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ORIGINAL ARTICLE

# Removal of divalent nickel from aqueous solutions using *Carissa carandas* and *Syzygium aromaticum*: isothermal studies and kinetic modelling

**Sanjay K. Sharma[1] · Suresh Mahiya[1] · Giusy Lofrano[2]**

**Abstract** Biosorptive removal of divalent nickel from aqueous solution using *Carissa Carandas* and *Syzygium aromaticum* was investigated in batch mode and the observations were correlated with the pH variation, agitation time, dose of the adsorbent and initial metal ion concentration in the solution. In the course of this study *Sorption efficiency of C. carandas leaf powder found higher than that of S. aromaticum* under identical experimental conditions. The maximum adsorption capacities estimated for Ni(II) through Freundlich isotherm model were 3.76 and 2.96 mg/g for *C. carandas* and *S. aromaticum*, respectively. In kinetic studies the correlation coefficient ($R^2 = 0.99$) for the pseudo-second order kinetics modal was higher than that of pseudo-first order kinetics model and the calculated value of $q_e$ for the pseudo-second order kinetic model resulted very close to the experimental value, which indicates that it fits well with the equilibrium data for Ni(II) sorption from aqueous solutions on biosorbents.

**Keywords** Green Chemistry · Divalent nickel · Adsorption · Biosorption · *Carissa carandas* · *Syzygium aromaticum* · Langmuir isotherm · Freundlich isotherm · Kinetics

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## Introduction

Heavy metal contamination of water and waste water is a widespread phenomenon mainly related to industrial activities (Volesky 2001; Saleem et al. 2015). Many plating and battery industrial, Mining, smelting activities, disposal of municipal sewage and industrial wastewater contain heavy metals such as Cr, Cu, Cd, Pb, Cr, Ni, Hg and Zn (Gautam et al. 2014; Denkhaus and Salnikow 2002). These heavy metals are very harmful when discharged into natural water resources and poses serious health hazard (Libralato et al. 2009a). Removal of heavy metals in water is a problem of Global concern and researchers all over the world are making tireless efforts to address this big issue with the best of their abilities and capabilities.

Among these heavy metals, Ni represents as hazardous pollutant of environmental concern, having been classified extremely toxic, embryo toxic and teratogen (Libralato et al. 2009b, 2010a, b). Nickel is the most toxic element, its higher concentration causes poisoning effects like cancer, reduction in cell growth, headache, dizziness, tightness of the chest, nausea, dry cough, chest pain, vomiting, shortness of breath, cyanosis, extreme weakness and rapid respiration (Akhtar et al. 2004). According to the World Health Organization (WHO 2006) the acceptable limit of Nickel is 0.01 and 2.0 mg/L in drinking water and industrial discharge, respectively (World Health Organization 2006).

In the last one and half decade the author (SKS) and his co-workers have also contributed significant volume of work in the field of water pollution, and applications of Green Chemistry principles in its treatment and remediation (Sharma 2003; Kulshrestha et al. 2004; Kaushik et al. 2007; Sharma et al. 2008, 2010, 2012; Yadav et al. 2008, 2010, 2011; Chandrawat et al. 2009a, b; Mudhoo et al.

2009; Sanghi et al. 2011; Rani et al. 2011; Ozha and Sharma 2011; Mudhoo and Sharma 2011; Gautam et al. 2012).

There are many promising techniques in practice to remove heavy metals from water and have already been reported including; precipitation (Esalah et al. 2000), flotation (Zouboulis et al. 1997), biosorption (Mahiya et al. 2014; Ho et al. 2001), membrane separation (Canet et al. 2002), adsorption on minerals (Buerge-Weirich et al. 2002; Ahmed et al. 2002; Chamila et al. 2015), Zeolites (Pankaj et al. 2015) and activated carbon (Khan et al. 2015; Ravindran et al. 1999). Many researchers also use Bacteria, fungi and algae for removal of heavy metals (Ankur and Chandrajit 2015; Hossein et al. 2015).

Green Chemistry plays a very important and vital role in removal of metal ions from water. There are some commonly applied green techniques including phytoremediation, bioremediation, use of functionalized magnetic nanoparticles, photocatalytic processes and biosorption using industrial and agricultural waste as a biosorbent have been developed in recent years. Adsorption, a physico-chemical process where the adsorbate accumulates at the interface of adsorbent, has become a useful green technique and attracts eyeballs worldwide (Grassi et al. 2012). Biosorption have many certain advantages including low cost and high efficiency, minimization of chemical and biological sludge, and possibility of metal recovery and most important regeneration of biosorbent.

Several investigations have been carried out to identify suitable and relatively cheap biosorbents that are capable of removing significant quantities of nickel(II) ions. Successful metal biosorption has been reported by a variety of biological materials including *Trachyspermum copticum* (Ajwain) (Rifaqat and Shaista 2015), Modified Chitosan (Ma et al. 2014), *Farfantepenaeus aztecus* (shrimp) biomass (Alejandro and Eliseo 2014), rice bran (Muhammad et al. 2015), *Nannorrhops ritchiana* (Mazri Palm) (Sefath et al. 2014), *Lycopersicum esculentum* (Tomato) (Yuvaraja et al. 2015).

Earlier, we have carried out biosorptive removal of divalent copper from aqueous solution using *Carissa carandas* and *Syzygium aromaticum* (Mahiya et al. 2014). In which, adsorption of Cu(II) onto *S. aromaticum* was best described by the Langmuir isotherm modal and the maximum adsorption capacities estimated for Cu(II) were 54.2 and 76.61 mg/g for *C. carandas* and *S. aromaticum*, respectively. Results of that study encouraged us to try the same adsorbents for removal of divalent nickel this time.

The purpose of the present research was to evaluate the efficiency of *C. carandas* and *S. aromaticum* as biosorbents for removal of divalent nickel from water. Maximum adsorption capacity of biosorbents, the adsorption intensity of the adsorbate on biosorbents surface and biosorption potentials of biosorbents was estimated by Langmuir and Freundlich isotherms, respectively. Batch adsorption experiments for removal of Ni(II) were carried out at ambient temperature (30 °C) as a function of solution pH (2–12), biosorbent dosage (2–10 g/100 mL), contact time (with a time interval of every 60 min) up to 300 min and initial metal ion concentration. Then, equilibrium isotherms and kinetic data parameters were evaluated. The sorption efficiency of adsorbents was explained with help of SEM image visualization and FTIR analysis.

## Materials and methods

### Chemicals

Analytical-grade chemicals were used in this work without further purification. To avoid any interference of other ions, all solutions were prepared using double distilled water. Ni(II) was prepared by dissolving 4.783 g of $NiSO_4 \cdot 5H_2O$ in 1000 mL volumetric flask and make up to the mark with double distilled water. All the required working solutions were prepared as per the reported method in earlier study of the present researchers (Mahiya et al. 2014). Dilute solutions of 1 M HCl and 1 M NaOH were used to adjust pH of metal ion solutions using a pH meter.

### Adsorbent

The leaves of *C. carandas* were collected from local field of Pushkar (India) and the buds of *S. aromaticum* were collected from local market of Jaipur (India). The leaves of *C. carandas* and the buds of *S. aromaticum* were extensively washed with running tap water for remove dirt and other particulate matter then washed by double distilled water and dried in sunlight, then at 60 °C for 24 h in hot air oven. Finally, the dried leaves of *C. carandas* and *S. aromaticum* were grinded in clean electric mixer and stored in a dry and clean plastic bag.

