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Kinetic Studies on Biosorption of Cadmium and Nickel from Aqueous Solutions with *Citrus limonum.*

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ABSTRACT

Biosorption by materials such as citrus peels could be a cost effective technique for removing toxic heavy metals from wastewater.Equilibrium, thermodynamic and kinetic studies were carried out for the biosorption of cd^{2+} and Ni^{2+} ions from aqueous solution using *citrus limonum*.Langmuir and freundlich isotherm models were applied to describe the biosorption of the metal ions on to *citrus limonum*.The influences of pH and contact time of solution on the biosorption were studied. Langmuir model fitted the equilibrium data better than the freundlich isotherm. The kinetics for Cd^{2+} and Ni^{2+} ions biosorption followed the pseudo second order kinetics.

Keywords: Biosorption, Langmuir, citruslimonum, equilibrium.

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INTRODUCTION

Water pollution is a major environmental problem faced by modern society that leads to ecological disequilibrium and health hazards. Heavy metal ions such as copper, cadmium, lead, nickel, and chromium, often found in industrial wastewater, present acute toxicity to aquatic and terrestrial life, including humans. Thus, the discharge of effluents into the environment is a chief concern. Many methods, such as chemical precipitation [1], ion exchange [2], membrane processes [3] and adsorption onto activated carbon [4] etc., have been used to remove heavy metal ions from various aqueous solutions. However, the application of such processes is often restricted because of technical or economic constraints [5,6]. Biosorption of heavy metals is one of the most promising technologies involved in the removal of toxic metal ions from wastewater. It is a potential alternative to conventional processes for the removal of metals due to the low cost, easily obtained, minimization of the volume of chemical and/or biological sludge to be disposed of, high efficiency in detoxifying very dilute effluents and no nutrient requirements [7–9]. A great interest has recently been directed to the biosorption of heavy metals from solutions using different bio- materials as adsorbents. Among the various resources in biological wastes, both dead and live biomass, exhibit particularly interesting metal-binding capacities [10,11]. In recent years, agricultural by-products have been widely studied for metal removal from water. These include peat, wood, pine bark, banana pith, soybean and cot- tonseed hulls, peanut, shells, hazelnut shell, rice husk, sawdust, wool, orange peel, and compost and leaves [12].

Biosorption, using waste biomass from other industries as sorbent materials, can be a cost effective metal removal technique. So far, very little research has been performed on Citrus peels; inspite of their great potential as biosorbents Citrus peels have a high metal binding capacity due to their pectin content. As a low cost, citrus peel is an attractive and inexpensive option for the biosorption removal of dissolved metals.

MATERIALS AND METHODS

Chemicals

All chemicals used in the present work were of analytical purity. The stock solution of Cd^{2+} and Ni^{2+} was prepared in 1.0 g L^{-1} concentration using $CdSO4{\cdot}8H_2O$ and $Ni(NO_3)_2$ then diluted to appropriate concentrations. 0.1 mol L^{-1} HCL and 0.1 mol L^{-1} NaOH were used for pH value adjustment.

Biosorption Experiments

Biosorption experiments were conducted at 30°C by agitating 0.050 g of biosorbent with 25 mL of metal ion solution of desired concentration in 100 mL Stoppard conical flask using a shaking thermostat machine at a speed of 120 rpm for 3 hours except for the contact time experiments. The effect of solution pH on the equilibrium biosorption of metal ions was investigated under similar experimental conditions between pH 2.0 and 7.0.In the kinetic experiments, 50 mg L^{-1} Cd^{2+} and Ni^{2+} ion solution were used. The sorption time was varied between 30 and 180 min. In the isotherm experiments, 0.050 g of biosorbent was added in 25 mL of Cd^{2+} and Ni^{2+} ions solution at various concentrations (50–250 mg L^{-1}). Once the preset contact time (3 h) reached, the samples were withdrawn and centrifuged at 4000 rpm for 5 min and the supernatant solutions were analyzed for the residual metal ion concentration by using Agilent model 3510 atomic absorption spectrophotometer. The amount of biosorption (q) was calculated by the following equation:

$$q = \frac{(C_0 - C_e)V}{m} \quad (1)$$

The biosorption efficiency, A %, of the metal ion was calculated from:

$$A\% = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

Where C_0 and C_e are the initial and equilibrium metal ion concentrations (mg L^{-1}), respectively. V is the volume of the solution (L) and m is the amount of biosorbent used (g).

