Universal Journal of Environmental Research and Technology
 eISSN 2249 0256
Available Online at: **www.environmentaljournal.org**
2016 Volume 6, Issue 3: 119-130

Open Access **Research Article**

Brassica Oleracea Botrylis Leaves (BOBL) Powder as Bioadsorbent to Remove Ni (II) Ions from Wastewater: Kinetic, Isotherm and Thermodynamic Studies

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Abstract:
Removal of Ni(II) ions from aqueous solution was carried out using brassica oleracea botrylis leaves (cauliflower leaves) and was characterized by SEM, XRD and EDAX techniques. The effect of solution pH, contact time, initial metal ion concentration and temperature was investigated in a systematic manner. Various thermodynamic parameters such as ΔG°, ΔH° and ΔS° have also been evaluated and it has been found that the adsorption process was spontaneous, endothermic and randomness in nature. The equilibrium data were analyzed by using Langmuir, Freundlich, Temkin and D-R isotherm models. Among these isotherm models Freundlich model was fitted well with its good correlation coefficient. The experimental data were analyzed by kinetic parameters such as Lagergen pseudo-first order and pseudo-second order models and found that the biosorption of Ni(II) followed pseudo-second order model by its good correlation coefficient values which are very close to unity. Desorption and recovery of the adsorbent was found that 12%. The results concluded that the BOBL powder was an efficient, eco-friendly and economically cheap adsorbent in the removal of Ni(II) ions from the aqueous solution.

Keywords: Adsorption, Bioadsorbent, Isotherms, Thermodynamic parameters, Kinetics, Desorption

1.0 Introduction:

Heavy metals are defined as metallic elements that have a relatively high density compared to water (Fergusson, 1990). In recent years, there has been an increasing ecological and global public health concern associated with environmental contamination by these heavy metals. Also human exposure has risen dramatically as a result of an exponential increase of their use in several industrial, agricultural, domestic and technological applications. Most commonly found at contaminated sites are lead, chromium, arsenic, zinc, cadmium, copper, mercury, and nickel. The wastewater commonly contains toxic heavy metals which are not biodegradable and their accumulation in ecological system can cause harmful effect to human, animals, and plants. The excessive exposure to nickel can lead to severe damage of lungs, kidneys, skin dermatitis and cancer (Bradl, 2002).

Nickel is the one of many trace metals widely distributed in the environment (Clatton and Clayton, 1994). Nickel finds its way into the ambient air as a result of the combustion of coal, diesel oil, the incineration of waste and sewage and miscellaneous source. Environmental sources of lower level nickel include tobacco, dental or orthopedic implants, stainless steel, kitchen utensils (Coogan *et al,* 1989). Drinking water generally contains nickel at concentration less than 10µg/L assuming a daily intake of 1.5L of water and level of 5-10µ Ni/L, the mean daily intake of nickel from water for adult would be between 7.5µ and 15.0µ. Tests conducted in the USA have revealed that 97% of the 2053 drinking water samples tested had nickel concentration below 20µg/L and 80% of the samples had less than 10µg/L. In exceptional cases values up to 75µg/L were found and those as high as 200µg/L were recorded only in the nickel ore mining areas. The incidence of health impairments due to higher nickel intake in drinking water is extremely infrequent (Bennett, 1982). The concentration of nickel in cold and hot water depends on the quality of the pipes. In the case of metal pipes the level of

Ni is hot water is lower than in cold water. However, when PVC pipes are used the concentrations are opposite (Rudzki, 2000).

As the low amount of these metals are highly toxic, removal of heavy metals from water has recently becomes the subject of considerable interest owing to strict legislation (Babel and Kurniawan, 2003). Heavy metals removal from wastewater and effluent can be achieved by conventional treatment process. Chemical precipitation, coagulation, complexation, activated carbon adsorption, ion exchange, solvent extraction, foam flotation, electro-deposition, cementation and membrane (Maity *et al,* 2003, Amriphate *et al*, 1992, Chandra sekhar *et al*, 2003, Prasad and Pandey, 2000, Voudrias *et al*, 2002). Adsorption is considered as one of the effective and economical technology for removal of heavy metal from wastewater. Natural materials or certain waste from industrial or agricultural waste is one of the resources for low cost adsorbents. Generally, these materials are locally and easily available in large quantities. Therefore, they are inexpensive and have little economic value. A fundamentally important characteristic of good adsorbents is their high porosity and consequent larger surface area with more specific adsorption (Patil Kishor *et al*, 2012). Some less expensive adsorbents are sphagnum peat, blast furnace slag, apple waste soybean, cotton seed husk, luffa husk, straw etc., (Periasamy and Namasivayam, 1995, Vashantha *et al*, 2016). Activated carbon prepared from activated rice husk, agriculture solid waste, peanut hull, fly ash (Viswakarma *et al* 1989, Swayampakula *et al,* 2007). The present study, cauliflower leaves waste, which is easily available, eco-friendly and low cost. This adsorbent material is belongs to cabbage family and the botanical name is *Brassica Oleracea Botrylis*(BOB). The parameters are pH, adsorbent dosage, concentration of metal ion, contact time and temperature (Ho and Mckay, 2000). The main objective of this study was to investigate the feasibility of using the brassica oleracea botrylis leaves for the maximum removal of Ni(II) ions from aqueous solution.