### Adsorption experiment

Batch adsorption studies were performed at room temperature. The adsorption equilibrium experiments for Ni(II) solution were carried out by taking 100 mL of nickel solution in 250 mL conical flask and then the flasks were agitated at 200 rpm in an incubator. At the end of predefined time intervals, the flasks were withdrawn from shaker, filtered by What man filter paper No. 41 and the supernatant solutions were analysed for Ni(II) ion concentration using an Atomic Absorption Spectrometer (Thermo scientific Solar S-series AA Spectrometer).

# Results and discussion

## Characterization of biosorbent by gas chromatography–mass spectroscopy

Gas Chromatography–Mass Spectroscopy (GC–MS) is one of the best techniques to identify the constituents of volatile matter, long chain, branched chain hydrocarbons, alcohols acids and esters etc. The GC–MS analysis of *C. carandas* leaves and *S. aromaticum* revealed the presence of 43 and 40 active compounds, respectively. The identification of the phytochemical compounds was confirmed based on the peak area, retention time and molecular formula.

Gas chromatography–mass spectroscopy analysis of *S. aromaticum* The *S. aromaticum* buds were analysed by GC–MS and eugenol identified as a major constituent. In the clove bud essential oil eugenol acetate is the second major component. The Results Revealed that, Phenol, 2-Methoxy-4-(2-Propenyl)- (Eugenol) (46.01 %), Phenol, 2-Methoxy-4-(2-Propenyl)-, Acetate (Eugenol Acetate) (23.42 %), Bicyclo[7.2.0]Undec-4-Ene, 4,11,11-Tri-methyl-8-Methylene- (12.43 %), 1,4,8-Cycloundecatriene, 2,6,6,9-Tetramethyl (3.00 %), 6-Octadecenoic Acid, (Z)-(2.18), (−)-5-Oxatricyclo[8.2.0.0(4,6)]Dodecane,12-Tri-methyl-9-Methylene- (2.00), Benzoic Acid, 2-Hydroxy-, Methyl Ester (0.11 %), 4-Allylphenol (0.88 %), Benzene,



**Fig. 1** GC–MS spectra of *C. carandas*
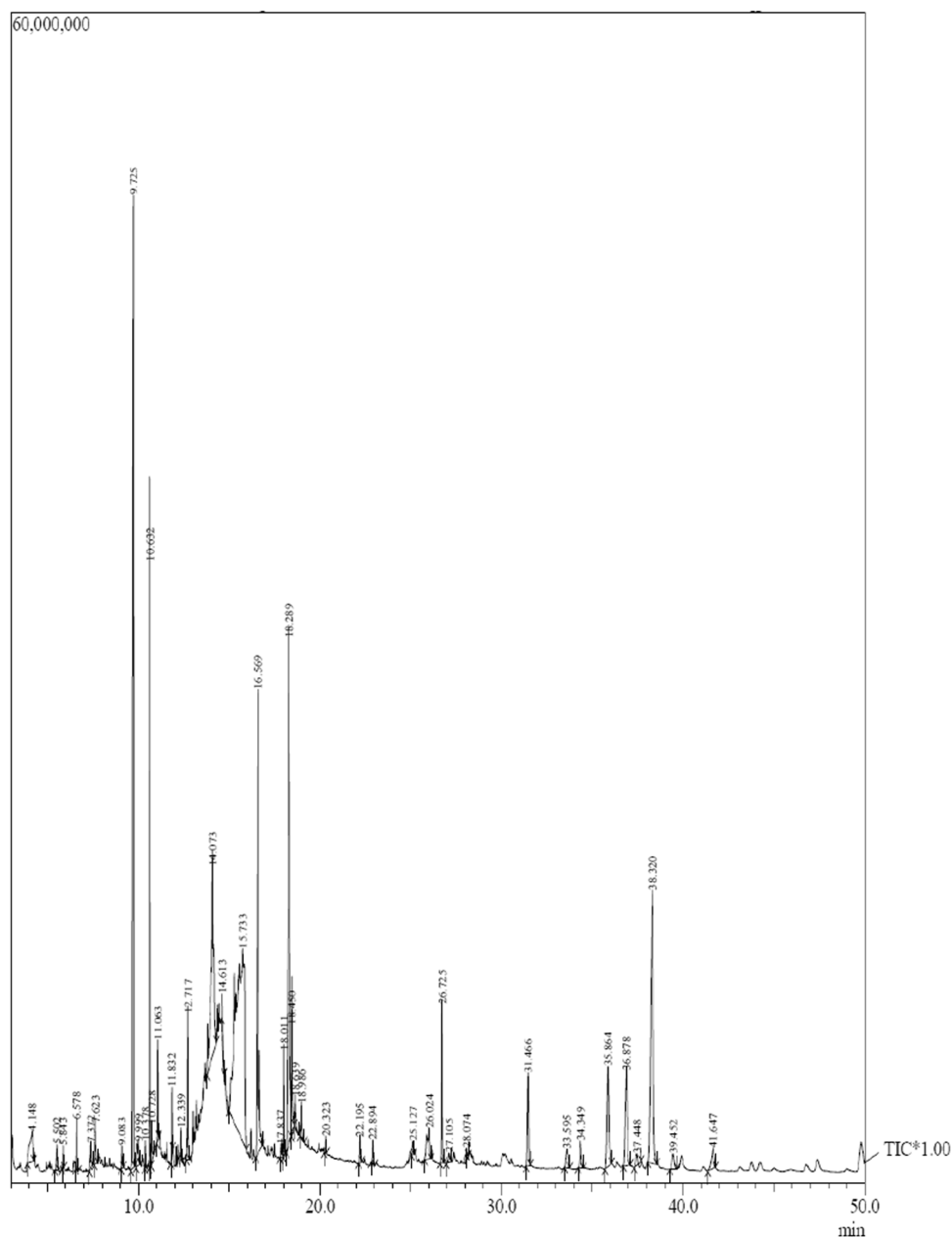
1-Methoxy-4-(1-Propenyl)- (0.13 %), 2-Acetyl-2-Methyl-phenyl Acetate (0.22 %), 1,2,3-Benzenetriol (1.58 %), Naphthalene, 1,2,3,4,4a,5,6,8a-Octahydro-7-Methyl-4-Methylene-1-(1-Methylethyl)- (0.13 %), 1,3,6,10-Dode-catetraene, 3,7,11-Trimethyl- (0.53 %), 1-(4-Isopropoxy-3-Methoxyphenyl)Acetone (0.09 %), Dodecanoic Acid (0.12 %), Epi-Alpha-Patschulene (0.19 %), Phenol, 2-Methoxy-4-(2-Propenyl)-, Acetate (0.11 %), 12-Oxabi-cyclo[9.1.0]Dodeca-3,7-Diene, 1,5,5,8-Tetramethyl- (0.16 %), 1-Naphthalenol, 1,2,3,4,4a,7,8,8a-Octahydro-1,6-Dimethyl-4-(1-Methylethyl)- (0.31 %), 4-(2,6,6-Tri-methyl-Cyclohex-1-Enyl)-Butyric Acid (0.13 %), 4-((1e)-3-Hydroxy-1-Propenyl)-2-Methoxyphenol (0.36 %), 4-(2,6,6-Trimethyl-1-Cyclohexen-1-Yl)-2-Buta (0.16 %), 10-Methoxy-Nb-.Alpha.-Methylcorynantheol (0.10 %),