Desorption and Regeneration Tests

To investigate the possibility of repeated use of biosorbent, desorption and regeneration experiments were also conducted. The metal ions-loaded biosorbent was filtered, and metal ions content was measured. The biosorbent was then transferred to another conical flask and treated with 25 mL of 0.05 mol L^{-1} HCl solution for 2 hours. It was again filtered and desorbed metal ions were determined in the filtrate. The biosorbent was washed several times with distilled water in order to remove excess acid. The biosorbent thus regenerated was used in further biosorption steps.

RESULTS AND DISCUSSION

Effect of pH on Metal Biosorption

It is well known that pH could affect the protonation of the functional groups on the biomass as well as the metal chemistry. The study of biosorption of Cd^{2+} and Ni^{2+} on *Citrus limonum* as a function of pH was accomplished; the results are presented in Fig. 1. As the pH of the heavy metal ions solution increased from 2.0 to 7.0, the biosorption yield of Cd^{2+} and Ni^{2+} ions was changed. The percent biosorption is minimum at pH 2.0 and increases as the pH increases from 2 to 6. The minimum biosorption at low pH 2.0 may be due to the fact that high concentration and high mobility of H^+ ions, the hydrogen ions are preferentially adsorbed rather than the metal ions. At higher pH values, the lower number of H^+ and greater number of ligands with negatives charges results in greater metal ions biosorption. The weakly acidic carboxyl groups (R–COOH) are regarded as the main ligands involved in the metal uptake by

OPAA. Because the pKa value of R–COOH is in the range of 3.5–5.5 [13], more carboxyl groups will be deprotonated at pH over this range, and thus resulting in more negative binding sites. Consequently, the attraction of positively charged metal ions would be enhanced.

Maximum biosorption for Cd^{2+} and Ni^{2+} by *Citrus limonum* was achieved at pH 6 as no increases in metal uptake were observed above pH 6. For this reason, further metal sorption studies were carried out at pH 6, which is well below the pH levels where Cd^{2+} and Ni^{2+} ions are precipitated.

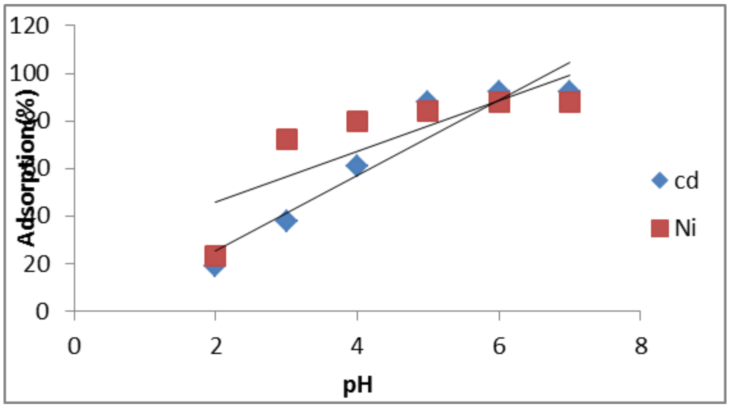

Figure 1: The effect of pH on biosorption of Cd^{2+} and Ni^{2+} ions.

