of nickel was performed to determine the vibrational frequency changes in the functional groups of the adsorbent (Figs. 1 and 2).

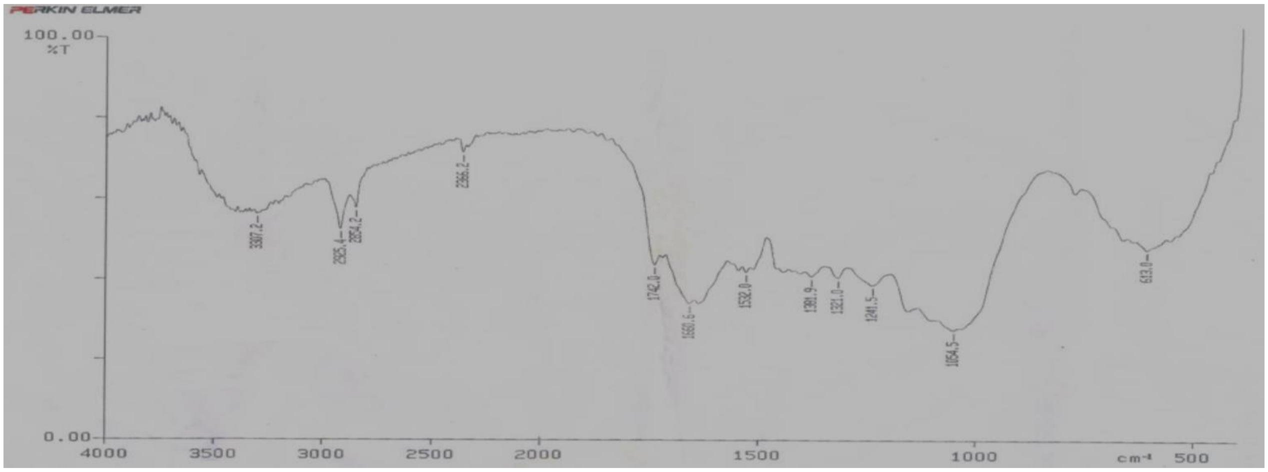

Fig. 1. FT-IR spectra of JOC before use

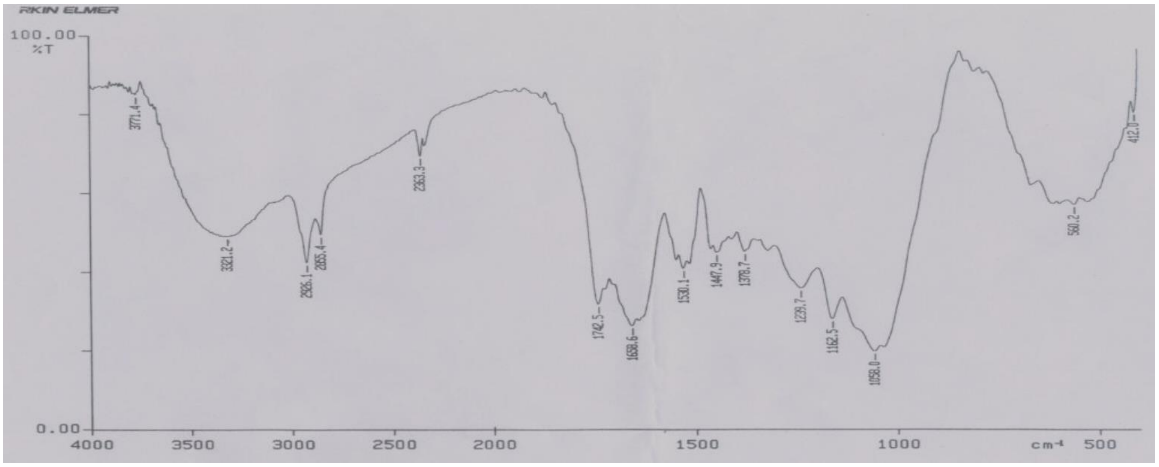

Fig. 2. FT-IR spectra of JOC loaded with Ni (II)

The spectra of the adsorbent were measured in the range of 500 to 4000 cm^{-1}. The FT-IR spectrum of the adsorbent displays a number of adsorption peaks, indicating the complex nature of the studied adsorbent. In the FT-IR analysis of the native JOC, a broad adsorption band is observed at 3307 cm^{-1} and can be attributed to the bonded –OH groups present in the structure. The other prominent peaks are due to the $–OCH_3$ groups and aromatic compounds. The presence of a peak near 2925.4 cm^{-1} indicates the presence of a C-H group in the structure. However, in the case of jatropha oil cake with Ni (II), there is a remarkable shift in the position of the –OH group, which is indicative of Ni (II) binding with –OH groups, and further shifts in the bending frequency of aromatics show the association with aromatic rings (Figs. 1 and 2).