4,4,8-Trimethyl-Tricyclo[6.3.1.0 1,5]Dodecane- (0.18 %), L-(+)-Ascorbic Acid 2,6-Dihexadecanoate (1.61 %), 1,2-Benzenedicarboxylic Acid, Dibutyl Ester (0.25 %), Octadecanoic Acid (0.12 %), Cyclobutane, 3-Hexyl-1,1,2-Trimethyl-, Cis- (0.11 %), 1,13-Tetradecadien-3-One (0.07 %), Octadecanoic Acid, Ethyl Ester (0.07 %), 3-(4-P-Tolyl-Thiazol-2-Yl)-4,5,6,7-Tetrahydro-Benzo[B]Thio-phen-2-Ylamine (0.29 %), Capsaicin (0.10 %), Dihydro-capsaicin (0.06 %), E,Z-1,3,12-Nonadecatriene (0.20 %), Phenol, 2-Methoxy-4-(1-Propenyl)- (0.20 %), Squalene (0.15 %), Vitamin E (0.28 %), Stigmast-5-En-3-Ol, (3.Beta.)- (1.52 %), Tetracyclo[5.4.3.0(7,11)]Tetradeca-2,5,10-Trione, 1,4,6,14-Tetramethyl-4-Vinyl- (0.17 %), Benzyl Myristate (0.27 %) and other compounds are available in it.



Fig. 2 GC–MS spectra of S. aromaticum
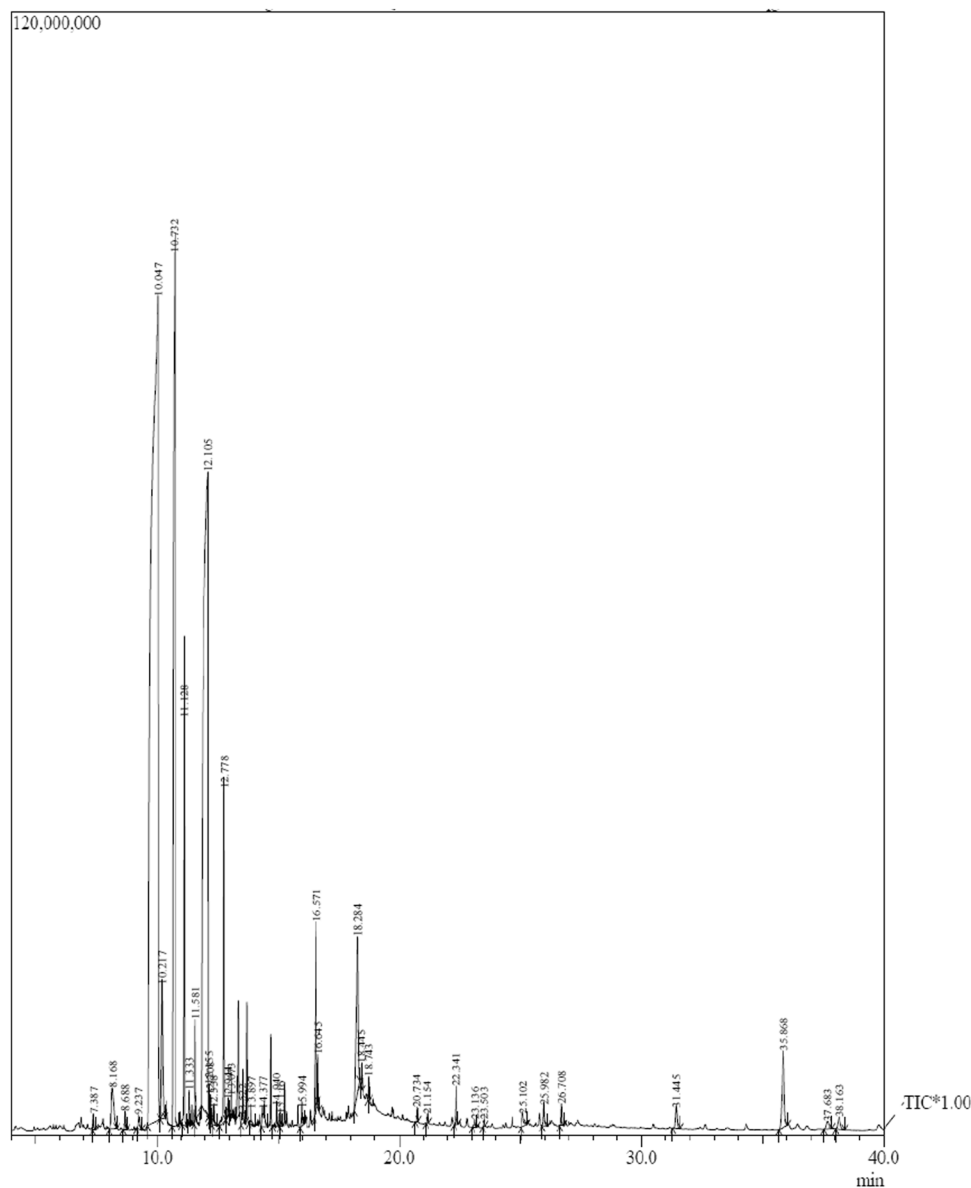
Gas chromatography–mass spectroscopy analysis of *C. carandas* It shows the presence of Mome Inositol (23.69 %), Phenol, 2-Methoxy-4-(2-Propenyl)- (12.52 %), Cis-9-Hexadecenal (10.97 %), 1,2,3-PROPANETRIOL (1.31 %), 1,3,5-Triazine-2,4,6-Triamine (0.32 %), Oxetane, 2-Propyl- (0.20&), 4 h-1,3,2-Dioxazine-2-Acetic Acid, Dihydro-.Alpha. (0.43 %), 4-(1-Hydroxy-Ethyl).Gamma.Butanolactone (0.37 %), 2,3-Dihydro-Benzofuran (0.48 %), 2-Methoxy-4-Vinylphenol (0.21 %), Tricyclo[4.4.0.0(2,7)]Dec-3-Ene, 1,3-Dimethyl-8-(1-Methylethyl)-, St (0.67 %), 1h-Cycloprop[E]Azulene, 1a,2,3,4,4a,5,6,7b-Octahydro-1,1,4,7-Tetramethyl-, [1ar-(1a.Alpha.,4.Alpha.,4a.Be (0.17 %), Bicyclo[7.2.0]Undec-4-Ene, 4,11,11-Trimethyl-8-Methylene-, [1r-(1r*,4e,9s*)]- (4.68 %), 3,5-Dimethylanisole (0.42 %), 1,4,7,-Cycloundecatriene, 1,5,9,9-Tetramethyl-, Z,Z,Z- (0.67 %), Phenol, 2-Methoxy-4-(2-Propenyl)-, Acetate (0.41 %), 4-Methyl-2,5-Dimethoxybenzaldehyde (0.18 %), 5-Oxatricyclo[8.2.0.0(4,6)]Dodecane,12-Trimethyl-9-Methylene- (1.18 %), L-(+)-Ascorbic Acid 2,6-Dihexadecanoate (7.15 %), 9,12-Octadecadienoic Acid (Z,Z)-, Methyl Ester (0.29 %), 2-Hexadecen-1-Ol, 3,7,11,15-Tetramethyl-, [R-[R*,R*-(E)]]-(0.78 %), Octadecanoic Acid (1.46 %), 9,12-Octadecadienoic Acid (0.43 %), 9,12-Octadecadienoic Acid (Z,Z)- (0.42 %), 4,8,12,16-Tetramethylheptadecan-4-Olide (0.12 %), Hexadecanoic Acid, 2-Hydroxy-1-(Hydroxymethyl)Ethyl Ester (0.35 %), 10-Methyldodec-2-En-4-Olide (0.26 %), Oleoyl Chloride (0.20 %), 10-Methyldodec-2-En-4-Olide (1.19 %), Squalene (1.56 %), 1-Pyrrolidinebutanoic Acid, 2-[(1,1-Dimethylethoxy)Carbonyl]-.Alpha.-Nitro-, 2,6-Bis(1,1-Dimethylethyl)-4-Methoxyphenyl Ester, [S-(R*,R*)]- (0.20 %), Vitamin E (1.59 %), ERGOST-5-EN-3-OL, (3.BETA.,24R)- (0.51 %), Stigmasterol (0.64 %), STIGMAST-5-EN-3-OL, (3.BETA.)-(2.55 %),.Beta.-Amyrin (2.77 %), 1H-3a,7-Methanoazulen-6-Ol, Octahydro-3,6,8,8-Tetramethyl-, Acetate, [3R-(3.Alpha.,3a.Beta.,6.Alpha.,7.Beta.,8a.Alpha.)]- (0.17 %), Lupeol (9.92 %),.Alpha.-Tocopherol-.Beta.-D-Mannoside (0.48 %), Lup-20(29)-En-3-Yl Acetate (0.81 %).