Biosorption Kinetics

Fig. 2 shows the kinetics of the biosorption of 50 mg L^{-1} Cd^{2+} and Ni^{2+} ions at 30^0C by *Citrus limonum*. The kinetic curve for heavy metal ions showed that the amount of biosorption sharply increases with increasing contact time in the initial stage (0–50 min), and then gradually increases to reach an equilibrium value in approximately 150 min. A further increase in contact time had a negligible effect on the amount of biosorption. According to these results, the shaking time was fixed at 2.5 hours for the rest of the batch experiments to make sure that the equilibrium was reached.

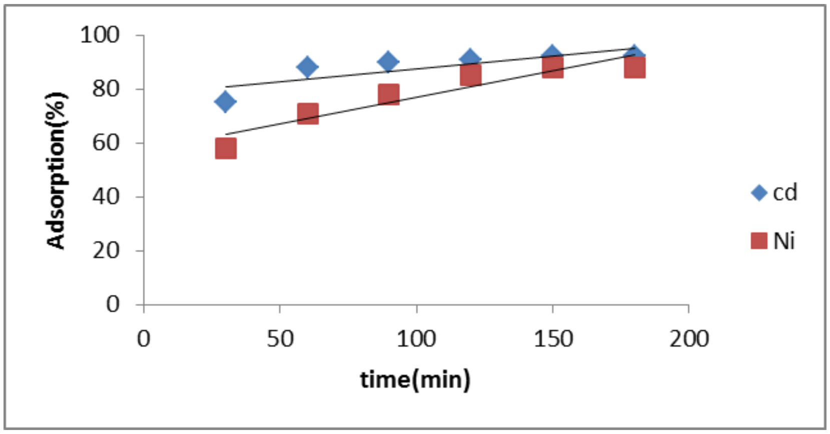

Figure 2: biosorption kinetics of Cd^{2+} and Ni^{2+} ions.

A good correlation of the kinetic data explains the biosorption mechanism of the metal ion on the solid phase [14]. In order to evaluate the kinetic mechanism that controls the biosorption process, the pseudo-first-order and pseudo-second-order models were applied for the biosorption of Cd^{2+} and Ni^{2+} ions on the biosorbent.

Biosorption kinetic data of Cd^{2+} and Ni^{2+} ions are analyzed using the Lagergren pseudo-first-order rate equation [15]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (3)$$

Where q_e and q_t are the amounts of biosorbed (mg g^{-1}) at equilibrium and at time t, respectively, and k_1 is the rate constant of pseudo-first-order biosorption (min^{-1}). The q_e and rate constants k_1 were calculated from the slope and intercept of the plot of log ($q_e - q_t$) vs. t (fig .3). In fact, it is required that calculated equilibrium adsorption capacity values, q_e (cal.), should be in accordance with the experimental q_e (exp.) values [16]. Although the correlation coefficient values (R^2) are very high, the experimental qe values do not agree with the calculated ones, obtained from the linear plots (Table 1). This suggests that the biosorption of Cd^{2+} and Ni^{2+} ions does not follow pseudo-first-order kinetics.

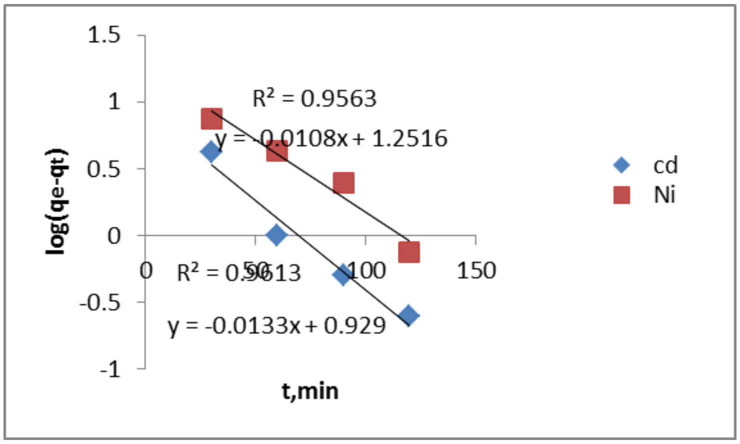

Figure 3: Lagergren pseudo first order kinetics for the biosorption of Cd^{2+} and Ni^{2+} ions.