Effect of Polymer and Biomass Ratio

Biomass beads were formed by binding JOC with sodium alginate polymer in different ratios of biomass to binding agent (*i.e.*, 1:1, 1:3, 1:5, 1:7, 1:9, and 1:11). As calculated from the preliminary experiments, a JOC:polymer ratio of 1:9 was found to be optimal, and the rest of the experiments were performed using the 1:9 ratios. The adsorption increases with an increase in the ratio of biomass to binding agent. Maximum adsorption was shown by the 1:9 ratios as compared to the 1:11 ratio due to its lack of stability in later experiments. The same process has already been used with other biosorbents for the removal of toxic metal ions and is reported in Mahajan and Sud 2011, 2012 (Fig. 3).

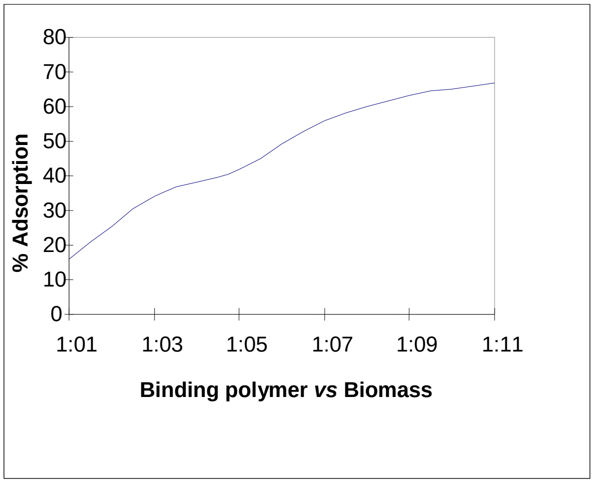

Fig. 3. Effect of variation of binding polymer and biomass ratio

Effect of pH

pH is an important controlling parameter in the adsorption process due to its influence on the surface properties of the adsorbent and the ionic form of the metal ion in solution. Adsorption experiments were carried out in the pH range of 1 to 7, keeping all the parameters constant (Ni concentration: 50 mg L^{-1}; stirring speed: 250 rpm; contact time: 60 and 90 min; adsorbent dose: 2.0 g L^{-1} for JOCN and JOCB at room temperature). The pH of the nickel solution was adjusted after adding the adsorbent. The maximum adsorptions of nickel were 62% and 63% for JOCN and JOCB, respectively, at pH 6.2. It was observed that when the pH increased from 1.5 to 6.2, the adsorption efficiency was increased from 7 to 62% in the case of JOCN and from 8 to 63% in the case of JOCB. Best adsorption occurred at pH 6.2; therefore, it was taken as the best pH value for further adsorption experiments. It was observed that there was no significant enhancement in the removal efficiency of the biosorbent increasing pH from 6.2 to 7.0 and the further increase resulted into the precipitation of the solution. On the basis of simulated studies, real industrial effluent containing Ni metal ion was taken from the electroplating industry, and studies were performed to determine the feasibility of the process on the real effluents. The removal efficiency was found to be near 95% with the biosorbent in various forms. The pH dependence of metal adsorption is largely related to the type and ionic state of the functional groups present on the adsorbent and the metal chemistry of the solution (Sekha *et al.* 2003). At lower pH values, the H_3O^+ ions compete with the metal ions for the exchange sites in the sorbent. As pH increases from the acidic range to the neutral range, nickel is present predominantly as Ni^{2+}. Moreover, due to the presence of vacant hydroxyl (-OH-) and carbonyl (C=O) groups, the formation of coordination complexes with the metal ion also occur. At low pH values, the H_3O^+ ions compete with the metal ions for the binding sites of the JOC, leaving the metal ions in solution. As the pH increases, the concentration of H_3O^+ ions decreases and the sites on the JOC surface become available for the metallic ions in the solution. Our results were found to be consistent with other studies that demonstrated that the removal of nickel decreases with a decrease in pH to 1.0 (Fig. 4). The same trends were shown in the case of immobilsed *Rhizomucor tauricus* (Kumar *et al*. 2012).