2.0 Materials and Methods:

Nickel sulphateAR graded chemical was used. The nickel ion solution prepared from 2.46g of nickel sulphate in 1L of distilled water. Different concentrations of metal solution were prepared by dissolving required amount of stock solution.

2.1 Preparation of Adsorbent:

Cauliflower leaves *(brassica oleracea botrylis)* were collected from local market. The collected material was cut into small pieces, washed with distilled water to remove the external dirt. The wetted bio-adsorbent was kept in an air for removing the water from the surface and dried in the sun light. The dried bio-adsorbent was powered and washed with distilled water to remove the colour and kept into the oven for removing the water and then kept in an air tight container for experimental uses. No other chemical modification was taken place. The bio-adsorbent was called as **brassica oleracea botrylis leaves (BOBL)**.

2.2 The characterization of Adsorbent:

The physical characteristics of the adsorbent samples are determined by known methods like pH, moisture content, total ash, surface morphology of the bio-adsorbent was examined with Scanning Electron Microscope(SEM) with Vega3 tescan model fitted with an Energy Dispersive X-ray Analyzer(EDAX), which allows a qualitative detection and the localization of elements present in the adsorbent (EDAX-Bruker Nano GMBH, Germany). X-ray diffraction (XRD) measurements were obtained using XRD 3003TT, GE, Inspection technology model to determine the crystalline phase present in the sorbents.

2.3 Batch Adsorption Studies:

The adsorption experiments were conducted batch mode method. 0.05g of BOBL is mixed with known concentration of Ni(II) ion taken in the 250mL conical flask and maintain the pH as constant then solution was stirred in mechanical shaker with 200 rpm at room temperature. For a wide range, contact time (0-60 minutes), the solution was filtered, absorption and concentration of the solution was determined by Atomic Absorption Spectrophotometer (Perkin Elmer, model AA400) at 232nm. The amount of adsorption for Ni(II) ion on the BOBL was calculated from the mass balance equation is

$q= (C_o-C_e) X v/m$

Where, q is the amount adsorbed (mg/g), C_o is initial concentration of metal ions(mg/L), C_e is equilibrium concentration of metal ions(mg/L), v is the volume of adsorbate (L) and m is the weight of the adsorbent (g).Percent of removal of metal ion was calculated using the formula

Percentage of removal (%) = $C_o – C_e /C_o \times 100$

3.0 Results and Discussion:

Table 1: The physical parameters of BOBL

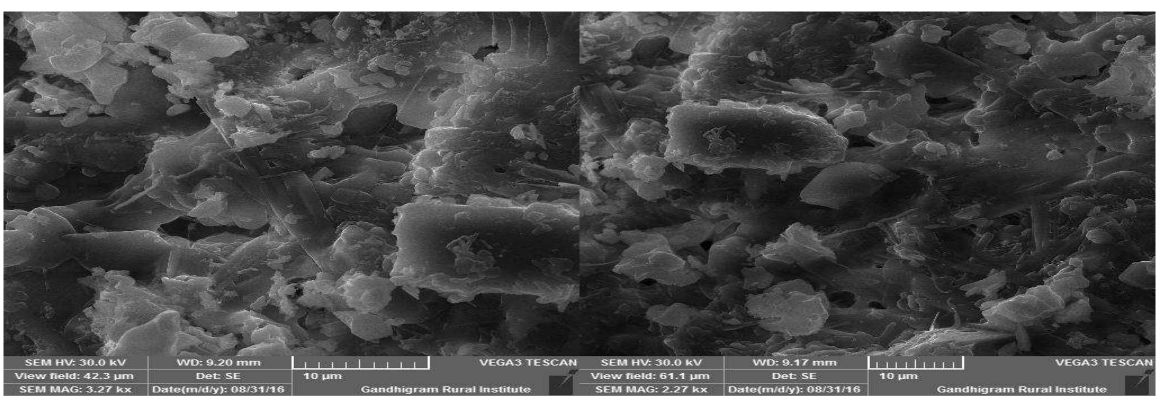
Sr. No.	Parameters	Result
1)	Loss of drying	13.7%
2)	Ash content	12.9%
3)	pH value at 20% W/V sol	5.8
4)	Specific gravity	0.65
5)	Bulk density	0.31 g/mL

3.1 Characterization of BOBL:

SEM Analysis: The SEM was used to observe the changes in the surface morphology of the materials. In **Figure 1** (a and b) are the raw BOBL and Ni(II) ion loaded BOBL bioadsorbent were shown, the adsorbent have irregular structure, thus makes possible for the adsorption of heavy metal ions on the different parts of the adsorbent. The figures illustrate the surface texture and porosity of BOBL adsorbent with holes and small opening on the surface which increased the contact area. These will lead to pores diffusion during adsorption (Achak *et al*, 2009). These images are clearly shown the difference in surface morphologies of these bioadsorbent after reaction with Ni(II) ions, the adsorbent porous was partly destroyed and this might be attributed to deposition of nickel over the pore of bio adsorbent surface.

