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Ghettoization Of Nickel II Ni2+ from Aqueous Solution By Maize Cob And Sugarcane Bagasse: Kinetic, Isotherm And Thermodynamics Studies.

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ABSTRACTS

Maize cob and sugarcane pulps (bagasse) were used for adsorption of different metal ions. The biosorption of Ni^{2+} was studied over a range of ion concentration, adsorption time, temperature and pH. With the aid of atomic absorption spectrophotometer (Buck scientific 210 VGP) the analysis of residual metal ions was done. The process of uptake obeyed both the Longmuir and Freundlich isotherms. According to the parameters of Langmuir isotherm, the maximum biosorption capacities of nickel ions on to maize cob and sugarcane pulp (bagasse) were 57.1mg/g and 83.3mg/g at 301k, respectively. The kinetic study shows that uptake of Ni^{2+} increases as the time increases and that maximum biosorption was obtained within 60min. Ion exchange is probably one of the main mechanisms during adsorptive process. The thermodynamics calculations indicate that maize cob and sugarcane pulp (bagasse) has potential for the removal of Ni^{2+} from industrial wastewater.

Keywords: Bagasse, biosorption, adsorption, isotherms, ghettoization.

Aims Research Journal Reference Format:
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1. INTRODUCTION

Heavy metal contamination is a man source of water pollution. The discharge of these heavy metals which has been on the increase, are from various industries such as electroplating, metal finishing, textile, mining, ceramic and glasses, etc. in both developed and developing countries (Aktar T. et al, 2006). The removal and recovery of these metals which are often in concentrations beyond the tolerance level, from waste water is important in protecting the environment and human health. According to the world health organization, the metals of most immediate concern are cadmium, chromium, cobalt, copper, lead, nickel, mecury and zinc. Hitherto various methods have been employed in removing these metals. This include chemical oxidation and reduction, membrane separation, solvent extraction, carbon adsorption, ion exchange, electrolytic treatment, coagulation, flotation ultrafiltration, reverse osmosis, electro-precipitation and crystallization (Ahmed Sari et al 2008, Paterson J. W. 1985; Battacharya S. N. et al 2006). As rightly observed by Ahmed Sari et al (2008), technical and or economic factors limit sometimes the feasibility of such processes.

Biosorption, a relatively new technology, has been considered to be an alternative for the uptake of toxic metal ions from waste water (Babarinde 2006, Ahmed Sari 2008). It is more economical than conventional methods and has thus been given much attention in the recent years (Aktar T. et al 2006). The mechanism of the biosorption process is explained in terms of the reaction between anionic groups present in the biomasses and the cationic metal ions (Pradhan et al 2007).
This paper investigates the removal of Ni II ions from aqueous solution using sugarcane pulp (bagasse) and maize cob. The aim is to study the influence of difference sorption conditions/environment in the update of Ni II by sugarcane pulp (bagasse) and maize cob.

2. EXPERIMENTAL PROCEDURES

Preparation of Biomass

The maize (Zea mays) cob was supplied as dry cobs by a local farm in Ijagun, Ogun State, Nigeria and used as the bio-sorbent. The dry cobs were rinsed with distilled water, dried in an oven at 333K until constant mass is attained and cut into pieces. Harvested sugar cane (saccharum officinarum) was crushed to extract the juice and the left over, pulp, was also washed with distilled water, cut into pieces and dried in an oven at 333K. The biomasses were stored in a dry place till the time of usage.

Metal Solution

The chemical used for the study were analytical grades of Nickel triocosulphate (vi) {$NiSO_4.6H_2O$} manufactured by M & B U.K., Trioxonitrate [v] acid {HNO_3} and sodium hydroxide (NaOH). Stock solution of 1000mg/L Ni (II) was prepared from $NiSO_4.6H_2O$ in distilled, deionized water that contained a few drops of 0.1 mol/L of HNO_3/NaOH to prevent precipitation of Ni (II) by hydrolysis. The solution as diluted as required to obtain working solutions. The initial pH of the working solutions was adjusted to 5.0, the optimum pH, by drop-wise addition of HNO_3 or NaOH except for the experiment examining the effect of pH. Fresh dilutions were used for each sorption study.