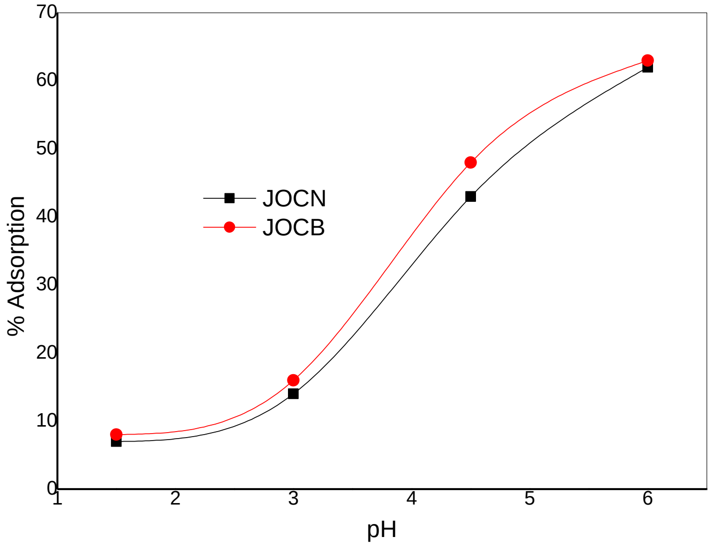

Fig. 4. Effect of pH on nickel removal by JOC in natural and bead form

Effect of Stirring Speed

Stirring influences the distribution of the aqueous solution. A range of stirring speeds from 50 to 300 rpm was selected for the adsorption experiments at a fixed nickel concentration (50 mg L^{-1}) and for experiments involving actual industrial effluent. Other parameters were kept constant at room temperature, pH 6.2, contact time 60 min for JOCN and 90 min for JOCB, and adsorbent dose of 2 g L^{-1} for JOCN and JOCB. The adsorption of nickel was low at 50 rpm, and it was observed that adsorption increased with an increase in agitation speed. The best value of stirring was found to be 250 rpm, as there was no remarkable change in the adsorption between 250 rpm and 300 rpm (Fig. 5). The results exhibited similar trends as shown by use of sugarcane bagasse by Garg *et al*. 2007.

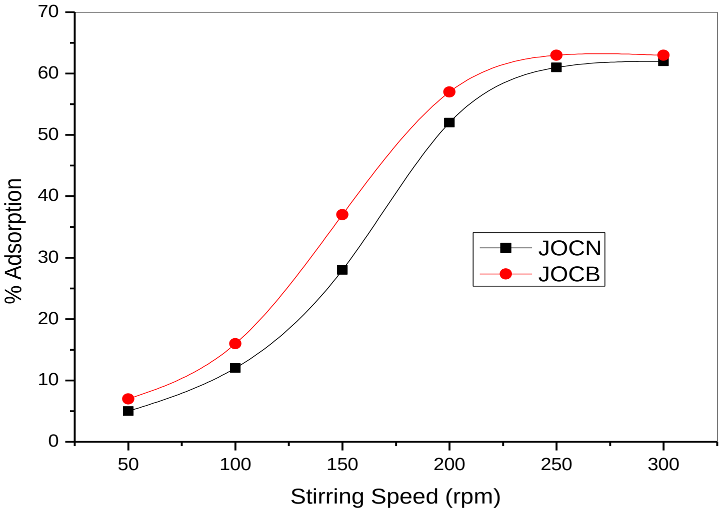

Fig. 5. Effect of stirring speed on nickel removal by JOC in natural and bead form

Effect of Adsorbent Dose

The adsorption of nickel was studied at different adsorbent doses (50 to 2500 mg) for both JOCN and JOCB, keeping Ni (II) concentration (50 mg L^{-1}), stirring speed (250 rpm), and pH (6.2), with the room temperature and contact time (60 min for JOCN and 90 min for JOCB) both held constant (Fig. 6).