XRD Analysis: The powered patterns of the bioadsorbent are shown in the **figure 2**. The average particle size was calculated using Debye Scherer's formula, **d= kλ / βcosθ**, where 'k' is the full width at half maximum(FWHM), 'λ' is the diffraction angle, is the wavelength, 'd' is the particle the average particle size of BOBL from XRD was found to be 4.64nm.

EDAX Analysis: This is further supported by EDAX analysis, which provides the direct conformation for the sorption of Ni(II) ions onto BOBL bioadsorbent. In **figure 3** (a and b) is the EDAX analysis of before and after analysis of BOBL conform the presence of respective ions present in the BOBL. The nickel peak in the figure 3b is conformed that the bioadsorbent was treated with Ni(II) ions.



(a) (b)

Figure 1 Scanning Electron Microscope images of (a) raw BOBL and (b) Ni(II) ions loaded BOBL

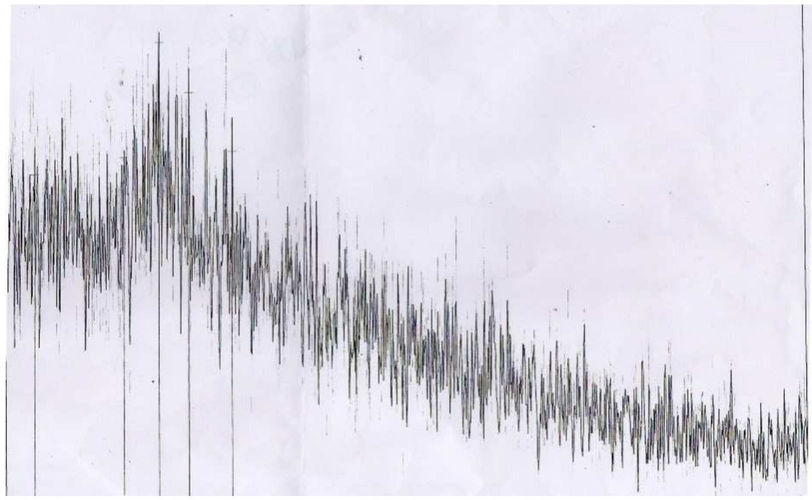


Figure 2: XRD curves of BOBL

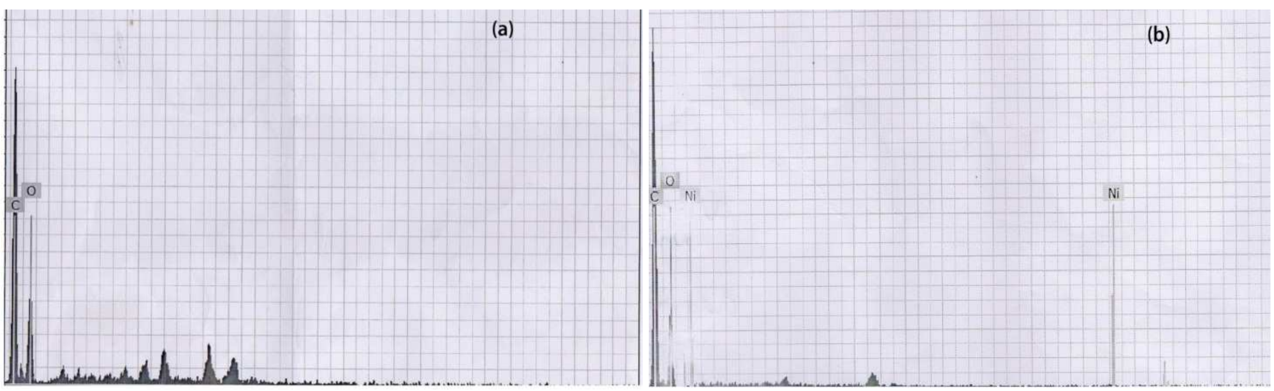


Figure 3: EDAX images of (a) raw BOBL (b) nickel ion loaded BOBL

3.2 Effect of pH:

The pH value of aqueous solution is an important parameter in adsorption process because it affects the surface charge of the adsorbent, the degree of ionization and specification of the adsorbate (Benaissa and Elouchdi, 2007). pH variation is one of the most important parameter controlling the uptake of toxic metals from wastewater and aqueous solution (Doan, et al 2007). From the **figure 4,** effect of pH on adsorption was conducted at range of 1-9 in each solution. The percentage adsorption increases with pH and it attains maximum at pH 7 and that after, it decreases with further increases in pH. This scenario will cause competition between H_3O^+ and the metal ions for active sites on the surface of adsorbents (Lu *et al*, 2007, Mungapati *et al*, 2010, Muthuselvi and Vashantha, 2016, Jalali *et al,* 2002, Karthikeyan *et al,* 2007). The optimum pH was recorded around pH 7 in figure 4. The decrease in removal of ions at higher pH may be due to solvation and hydrolysis of metal ions to form soluble hydroxylated complexes that complete for active sites. Moreover, the nature of ionization on the surface of adsorbents at specific pH may also cause the reduction of metal ion removal (Ucun *et al,* 2008). Some sorption was >80% at the natural pH of aqueous solution as prepared therefore, all the subsequent experiments were carried out without adjusting the pH.