The whole FTIR discussion about *C. carandas* and *S. aromaticum* reported in previous study (Figs. 1 and 2) seems well according to the reported absorption data of various expected groups present in *C. carandas* and *S. aromaticum* (Silverstein et al. 1981) and supported by the given data of GC–MS analysis. However, the exact functional groups, their native at adsorption mechanism and site of bonding between various functional groups present and Ni(II) are yet to be explored for better understanding of whole absorption process which will be surely an interesting objective in our future experiments and publications.

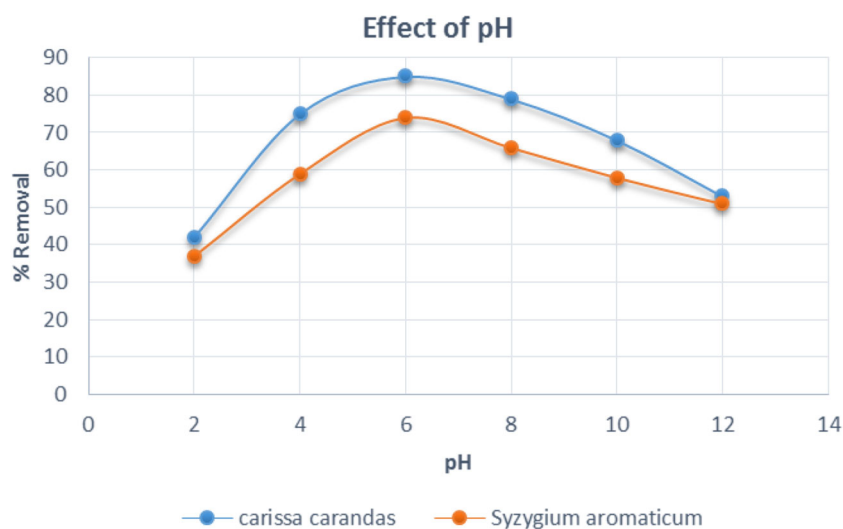## Effect of pH on biosorption

The effect of pH on the removal of divalent nickel was studied and it was observed that the metal sorption is

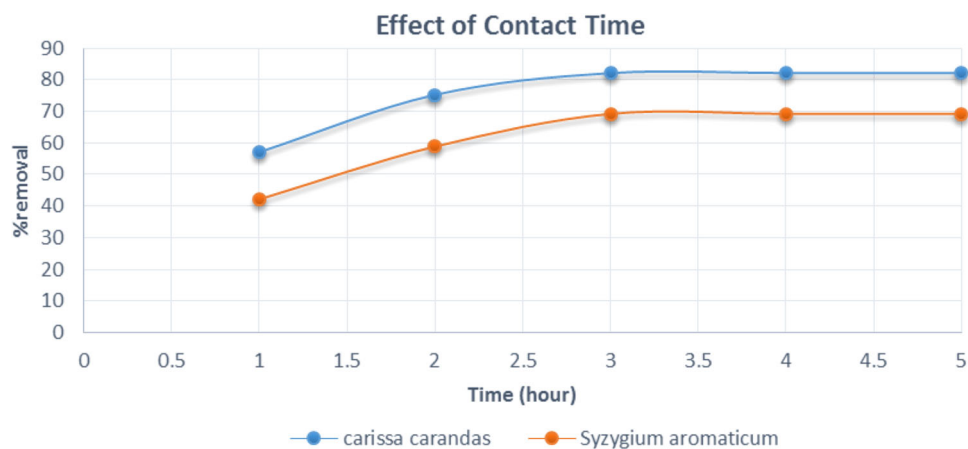**Table 1** Effect of solution pH on biosorption of Ni(II) by *C. carandas* and *S. aromaticum*

| S. No. | pH | Removal of Ni(II) (%) | |
|---|---|---|---|
| | | *Carissa carandas* | *Syzygium aromaticum* |
| 1 | 2 | 42 | 37 |
| 2 | 4 | 75 | 59 |
| 3 | 6 | 85 | 74 |
| 4 | 8 | 79 | 66 |
| 5 | 10 | 68 | 58 |
| 6 | 12 | 53 | 51 |

$C_0 = 100$ ppm, dosage = 2 g/100 mL, contact time = 180 min, $T = 300$ K

**Fig. 3** Effect of solution pH on biosorption of Ni(II) by *C. carandas* and *S. aromaticum* ($C_0 = 100$ ppm, dosage = 2 g/100 mL, contact time = 180 min, $T = 300$ K)

**Fig. 4** Effect of contact time on biosorption for Ni(II) by *C. carandas* and *S. aromaticum* ($C_0 = 100$ ppm, dosage = 2 g/100 mL, pH 6, $T = 300$ K)
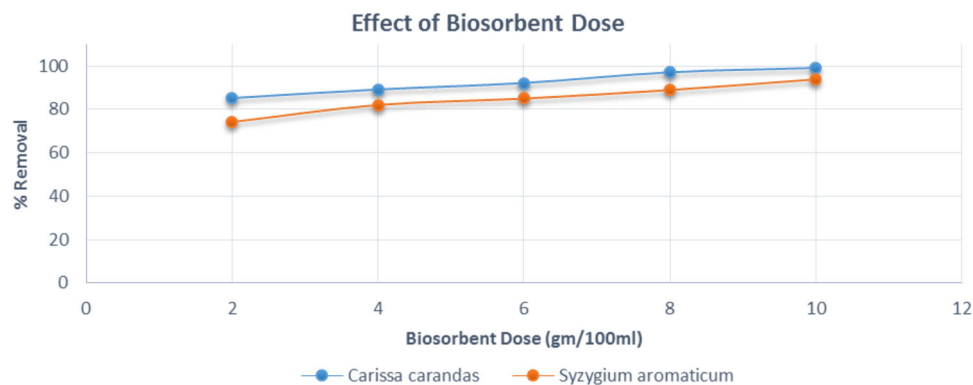