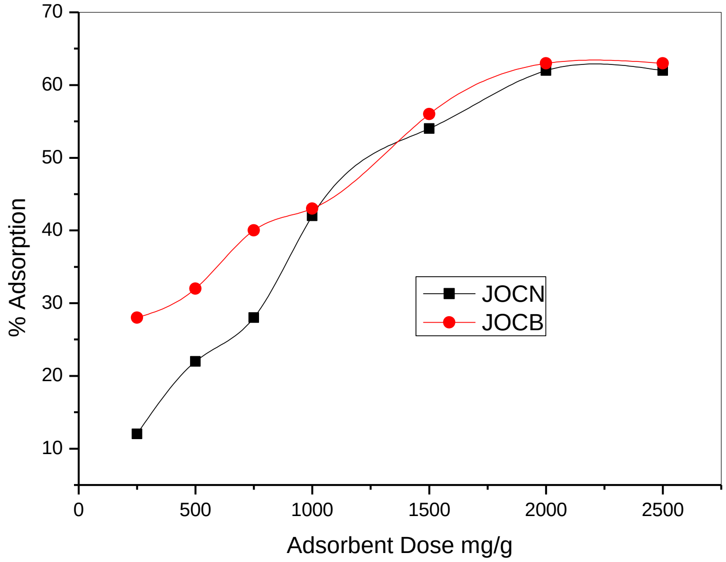

Fig. 6. Effect of adsorbent dose on nickel removal by JOC in natural and bead form

It was observed from the kinetics study that most of the nickel removal by JOCN was achieved in 60 min and by JOCB in 90 min, so these experiments were conducted at 60 min and 90 min of contact time. There was a constant increase in the adsorption of nickel with an increase in the adsorbent dose. The increase in the adsorption with adsorbent dose may be due to the increase in adsorbent surface area and availability of more adsorption sites. It was found that JOCB is more efficient than JOCN at sequestering nickel ions. The plausible explanation may be due to the presence of more available binding sites and least overlapping of sites due to immobilization (Fig. 6, Table 2). Similar trends have been found by and Mahajan and Sud (2011, 2012).

Table 2. Adsorption Capacity of JOC in Natural and Immobilized Form at Different Adsorbent Doses

Adsorbent Dose (g L^{-1})	**JOCB (q_e, mg g^{-1})**	**JOCN (q_e, mg g^{-1})**
2.0	5.6	2.4
5.0	3.2	2.2
7.5	2.67	1.87
10	2.15	2.1
15	1.87	1.8
20	1.57	1.55
25	1.26	1.24

Effect of Contact Time/ Kinetics Studies

Kinetics studies play a major role in finding the equilibrium during a reaction. Studies on both forms of adsorbent (JOCN, JOCB) were conducted by varying the contact time from 5 to 120 min at a fixed Ni concentration (50 mg L^{-1}), stirring speed (250 rpm), room temperature, and pH (6.2). Maximum Ni was sequestered from the solution in 60 and 90 min by JOCN and JOCB, respectively. The Ni removal was 62% with JOCN and 63% with JOCB in 60 and 90 min of contact time, respectively. There was little increase in the adsorption after 120 min of contact time (Fig. 7). The results shown are in agreement with the trend shown by Lie *et al*. (2012).