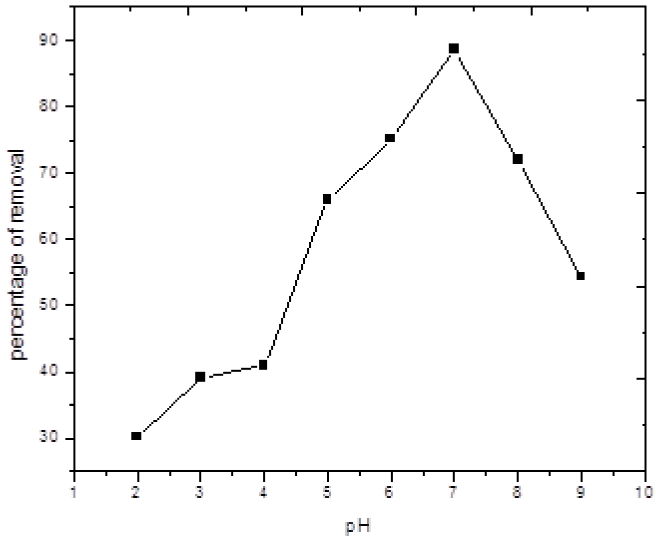


Figure 4: Effect of pH for adsorption of Ni(II) ions onto BOBL. Condition: initial concentration of Ni(II) ion 25mg/L, adsorbent dosage 0.05g/100mL and room temperature.

3.3 Effect of Contact Time:

Contact time is important factor in batch sorption process (Demirbas *et al,* 2008). **Figure 5** shows the effect of contact time on adsorption of Ni(II) ion onto BOBL. The initial rapid phase is due to the large number of active sites were available for adsorption. The binding site were shortly becomes limited and the remaining vacant surface site are difficult to be occupied by ions due to the formation of repulsive forces between the ions on the solid surface and the liquid phase. So, the removal of nickel ion increased with increase in contact time (Sengil and Ozacar, 2008, Anwar *et al*, 2010).

3.4 Effect of Initial Concentration:

Effect of initial concentration of Ni (II) ions were conducted at ranges of 5,10,15,20 and 25 mg/L. **Figure 6** shows that amount adsorbed for Ni(II) ion increases from 9.3mg/g to 44.3mg/g respectively. At lower initial metal ion concentration, sufficient adsorption site are available for adsorption of metal ions. The amount adsorbed was increases with increase in initial concentration of the metal ion, simply due to the presence of more surface site for sorption (Mohan and Karthikeyan, 1997). The adsorption of Ni(II) ion by BOBL bioadsorbent depends on the initial concentration and it can be seen that the amount adsorbed increases with increase in the metal ion concentration.

3.5 Effect of Temperature:

The temperature plays a major role in the adsorption of heavy metals on the surface of adsorbent. The effect of temperature was carried out in different temperature like 301, 311 and 321K remaining parameter kept constant. In **Figure 7** the amount adsorbed for Ni(II) ion was found to be almost same for three different temperatures. There is slight change in adsorption level. The internal pores of the adsorbate particles as the liquid viscosity decreases with increases in temperature and other affect the equilibrium capacity of the adsorbate (Hawari *et al* 2009; Aksu, 2002).