**Table 2** Effect of contact time on biosorption for Ni(II) by *C. carandas* and *S. aromaticum*

| S. No. | Contact time (min) | Removal of Ni(II) (%) | |
| --- | --- | --- | --- |
| | | *Carissa carandas* | *Syzygium aromaticum* |
| 1 | 60 | 56.91 | 42.11 |
| 2 | 120 | 75.23 | 58.84 |
| 3 | 180 | 82.22 | 69.23 |
| 4 | 240 | 82.22 | 69.23 |
| 5 | 300 | 82.22 | 69.23 |

$C_0 = 100$ ppm, dosage = 2 g/100 mL, pH 4, temp = 300 K

critically linked with pH and it was found that the pH of the solution is a very important controlling and contributing factor in the adsorption process. The effect of pH was studied at 100 mg/L Ni(II) concentration, biosorbent dosage of 2 g/100 mL at the pH range 2–12. According to Fig. 3 the percentage of Ni(II) removal increased with the increase in the pH up to the pH 6. After pH 6, further increase in pH value decrease the percentage of Ni(II) removal (Table 1; Fig. 3) possibly due to the formation of soluble hydroxide complexes of Ni(II), which competes with the biosorption of Ni(II) by biomass. Similar results of the effect of pH on the biosorption have also been observed

earlier for Ni(II) biosorption using dried green alga (Aksu and Dönmez 2006), activated sludge (Ajay Kumar et al. 2009), waste tea material (Aikpokpodion et al. 2010) and coconut copra meal (Saleem et al. 2015); which strengthen our point of view.

### Effect of contact time on biosorption

Effect of contact time on biosorption was studied for designing batch biosorption experiments. Contact time between biosorbent and adsorbate play a key role in influencing the biosorption process (Saleem et al. 2015). As shown in Fig. 4 the biosorption efficiency of Ni(II) increased substantially until the contact time reached at 180 min and then it proceeds at slower rate of increases and finally attained saturation. So, the optimum contact time was selected as 180 min for further experiments. The equilibrium time was independent of adsorbent type. The Ni(II) adsorption rate at the initial stage depends on increased availability in the number of active binding sites on the adsorbent surface. At later stage, no significant sorption takes place due to non-availability of sorption sites. Therefore, further experiments were carried out at 180 min as a significant contact time for Ni(II) adsorption (Table 2; Fig. 4).

**Fig. 5** Effect of biosorbent dose on biosorption capacity of Ni(II); ($C_0 = 100$ mg/100 mL, contact time = 180 min, pH 6, $T = 300$ K)

**Table 3** Effect of biosorbent dosage on biosorption capacity of Ni(II)

| S. No. | Biosorbent (g/100 mL) | Removal of Ni(II) (%) | |
|---|---|---|---|
| | | Carissa carandas | Syzygium aromaticum |
| 1 | 2 | 85 | 74 |
| 2 | 4 | 89 | 82 |
| 3 | 6 | 92 | 85 |
| 4 | 8 | 97 | 89 |
| 5 | 10 | 99 | 94 |

$C_0 = 100$ ppm/100 mL, contact time = 180 min, pH 6, $T = 300$ K
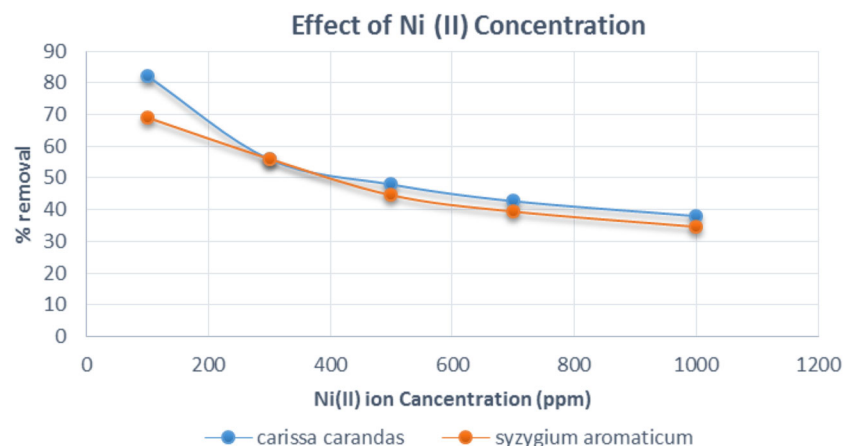
### Effect of biosorbent dose

As shown in Fig. 5 the effect of biomass dosage on the Ni(II) biosorption was studied using different doses ranging from 2 to 10 g/100 mL. An increase in nickel removal from 85 to 99 % for *C. carandas* and from 74 to 94 % for *S. aromaticum* (Table 3; Fig. 5) was observed with increasing biomass concentration (2–10 g/100 mL).

### Effect of initial metal concentration

The effect of initial concentration of Ni(II) metal and its removal using *C. carandas* and *S. aromaticum* biomass is shown in Fig. 6. The biosorbents dose, pH and contact time for the batch experiment were found best recorded at 2 g/100 mL, pH 6 and 180 min, respectively.

By increasing the initial concentration of Ni(II) in a batch study, a saturation point appears which resulted in decreased percentage of Ni(II) removal (Saleem et al. 2015). In batch study using *C. carandas* and *S. aromaticum* biomass percentage removal of Ni(II) decreased from 82.22 to 38.16 % and 69.23 to 34.49 % when the initial concentration of Ni was increased from 100 to 1000 mg/L (Table 4; Fig. 6).

### Effect of temperature

Figure 7 shows the biosorption of Ni(II) for varied temperatures at 180 min of contact time. As shown in Fig. 7 biosorption capacities were found for Ni(II) at 20, 30, 40 and 60 °C as 56.76, 82.22, 69.17 and 61.53 mg/100 mL for *C. carandas* and 52.12, 69.23, 65.91, 54.15 mg/100 mL for *S. aromaticum*, respectively. The biosorption capacities of *C. carandas* and *S. aromaticum* were best recorded at 30 °C. The decrease in biosorption capacity of *C. carandas* and *S. aromaticum* above 30 °C may be attributed to the deactivation of the biosorbent surface or the destruction of some active sites on the biosorbent surface. As a result, the optimum temperature for Ni(II) biosorption was chosen as 30 °C for subsequent experiments (Table 5).

### Isothermal studies

To better understanding of the Ni(II) ion adsorption to the *Carissa carandas* and *S. aromaticum*, we first analysed the adsorption isotherms that give comprehensive information about the nature of interaction. The adsorption isotherm shows that adsorbate ($C_e$) interacts with adsorbent ($q_e$) at a constant temperature and reflects the nature of adsorption reaction (Mondal et al. 2013).