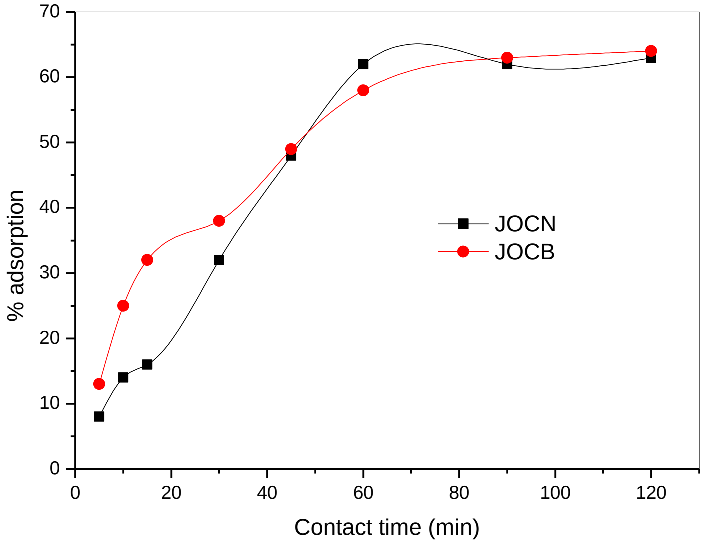

Fig. 7. Effect of contact time on nickel removal by JOC in natural and bead form

Effect of Initial Concentration

The initial concentration of the industrial solution is a major parameter. Considering the possible concentration of heavy metals that can be discharged, a wide range of metal ion concentrations was selected from 5 ppm to 500 ppm. The adsorption of nickel with JOCN and JOCB was studied by varying the nickel concentration (5, 10, 25, 50, 75, 100, 250, and 500 mg L^{-1}) and keeping the adsorbent dose (2 g L^{-1} for JOCN and JOCB), stirring speed (250 rpm), pH (6.2), and contact time (60 and 90 min for JOCN and JOCB, respectively) constant. A higher concentration of metal ions was used to study the maximum adsorption capacity of the adsorbent (Karthikeyan *et al.* 2005; Mohanty *et al.* 2006). The experimental results showed that nickel adsorption decreased with an increase in initial nickel concentration. However, the actual amount of nickel adsorbed per unit mass of the adsorbent increased with an increase in the nickel concentration in the test solution (Table 3).

Table 3. Adsorption Capacity of JOC in Natural and Immobilized Form at Different Initial Nickel Concentrations

Ni (II) concentration (mg L$^{-1)}$	JOCN (q$_e$, mg g^{-1})	JOCB (q$_e$, mg g^{-1})
05	0.25	0.25
10	0.5	0.5
25	0.9	0.95
50	1.55	1.57
100	2.2	2.3
250	2.88	3.0
500	4.5	3.75

Adsorption Isotherms

The experimental results obtained for the adsorption of nickel on jatropha oil cake at a constant room temperature (25±1 °C) under predefined conditions of pH, adsorbent dose, and stirring speed obeyed the Freundlich adsorption isotherm. The Freundlich adsorption isotherm represents the relationship between the amount of metal adsorbed per unit mass of the adsorbent (x/m) and the concentration of the metal ion in solution at equilibrium (C_e) (Mahajan and Sud 2011)

$$\log \frac{x}{m} = \log K_f + \frac{1}{n} \log C_e \tag{2}$$

where K_f (L g^{-1}) is an indicator of adsorption capacity and n (dimensionless) indicates the effect of the concentration on the adsorption capacity and represents the adsorption intensity (dimensionless). The plot of log (*x*/m) versus log (C_e) for various initial concentrations was linear, indicating the applicability of the classical adsorption isotherm to the jatropha oil cake natural-Ni (II) and jatropha oil cake beads-Ni (II) systems. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption on to the surface and no transmigration of adsorbate in the plane of the surface. The Langmuir isotherm is represented by the following equation,

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \tag{3}$$

where C_e is the equilibrium concentration (mg L^{-1}), q_e is the amount adsorbed at equilibrium time (mg g^{-1}), Q_o is the maximum quantity of metal ions per unit weight of biomass to form a complete monolayer on the surface (mg g^{-1}), and *b* is a constant related to the affinity of binding sites with the metal ions (L mg^{-1}) (Goel *et al.* 2005; Bansal *et al*. 2009). The plots of C_e/(x/m) versus C_e are linear, which shows that the adsorption of Ni (II) followed the Langmuir isotherm model. The correlation coefficient (R^2) values were very high for all the adsorbents, which indicates that the data fit reasonably well to the Langmuir isotherm in the present adsorption studies. The value of the slope was found to be less than unity, implying that significant adsorption took place at a low metal ion concentration (Fig. 8 (a,b) and Fig. 9 (a,b) and Table 4).