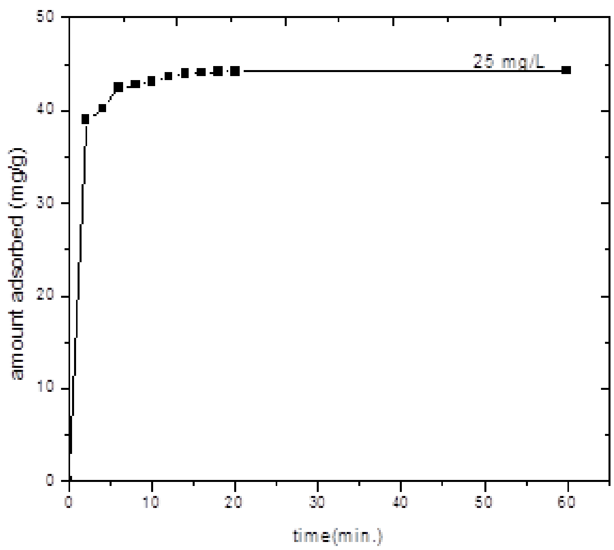


Figure 5: Effect of contact time on the adsorption of Ni(II) ion onto BOBL

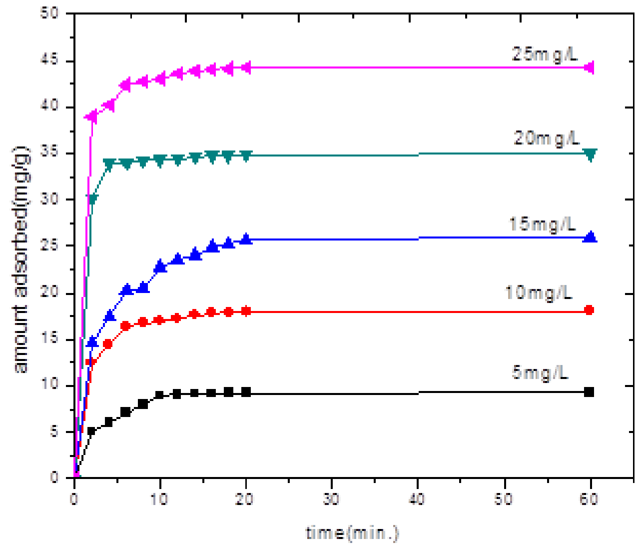


Figure 6: Effect of initial concentration on adsorption of Ni(II) ion onto BOBL

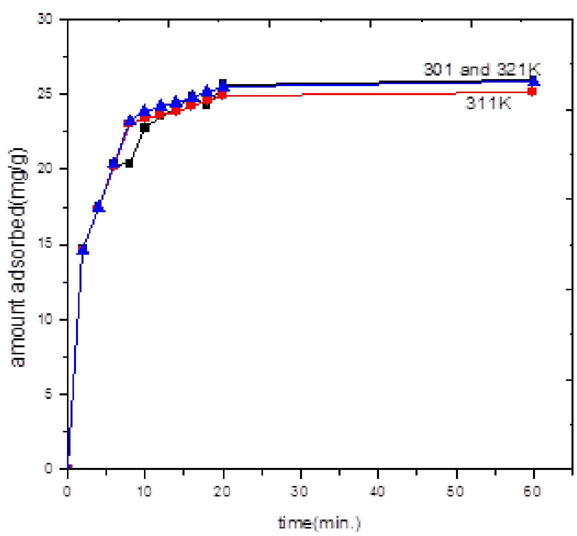


Figure 7: Effect of the temperature on the adsorption of Ni (II) ion onto BOBL

3.5.1 Thermodynamic Parameters:

In order to explain the effect of temperature on the adsorption of Ni(II) ion on BOBL bioadsorbent, thermodynamic parameters like standard Gibbs free energy(ΔG°), standard enthalpy(ΔH°), standard entropy(ΔS°) and activation energy $E_a$were calculated from the following equations.

$\Delta G^o = -RT \ln K_c$

$\log K_c = \Delta S°/2.303R - \Delta H°/2.303RT$

$\log k = \log A - E_a/RT$

Where R = the gas constant, T= absolute temperature, K_c = the adsorption equilibrium constant, k is rate constant, E_a is activation energy and A is Arrhenius pre-exponential factors (J/mol).The negative values of ΔG° indicates at all temperatures studied are due to the fact that adsorption is spontaneous and the adsorption process which no external energy source is required for the system and feasible (Vermeulan *et al,* 1966).

The negative value of ΔH° indicates that the adsorption reaction was exothermic for Ni(II) ion. The positive value of ΔS° indicates increased randomness at the solid/liquid interface during Ni(II) ion adsorption (Webber and Chakravarti, 1974). The E_a value calculated from the slope of the plot was found to be – 23.06kJ/mol (lesser Ea value faster the reaction) the negative value of E_a indicates that lower solution temperatures favours metal ion removal by adsorption onto BOBL surface.