To determine the surface properties of adsorbents and its affinity with nickel, the isotherm data were tried to different isotherm models. In this research, biosorption isotherm study was carried out on two well-known 'two-parameter isotherms', namely Langmuir and Freundlich isotherms. The well-known expression of Langmuir isotherm model (Langmuir 1918) is presented in Eq. 1

$$q_e = Q_0 b C_e / (1 + b C_e), \tag{1}$$

where $C_e$ (mg/L) and $q_e$ (mg/g) are the liquid phase concentration and solid phase concentration of adsorbate at

**Fig. 6** Effect of initial metal concentration on biosorption of Ni(II); (Dosage = 2 g/100 mL, contact time = 180 min, pH 6, $T = 300$ K)

**Table 4** Effect of initial metal concentration on biosorption of Ni(II)

| S. No. | Concentration of metal (mg/100 mL) | Removal of Ni(II) (%) | |
|---|---|---|---|
| | | *Carissa carandas* | *Syzygium aromaticum* |
| 1 | 100 | 82.22 | 69.23 |
| 2 | 300 | 56.07 | 56.12 |
| 3 | 500 | 48.12 | 44.56 |
| 4 | 700 | 42.87 | 39.34 |
| 5 | 1000 | 38.16 | 34.49 |

Adsorbent dosage = 2 g/100 mL, contact time = 180 min, pH 6, $T = 300$ K

**Table 5** Effect of temperature on biosorption of Ni(II)

| S. No. | Temperature (°C) | Removal of Ni(II) (%) | |
|---|---|---|---|
| | | *Carissa carandas* | *Syzygium aromaticum* |
| 1 | 20 | 56.76 | 52.12 |
| 2 | 30 | 82.22 | 69.23 |
| 3 | 40 | 69.17 | 65.91 |
| 4 | 50 | 61.53 | 54.15 |

$C_0 = 100$ ppm, adsorbent dosage = 2 g/100 mL, contact time = 180 min, pH 6

equilibrium, respectively, and $Q_0$ (mg/g) and $b$ (L/mg) are the Langmuir isotherm constants.

Kratochvil and Volesky (1998) suggested that high $Q_0$ and $b$ values indicate to good quality of biosorbents. The constants $b$ is related to monolayer adsorption capacity and energy of adsorption and the high values of constants indicating a high affinity of the adsorbate for the adsorbent.

The Freundlich isotherm model (Freundlich 1907) is as follows (Eq. 2)

$$q_e = K_F C_e^n, \qquad (2)$$

where $K_F$ [mg/g (L/g)$^{1/n}$] is the Freundlich constant related to the bonding energy, $n$ is the Freundlich exponent which depicts the extent of deviation from linearity of the adsorption.

Table 6 lists the calculated Freundlich and Langmuir isotherm constants. Based on regression coefficient ($R^2$) values, the experimental data for adsorption of Ni(II) onto *C. carandas* and *S. aromaticum* powder fit better to Freundlich isotherm model than the Langmuir isotherm model. The adsorption of Ni(II) onto *C. carandas* was best described by the Freundlich isotherm model. The maximum adsorption capacities ($K_L$) estimated from the Freundlich isotherm model for Ni(II) were 3.76 and 2.96 mg/g

for *C. carandas* leaves and *S. aromaticum*, respectively (Figs. 8, 9).

## Adsorption kinetics

Adsorption kinetic studies are important to determine the efficacy of adsorption. The purpose of adsorption kinetic studies is to investigate about the mechanism of biosorption and its potential rate-controlling steps that include mass transport and chemical reaction processes. In batch adsorption system, kinetic models such as pseudo-first order and pseudo-second order have been widely used. The linearized pseudo-first-order kinetic model takes the following form as

$$q_t = q_e - q_e \exp(-K_1 t) \qquad (3)$$

$$\log(q_e - q) = \log q_e - \frac{K_1}{2.303} t, \qquad (4)$$

where $q$ is the amount of Ni(II) (mg/g) at time $t$ (minute), $q_e$ is the amount of nickel adsorbed at equilibrium (mg/g) and $K_1$ is the equilibrium rate constant of pseudo-first order adsorption (min$^{-1}$). The plot of log ($q_e$–$q_t$) versus $t$ gave a straight line for the first order adsorption kinetics.
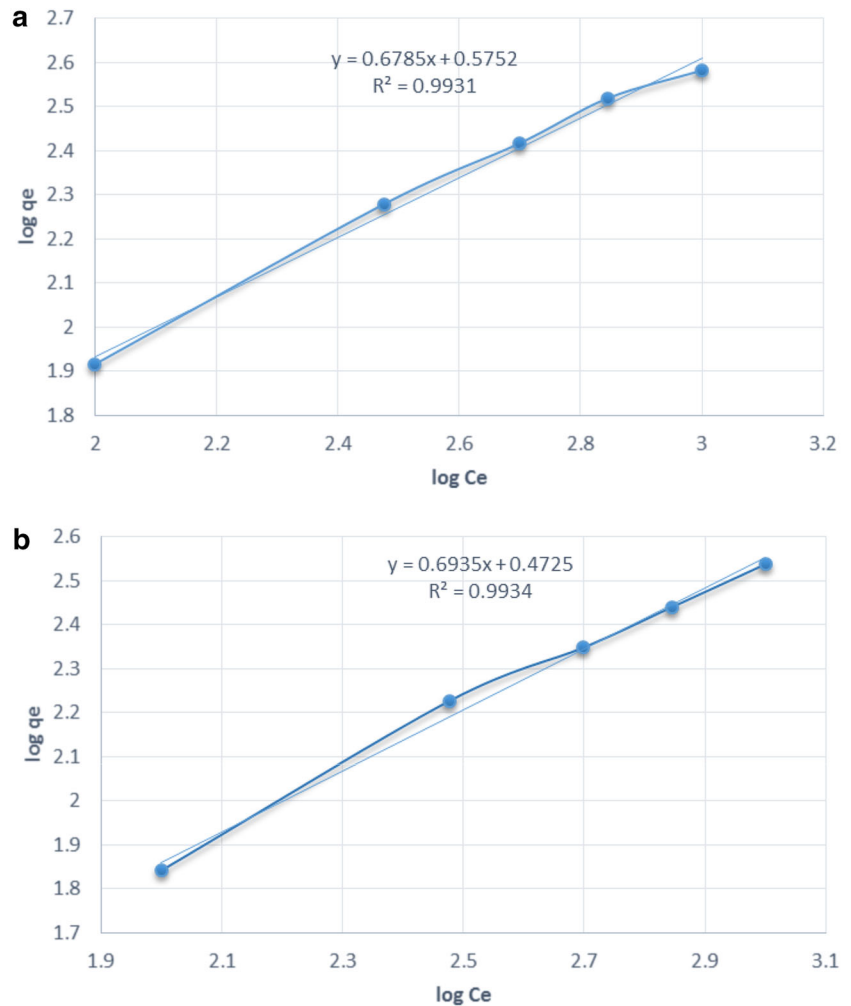
The pseudo-second order kinetic model considered in this study is given as

**Fig. 7** Effect of Temperature on biosorption of Ni(II); ($C_0 = 100$ ppm, dosage = 2 g/100 mL, contact time = 180 min, pH 6)

**Table 6** Langmuir and freundlich isotherm constants for Ni(II) ion biosorption

| Adsorbent | Langmuir isotherm | | | Freundlich isotherm | | |
|---|---|---|---|---|---|---|
| | $q_{max}$ | $K_L$ | $R^2$ | $K_F$ | $N$ | $R^2$ |
| *Carissa carandas* | 60.81 | 0.33 | 0.98 | 3.76 | 1.47 | 0.99 |
| *Syzygium aromaticum* | 57.02 | 0.30 | 0.97 | 2.96 | 1.44 | 0.99 |

**Fig. 8** Freundlich isotherm for **a** *C. carandas* and **b** *S. aromaticum*

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}, \tag{5}$$

where $K_2$ (g mg$^{-1}$ min$^{-1}$) is the second-order reaction rate constant.