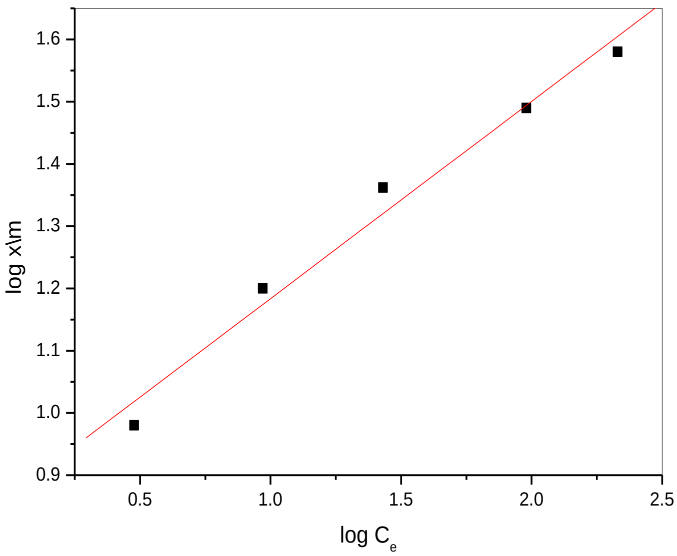

Fig. 8 (a). Freundlich isotherm model for JOC in natural form

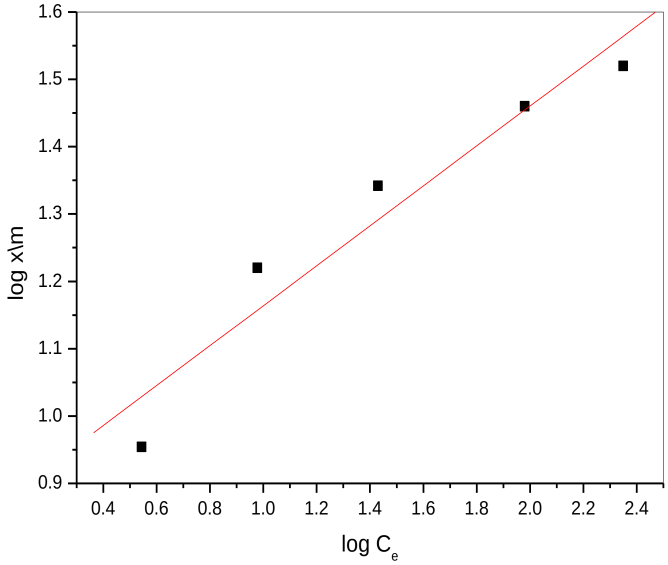

Fig. 8 (b). Freundlich isotherm model for JOC in immobilized form

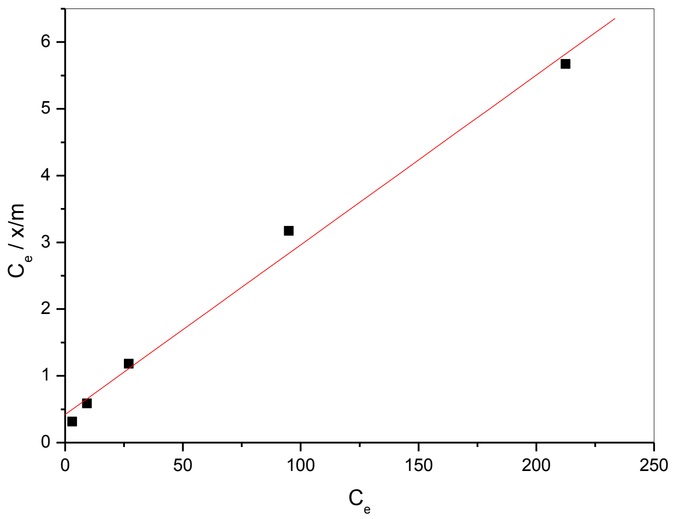

Fig. 9 (a). Langmuir isotherm model for JOC in natural form

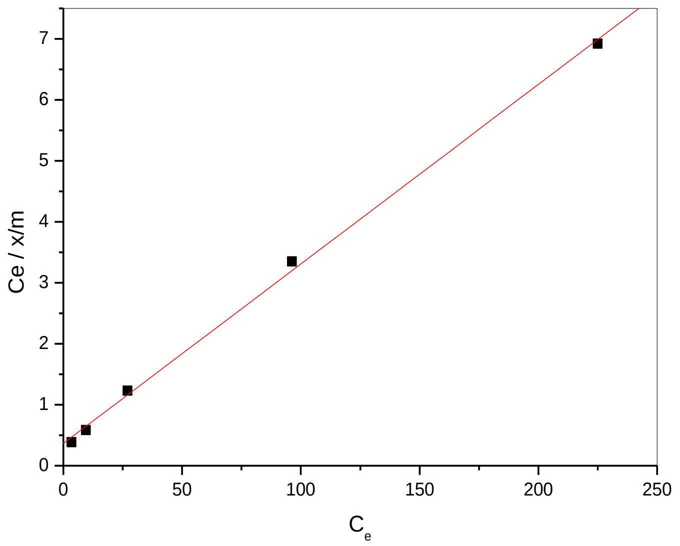

Fig. 9 (b). Langmuir isotherm model for JOC in immobilized form

Desorption Efficiency and Reusability

The regeneration of the biosorbent is one of the key factors in assessing its potential for commercial applications. Two different desorption agents (1 M HCl and 1 M HNO_3) were used to desorb the Ni (II) from the biosorbent. The desorption efficiency of Ni (II) was found to be 98% and 65% using 1 M HCl and 1 M HNO_3, respectively. Therefore, the 1 M HCl solution was selected as the desorption agent. The reusability of the biosorbent was also tested in 10 consecutive sorption-desorption cycles. It has been found that the biosorbent slowly becomes exhausted after repeated reuse. Initially the sorption of metal ion was high, as shown in the graph; and after every acid wash, the next sorption capacity was found to be reduced until the biosorbent was finally exhausted completely. It has also been observed that initially after one-two washes, the sorption capacity per unit mass was found to be high, indicating that the mild acid had caused certain surface modifications leading to the better sorption capacity; however the changes later had a negative impact, resulting in poor sorption ability for metal ions. Regeneration efficiency was found to be high in the 1st cycle. The efficiency gradually decreased in successive cycles; in the 2nd cycle it was 86 percent followed by 79, 64, 58, 52, 47, 39, 31, and 24 percent, respectively. The results showed that the biosorbent has the potential to be used repeatedly in the Ni (II) sequestering process (Fig. 10).