The biosorption kinetic data can also be described by pseudo- second-order equation [17]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (4)$$

Where k_2 is the rate constant of pseudo-second-order biosorption (g mg^{-1} min^{-1}). The pseudo-second-order rate constant k_2 and qe values were calculated from the slope and intercept of the plots t/q vs. t (fig .4.). It was found that the calculated q_e values agree well with experimental qe values (Table 1). This suggests that the pseudo-second-order kinetic model based on the assumption that the rate-limiting step may be chemical sorption involving valance forces through sharing or exchange of electrons between heavy metal ions and the adsorbent provides the best correlation data for the heavy metal ions.

Table 1: Kinetic parameters for biosorption of Cd^{2+} and Ni^{2+} ions on Citrus limonum

Metal ions	q_e (exp)	Pseudo first order			Pseudo second order		
		q_e(cal)mg/g	k1(min^{-1})	R^2	q_e(cal)mg/g	k1(min^{-1})	R^2
Cd2+	23	8.491	0.0306	0.961	24.3	0.0060	0.999
Ni2+	22	17.848	0.0248	0.956	25.64	0.0016	0.998

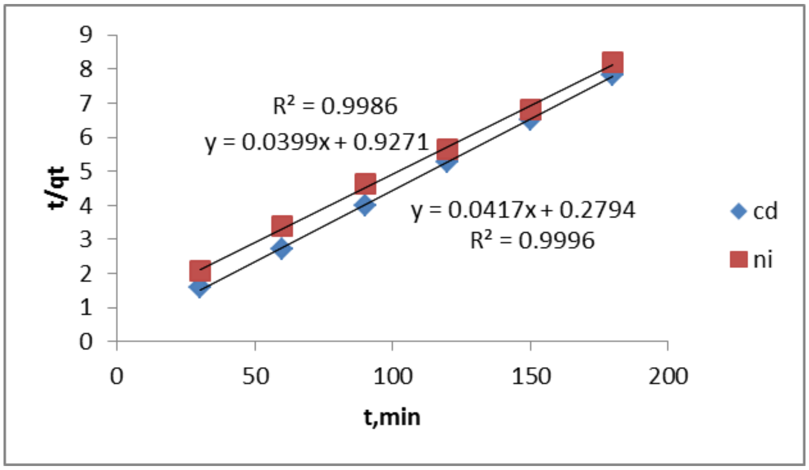

Figure 4: Lagergren pseudo second order kinetics for the biosorption of Cd^{2+} and Ni^{2+} ions.

Biosorption Isotherms

Biosorption isotherms describe how adsorbate interacts with biosorbents and equilibrium is established between adsorbed metal ions on the biosorbent and the residual metal ions in the solution during the surface biosorption. Equilibrium isotherms are measured to determine the capacity of the biosorbent for metal ions. The most common types of models describing this type of system are the Langmuir and Freundlich isotherms.

The Langmuir isotherm assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface, and the biosorption of each molecule onto the surface has equal biosorption activation energy. While the Freundlich isotherm supposes a heterogeneous surface with a non-uniform distribution of heat of biosorption over the surface and a multilayer biosorption can be expressed.

The Langmuir isotherms can be expressed as [18]:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \qquad (5)$$

Where qmax is monolayer capacity of the biosorbent (mg g^{-1}), and b is the biosorption constant (L mg^{-1}). The plot of C_e /q_e versus C_e should be a straight line with slope 1/q_{max} and intercept 1/(q_{max} b) when the biosorption follows the Langmuir equation. Fig.5a,5b. Presents the experimental biosorption langmuir isotherms of Cd2+ and Ni2+ ions on *Citrus limonum*.