The experimental data and the parameters of both models are reported in Table 7. The coefficient of correlation ($R^2 = 0.99$) for the pseudo-second-order kinetic model was higher in comparison with the pseudo-first-order kinetic model and the kinetic data fits well with a pseudo-second order model for Ni(II) ion sorption as compared to a pseudo-first order model.

## SEM images

The SEM images of adsorbents before and after adsorption are given in Figs. 10 and 11, respectively, for *C. carandas* and *S. aromaticum*. A significant difference in the appearance of the adsorbent surfaces could be noticed.

**Fig. 9** Langmuir isotherm for **a** *C. carandas* and **b** *S. aromaticum*
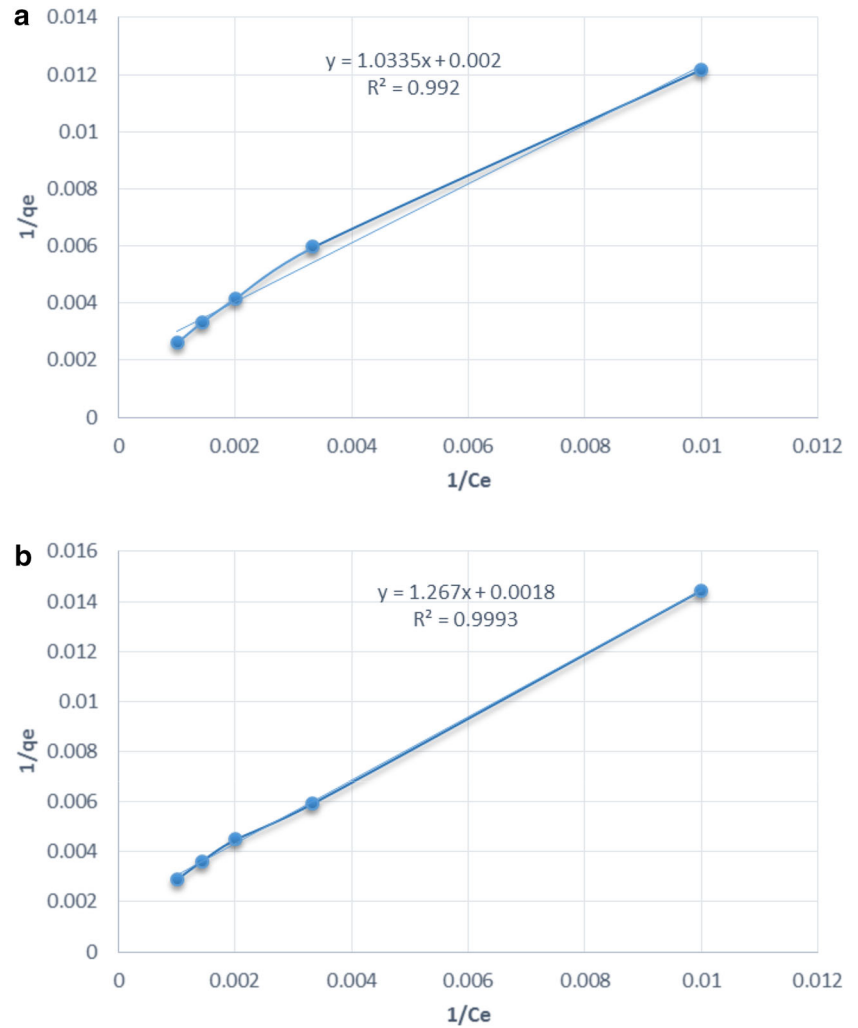


**Table 7** Kinetics studies of biosption of Ni(II) on *C. carandas* and *S. aromaticum*

| Biosorbent | Metal ion concentration (ppm) | $q_e$,exp (mg/g) | Pseudo-first-order kinetic model | | | Pseudo-second-order kinetic model | | |
|---|---|---|---|---|---|---|---|---|
| | | | $q_{e,cal}$ (mg/g) | $K_1$ (min$^{-1}$) | $R^2$ | $q_{e,cal}$ (mg/g) | $K_2$ (g mg$^{-1}$ min$^{-1}$) | $R^2$ |
| *Carissa carandas* | 100 | 4.11 | 36.96 | $4.60 \times 10^{-3}$ | 0.92 | 105.26 | $1.6 \times 10^{-4}$ | 0.99 |
| | 300 | 8.4 | 99.48 | $2.99 \times 10^{-3}$ | 0.95 | 185.18 | $1.9 \times 10^{-4}$ | 0.99 |
| | 500 | 12.03 | 177.68 | $1.84 \times 10^{-3}$ | 0.96 | 256.41 | $2.5 \times 10^{-4}$ | 0.99 |
| | 700 | 15.00 | 249.63 | $9.21 \times 10^{-4}$ | 0.96 | 312.5 | $3.9 \times 10^{-4}$ | 0.99 |
| | 1000 | 19.08 | 307.96 | $1.15 \times 10^{-3}$ | 0.96 | 400 | $2.6 \times 10^{-4}$ | 0.99 |
| *Syzygium aromaticum* | 100 | 3.46 | 36.96 | $3.68 \times 10^{-3}$ | 0.91 | 83.33 | $3.0 \times 10^{-4}$ | 0.99 |
| | 300 | 8.41 | 120.30 | $1.84 \times 10^{-3}$ | 0.95 | 181.81 | $3.1 \times 10^{-4}$ | 0.99 |
| | 500 | 11.14 | 169.01 | $1.38 \times 10^{-3}$ | 0.95 | 232.58 | $3.3 \times 10^{-4}$ | 0.99 |
| | 700 | 13.76 | 228.14 | $1.15 \times 10^{-3}$ | 0.94 | 285.71 | $3.9 \times 10^{-4}$ | 0.99 |
| | 1000 | 17.24 | 281.46 | $1.15 \times 10^{-3}$ | 0.96 | 357.14 | $3.0 \times 10^{-4}$ | 0.99 |