Table 4. Freundlich and Langmuir Models' Regression Constants for Different Adsorbents

Adsorbent	**Freundlich Isotherm**			**Langmuir Isotherm**		
	K_f (1 g^{-1})	N	R^2	Q_0 (mg g^{-1})	B (1 mg^{-1})	R^2
JOCN	0.86	3.15	0.9801	0.62	0.031	0.9911
JOCB	0.86	3.37	0.9305	0.63	0.0315	0.9911

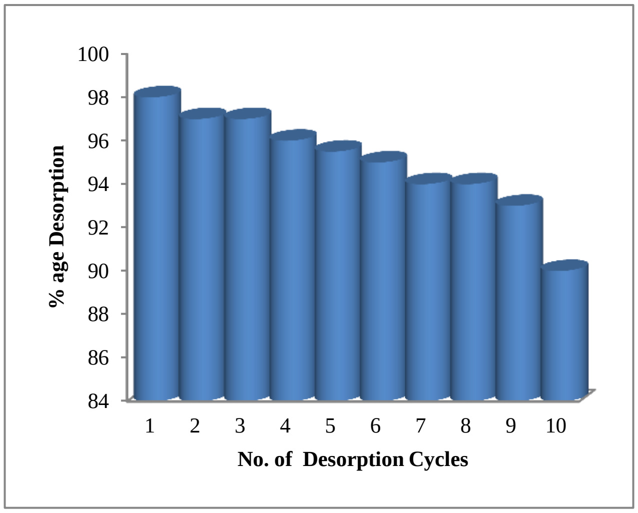

Fig. 10. Desorption cycles of biosorbent during recycling

CONCLUSIONS

1. The findings of the study show the capability of jatropha oil cake (JOC) to be used as a potential biosorbent in its natural and also immobilized form. Potential removal efficiency and stability of the beads explores the utilization of JOC at the commercial level in small scale continuous flow systems in the form of beads.
2. The adsorption of nickel is heavily dependent on the amount of JOC, contact time, and pH of the metal ion solution. Best removal efficiency of Ni is at pH 6.2 in both forms, although the actual amount of biomass in the bead form is very low compared to the natural form, because the beads are swollen from the weight of deionized water and the binding agent.

3. The experimental data were well fit to the Langmuir equation, with good correlation coefficients. Using these models, the adsorption capacity of JOC in both forms was also calculated.
4. Studies on real effluent from the electroplating process also revealed the potential capability of the biosorbent for practical utilization in the real and complex matrix, making it of great potential for commercial use.

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