The Freundlich equation can be expressed as [19]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (6)$$

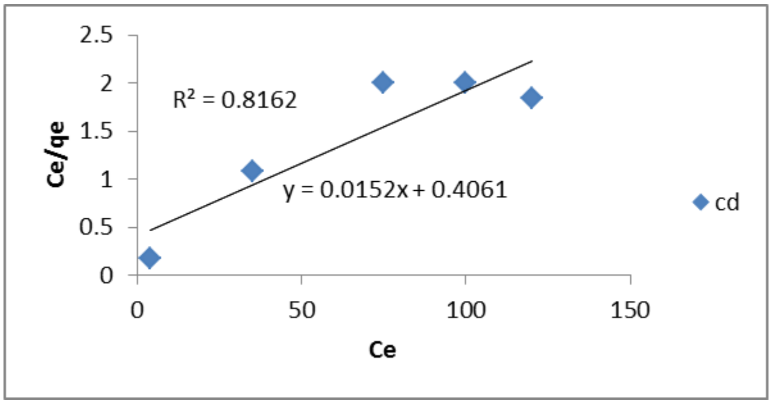

Figure 5a: Langmuir isotherm of Cd^{2+} ions on Citrus limonum

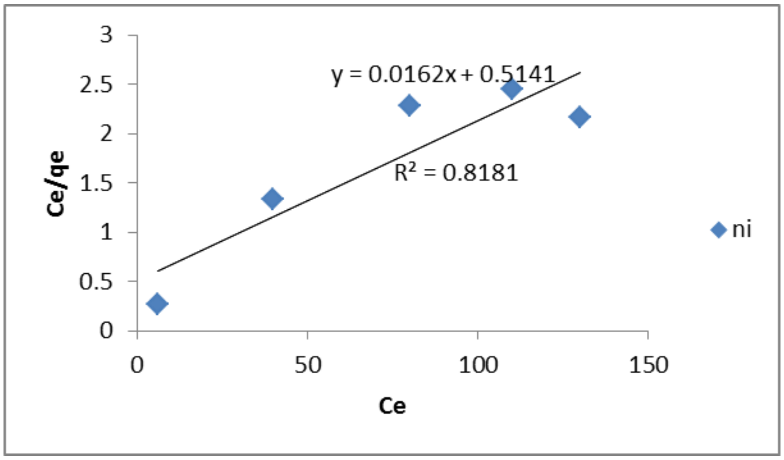

Figure 5b: Langmuir isotherm of Ni^{2+} ions on Citrus limonum

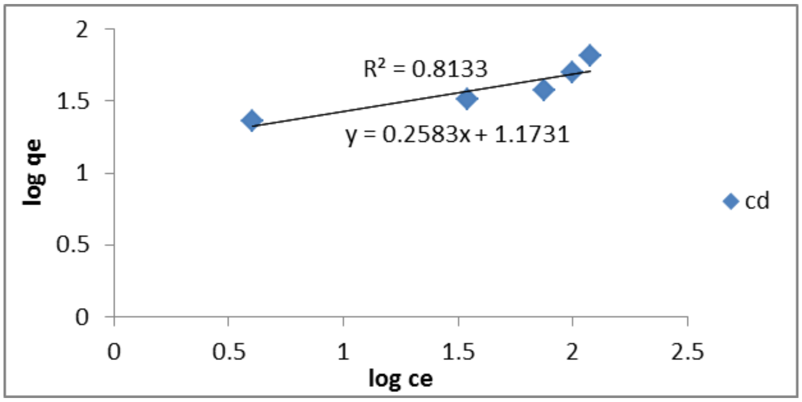

Figure 5c: Freundlich isotherm of Cd^{2+} ions on Citrus limonum

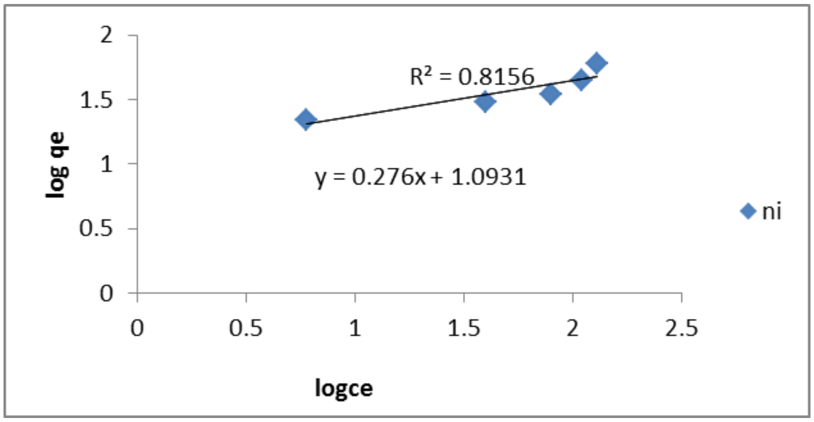

Figure 5d: Freundlich isotherm of Ni^{2+} ions on *Citrus limonum*

Where K_F and 1/n are Freundlich isotherm constants related to biosorption capacity and intensity of biosorption, respectively. If Eq. (6) applies, a plot of log q_e versus log C_e will give a straight line of slope 1/n and intercept K_F. Fig.5c,5d. Presents the experimental biosorption Freundlich isotherms of Cd^{2+} and Ni^{2+} ions on *Citrus limonum*.

The Langmuir and Freundlich biosorption constants evaluated from the isotherms with the correlation coefficients are listed in Table 2. As it can be seen that the Langmuir isotherm gave better fit than the Freundlich isotherm, which illustrated that the biosorption on the surface of *Citrus limonum* was a monolayer biosorption. According to the Langmuir equation, the maximum uptake capacity for Cd^{2+} and Ni^{2+} ions were 66.66 and 62.5 mg g−1, respectively.

Table 2: Isotherm parameters for biosorption of Cd^{2+} and Ni^{2+} ions on Citrus limonum