**Fig. 10** SEM image of *C. carandas* **a** *before* Adsorption; **b** *after* Adsorption
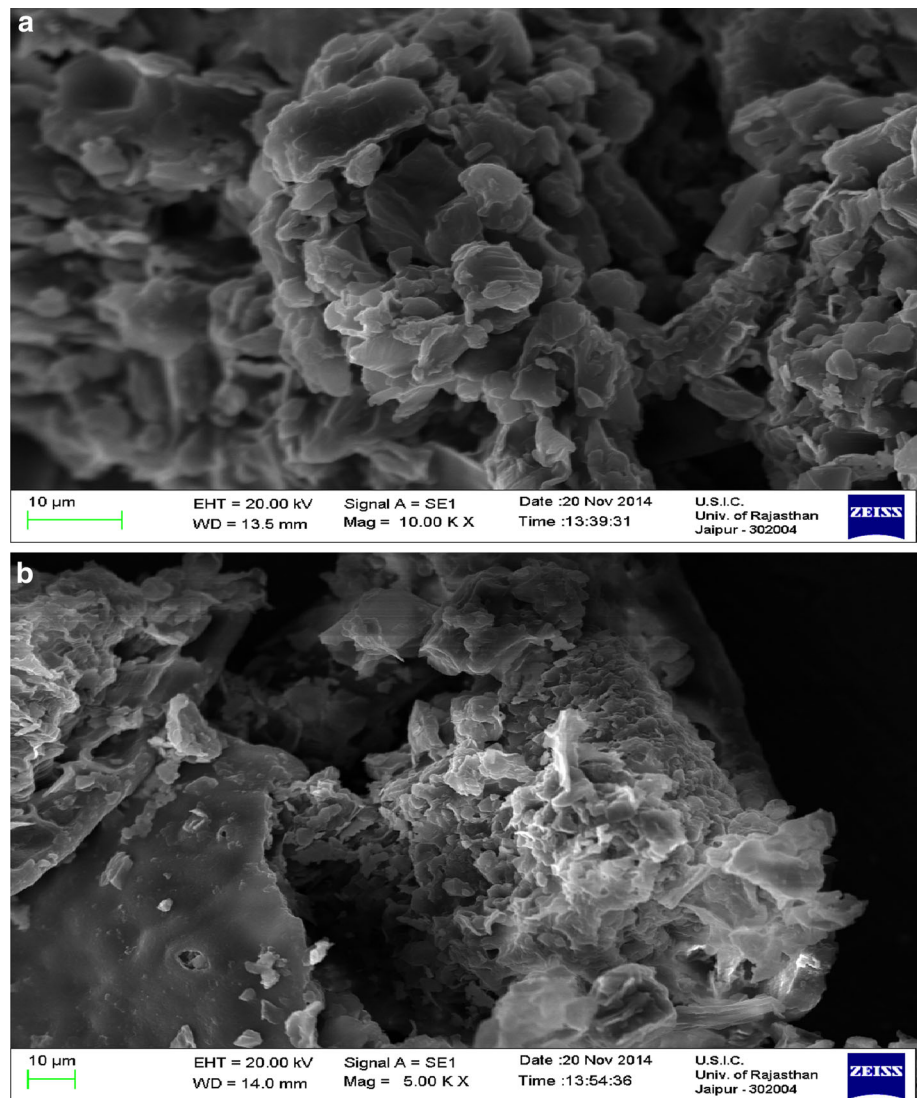


Images clearly highlight the action of adsorption on the surfaces of both the adsorbents and strengthen the view point of the researchers.

## Conclusions

This study was focused on the biosorption of Ni(II) ion onto of *C. carandas* and *S. aromaticum* biomass from aqueous solution. The operating parameters, pH of solution, biomass dosage, contact time, initial metal ion concentration, and temperature were effective on the biosorption efficiency of Ni(II). Biosorbent *C. carandas* leaf powder showed higher sorption efficiency than that of biosorbent *S. aromaticum* powder under identical experimental conditions. Adsorption isotherm studies revealed that the Freundlich isotherm model showed a better experimental data in comparison of the Langmuir isotherm model. The maximum adsorption capacities estimated from Freundlich isotherm model for Ni(II) were 3.76 and 2.96 mg/g for *C. carandas* and *S. aromaticum*, respectively.

Since, several parameters including migration of metal ions from bulk solution to the surface of the adsorbent through bulk diffusion and the adsorption of metal ions at an active site on the surface of the adsorbent by chemical

**Fig. 11** SEM image of *S. aromaticum* **a** *before* Adsorption; **b** *after* Adsorption
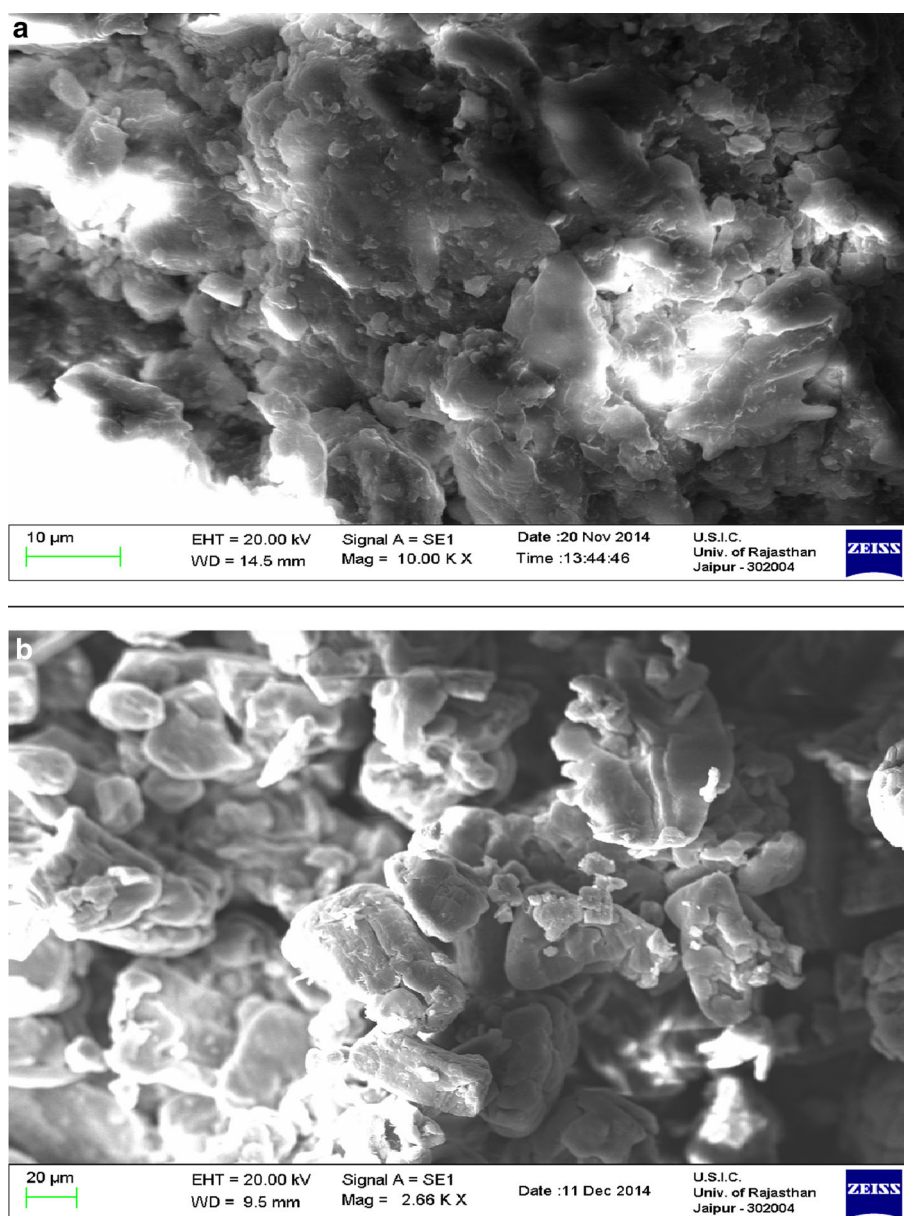


reactions play very important role in deciding the adsorption kinetics and adsorption mechanism; the actual adsorption mechanism is yet to be discussed and explained.

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