Table 2: Thermodynamic parameters for adsorption of Ni(II) ion onto BOBL

Temp.(K)	ΔG° (kJ\mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol)	E_a (kJ/mol)
301	-4999.32	-1.206	0.0122	-23.06
311	-4706.40			
321	-5247.64			

3.6 Adsorption Isotherm:

The equilibrium study is important for an adsorption process as it shows the capacity of the adsorbent and describes the isotherm to express the surface properties and affinity of the adsorbent. The equilibrium data for Ni(II) ion adsorption on BOBL bioadsorbent were evaluated by the Langmuir (Langmuir, 1918), Freundlich (Freundlich, 1906), Temkin (Temkin and Pyzhev, 1940) and D-R (Dubinin, 1960) isotherm models. In Figure 8 shows the Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The Langmuir constants b and Q_o were calculated, it shows the adsorption constant (b) is related to the affinity of binding sites (L/mg) and value of (b) is 0.2587 and Q_o is 90.09 mg/g for Ni(II) ions. $R_L = 1/(1+bC_0)$. The R_L value indicate the type of adsorption as either unfavourable (R_L>1), linear(R_L=1), favourable (0<R_L<l) or irreversible(R_L=0). The R_L value of Ni(II) ion is 0.2430 revealed that this adsorption onto BOBL is favorable as the value lie between 0 and 1. Freundlich isotherm is describe the adsorption characteristics for the heterogeneous surface ((Freundlich, 1906). These data often fit the empirical equation proposed by Freundlich. The linearised adsorption isotherms are obtained at room temperature as shown **Figure 9** and the adsorption coefficients values are calculated from intercept and slope and these values are given in **Table 3.** All the curves had good linearity indicating strong binding of Ni(II) ion to surface particles. Correlation coefficients (R^2) for Langmuir isotherm of Ni(II) ion is 0.8024 and Freundlich isotherm is 0.9856, it clearly suggest that Freundlich isotherm follows a good relation of Ni(II) ions with BOBL. The Freundlich constant, K_F is 17.94mg/g/L^{-n}/mg^{-n} and n (1.37) value prove that the adsorption of Ni(II) ion onto BOBL is favorable as the magnitude lies between 1 to 10 (Gunay *et al,* 2007).

The Temkin isotherm equation assumes that the heat of adsorption of all the molecules in layer decreases linearly with coverage due to adsorbent-adsorbate interactions and that the adsorption in characterized by a uniform distribution of the bonding energies up to some maximum binding energy. The Temkin adsorption isotherm model was chosen to evaluate the adsorption potentials of the adsorbent for the adsorbates (Dabrowski, 2001, Hobson, 1969). The Temkin isotherm plot for the Ni(II) ions as shown in **Figure 10** and the parameters are given in Table 3. The Temkin adsorption potential, K_T is 2.649(L/mg), the Temkin constant, b_T is 26.86kJ/mol related to heat of sorption for the metal ion.

Dubinin–Radushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface (Dubinin, 1960). The approach was usually applied to distinguish the physical and chemical adsorption of metal ions with its mean free energy, E per molecule of adsorbate can be computed by the relationship (Foo and Hameed, 2010, Aharoni and Ungarish, 1977).

$E=[1/\sqrt{2\beta}]$ where, β is denoted as the isotherm constant, the parameter ε can be calculated as

$\varepsilon=RT\ln[1+1/C_e]$

Where R is gas constant, T is absolute temperature (K) and C_e is adsorbate equilibrium concentration (mg/L) respectively. One of the unique features of the Dubinin-Radushkevich isotherm model plotted **(Figure 11)** as a function of logarithm of amount adsorbed $\ln q_e$ vs ε^2 the square of potential energy, all suitable data will lie on the same curve, named as the characteristic curve (Aharoni and Ungarish, 1977) the regression coefficient is 0.919. The constant such as q_m, and β were determined from the appropriate plot using known equation and the free energy, E=5.2kJ/mol indicating a physiosorption.