Metal ions	Langmuir model			Freundlich model		
	$q_{max(}$mg/g)	b	R^2	K_F	n	R^2
Cd2+	66.666	27.066	0.816	14.893	0.258	0.813
Ni2+	62.5	32.125	0.818	12.387	0.276	0.815

Table3: Biosorption capacities of various biosorbents.

Biosorbents	q_{max}(mg/g)		References
	Cd^{2+}	Ni^{2+}	
Rice husk	16.7	5.52	[20]
Sugar beet pulp	24.39	11.86	[21]
Corncobs	8.99	13.49	[22]
NaOH-modified biomass of Solanum elaeagnifolium	18.63	7.55	[23]
Solanum elaeagnifolium	18.94	6.50	[23]
Ulva sp.	65.20	17.02	[24]
Gracillaria sp.	33.72	16.43	[24]
Orange peel (OP)	63.35	9.82	[25]
Citrus limonum	66.666	62.5	This study

CONCLUSIONS

Removal of Cd^{2+} and Ni^{2+} ions from aqueous solution by *Citrus limonum* was found to be effective. The results clearly show that *Citrus limonum* is more effective than many other adsorbents for the biosorption of Cd^{2+} and Ni^{2+} ions. Optimum pH for Cd^{2+} and Ni^{2+} ions removal was found to be pH 6.Equilibrium biosorption data showed good fit to Langmuir isotherms. The biosorption equilibriums were reached at 150 min and biosorption processes followed pseudo-second-order kinetic model. It can be concluded that the *Citrus limonum* is an effective and alternative biomass for the removal of Cd^{2+} and Ni^{2+} ions from wastewater in terms of high biosorption capacity, natural and abundant availability and low cost.

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