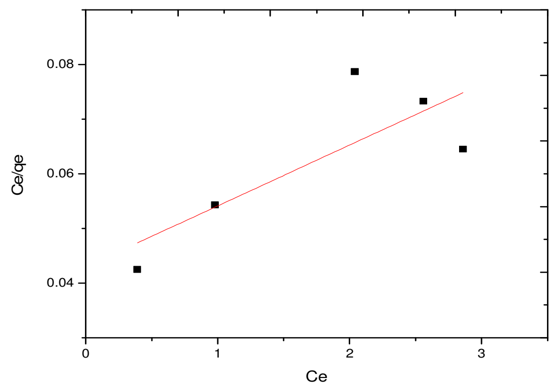


Figure 8: Langmuir isotherm for adsorption of Ni(II) ion onto BOBL

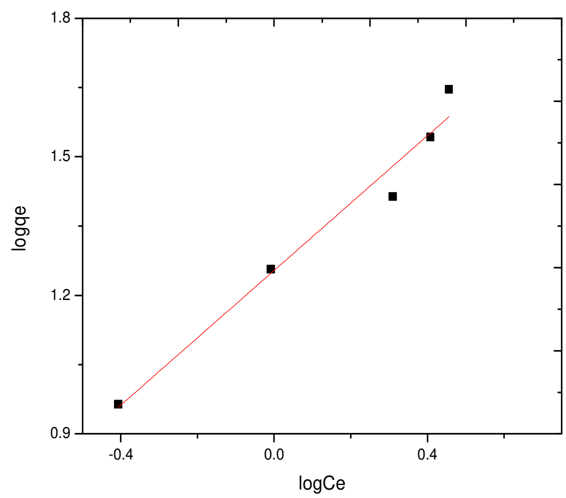


Figure 9: Freundlich adsorption isotherm for adsorption of Ni(II) ion onto BOBL

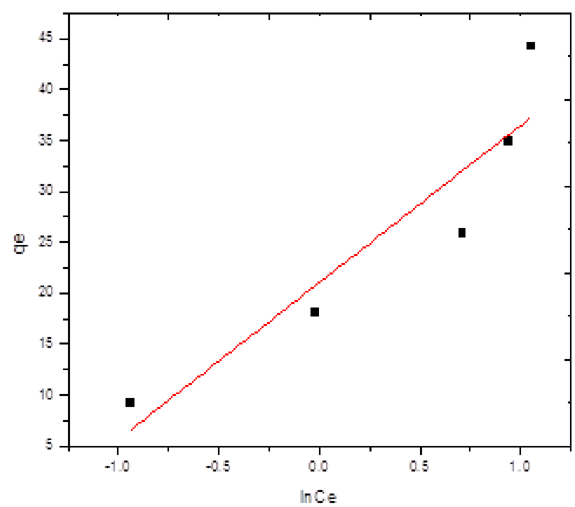


Figure 10: Temkin adsorption isotherm for adsorption of Ni(II) ion onto BOBL

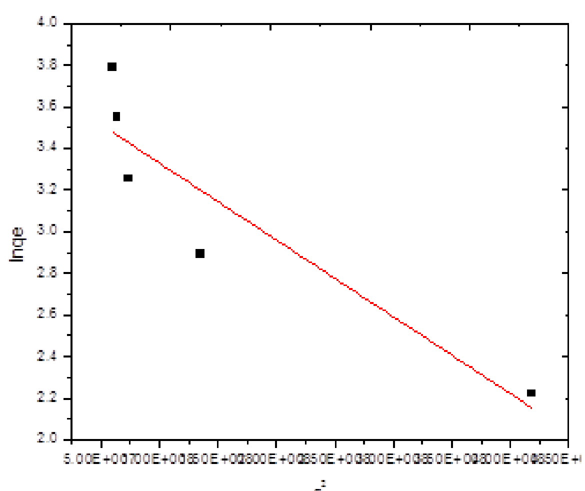


Figure 11: D-R adsorption isotherm for adsorption of Ni(II) ion onto BOBL

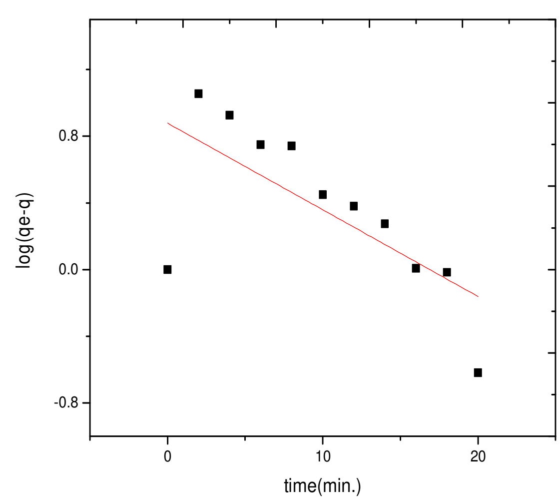


Figure 12: pseudo–first order kinetics for adsorption of Ni(II) ion onto BOBL

Table 3: Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherm constants for the adsorption of Ni (II) ion onto BOBL

Isotherm models	Parameters
Langmuir	Q_o = 90.99 b = 0.2587 R_L = 0.243 R^2 = 0.824
Freundlich	K_F = 17.94X10^{-2} n= 1.371 R^2 = 0.986
Temkin	K_T = 2.649 B_T = 26.86 R^2 = 0.938
Dubinin–Radushkevich	q_m= 20.33 β = 3.693X10^{-8} E= 5.2 R^2 = 0.919

According to regression coefficient values the isotherm adsorption was increases from the following order Langmuir<D-R<Temkin<Freundlich isotherm.

3.7 Adsorption Kinetics:

Kinetic studies were carried out under the optimized condition from 0 to 60 min**.** Kinetic of adsorption initially increased and reach equilibrium. There are three common steps involved in adsorption process the first step is mass transfer across the external boundary layer film of liquid surrounding the outside of the particle. Second is the adsorption process (physical or chemical adsorption) this step is often assumed to be extremely rapid. Finally, diffusion of the adsorbate molecule to an adsorption site either by a pore diffusion process through the liquid filled pore or by a solid surface diffusion mechanism (Hutsonand and Yang , 2000). One or any combination of this adsorption process could be the rate-controlling mechanism. The kinetic data obtained were to linear form of pseudo-first order and pseudo-second order.

3.7.1 Pseudo-First Order:

The pseudo- first order model is used to describe the reversibility of the equilibrium between liquid and solid. The pseudo – first is explain by the Lagergen equation (Lagergren 1898). By plotting of $\log(q_e-q_t)$ vs t gives the intercept and slope value. From this value we can calculate first order rate constant(k_{ad}). The linear plot of experimental data and the calculated parameters are shown in F**igure 12** and **table 4**, respectively.

3.7.2 Pseudo- Second Order:

The pseudo–second order kinetic data were also analyzed by using known equation (Ho and Mckay, 1999). By plotting t/q_t vs t gives the intercept and slope value. From this value we can calculate second order rate constant. The graphical interpretation of the data for second order kinetic model and calculated parameter are shown in **figure 13** and **table 4** respectively. Kinetic studies were conducted at five different initial metal ion concentrations at room temperature. From the table 4 the coefficient, R^2 of pseudo second order is approaching one. And it was found that equilibrium adsorption capacity (q_e) increased with an increasing in initial Ni(II) ion concentration. The adsorption capacity increased from 9.3mg/g to 44.3mg/g (from 5 to 25 mg/L). From, **figure 12 and 13** we found that pseudo-second order had good linearity, it clearly suggest that pseudo second order follows a good relation of Ni(II) ion adsorption with BOBL.

3.8 Desorption:
The possibility or regeneration of the adsorbent and recovery of the metal ion can be explored using desorption study. Desorption was carried out using batch experimental method. In this study, the adsorbent was regenerated using 50mL of distilled water and 0.05g of metal loaded adsorbent. The extent desorption was found 12% .

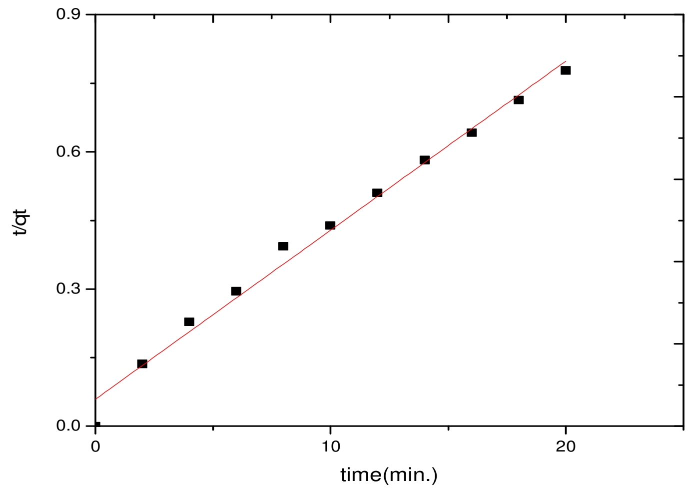


Figure 13: pseudo–second order kinetics for adsorption of Ni(II) ion onto BOBL

Table 4: Kinetic parameter for adsorption of Ni(II) ion onto BOBL

Kinetic model	parameter	5 mg/L	10 mg/L	15 mg/L	20 mg/L	25 mg/L
1st order	k_{ad}	0.325	0.285	0.194	0.206	0.241
	R^2	0.991	0.942	0.976	0.968	0.992
2nd order	k_2	0.038	0.047	0.014	0.114	0.053
	R^2	0.997	0.999	0.998	0.999	0.999
	q_e	10.55	19.01	28.65	35.03	45.25

4.0 Conclusions:

To avoid environmental hazards, it is essential to remove metal contaminants from industrial effluents before discharging in water bodies. Overall of this study explain that adsorption technique is a cost effective and technically feasible method. Replacement of expensive adsorbent by low cost, more effective and readily available waste bio product as adsorbents like vegetable waste product BOBL(brassica oleracea botrylis leaves) are very effective bioadsorbent for Ni(II) ion removal from waste water. The bioadsorbent was characterized by scanning electron microscope, X-ray diffraction and EDAX method. The Freundlich adsorption isotherm was fitted to the experimental data with the maximum adsorption capacity. Adsorption kinetics of Ni(II) ion adsorption onto BOBL followed the pseudo-second order kinetic model. Thermodynamic analysis suggest the removal of Ni(II) onto bioadsorbent are spontaneous, endothermic and randomness. Therefore, the present study finding that the bioadsorbent BOBL (*Brassica Oleracea Botrylis* leaves) used as an inexpensive, eco- friendly and effective adsorbent for the removal of Ni(II) ions from wastewater.

5.0 Acknowledgements: Authors expressing sincere thanks to our principal Dr. JAYASHREE GHOSH and Management, Punjab Association for providing the financial support.

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