Method Of Absorption Study

Each of the batch biosorption studies was carried out by contacting the biomass with the metal ions under different conditions for a period of time in a glass tube. Studies were conducted at 28^{0}C (301K) to determine the effect of initial solution pH, contact time and initial ion concentration on the biosorption of Ni (II) ions. The effect of varying temperature was also studied. Each experiment was conducted in a thermostated water bath {HH-S model quality standard YY91037} and the residual metal ions analyzed using Atomic Adsorption spectrophotometer {Buck scientific 210 VGP}. The amount of metal ions biosorbed from solution was determined by difference and the mean value was calculated for each set of experiment.

Effect Of Solution pH On Biosorption

The effect of pH on the adsorption capacity of maize cob and sugarcane pulp on Ni (II) was carried out within the range that would not be influenced by the metal precipitated {Pavasant et al, 2006}. Since the suitable pH ranges for the sorption of different metal ions were slightly different, the suitable pH ranges for Ni (II) ions should be 2-7. The procedure used is similar to those earlier reported (Vasuderan et al, 2003; Xu et al 2006; Babarinde et al, 2006). Experiment were conducted at 28^{0}c to study the effect of initial solution pH on the biosorption of Ni (II) by contacting 0.5g of the sugarcane pulp and maize cob with the Ni (II) solution in a glass tube.

Using pH meter Jenway 3510, the pH of each of the solutions was adjusted to the desired value (2 – 7), with drop-wise addition of 0.1M sodium hydroxide and or 0.1M trioxonitrate [v] acid. The glass tubes containing the mixture were left in a water bath for 24hrs. The biomass was removed from the solution by decantation and the residual Ni (II) concentration in the solution was analyzed. All studies were conducted in triplicate and the mean value was determined for each. Subsequent biosorption experiments were performed at the optimum pH 5.

Effect Of Contact Time On Biosorption

Batch biosorption tests were done at different contact time at initial concentration of 100mg/L for Ni (II) using 0.5g of maize cob and sugarcane pulp at the optimum pH. The temperature was controlled with a water bath at the temperature of 301K. The samples were then collected at different intervals (0, 15, 30, 45, to 120 minutes), and were centrifuged. The concentration of metal ions in the supernatant solution was analyzed using Atomic Absorption spectrophotometer. Each determination was repeated three times and the results, which were the average values, plotted against time.

Effect Of Temperature On Biosorption

Using the biomass dose of 0.5g each, pH 5.0 and constant initial concentration of Ni (II), the flasks were shaken at a contant speed of 120rpm in a shaking water bath at temperature 28, 33, 38, 43 and 50^{0}C respectively. The samples were then centrifuged, and analysed as described above.

Effect Of Concentration On Biosorption

Batch sorption test were done at different concentration range of 200mg/L – 1800mg/L at optimum pH for a contact time of 20hrs at 301k with 0.5g of the maize cob and sugarcane pulp weighted into each of the metal ion solution. The maize cob and sugarcane pulp were removed from the mixture by decantation and the residual ions in the solution were determined.

The biosorption capacity q_e of the sludge is expressed as milligrams of biosorbed ions per gram of dry mass of the biomass [mg g-1] and the removal efficiency of metallic ion [%E] were calculated by equations 1 and [2] respectively.

$$q_e = v\left(\frac{C_i - C_e}{m}\right) \text{ -- (1)}$$

$$\%E = 100\frac{C_i - C_e}{C_i} \text{ ------------------------------------- (2)}$$

Where q_e is the amount of metal ions absorbed per unit weight of cob and bagasse in mg/g, v the volume of solution treated in L, C_i the initial metal ion concentration in mg/L, C_e the equilibrium metal ion concentration in mg/L and m is the dry weight of biomass in g.

The results obtained were analyzed using both Freundlich (Freundlich 1906) and Langmuir (Langmuir, 1918) isotherms. The Freundlich isotherm in linearized form is

$$\log q_e = \frac{1}{n}\log C_e + \log K_F \text{ ------------------------- (3)}$$

Where n and K_F are Freundlich constants. While the Langmuir isotherm (T. J. Cassey 2001) in linearized form is

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{-1}{b_m}\frac{1}{C_e} \text{ -- } (4)$$

Where b_m is a coefficient related to the affinity between the sorbent and the sorbate, and q_m is the maximum sorbate uptake under the given condition.

4. RESULT AND DISCUSSION

Kinetics of the biosorption process

The effect of contact time on nickel biosorption by maize cob and sugarcane pulp were shown in fig 1. It could be seen that the adsorptive quantity of nickel on maize cob and sugarcane pulp (bagasse) initially increased as the contact time increased and got to its maximum biosorption within 40 min.

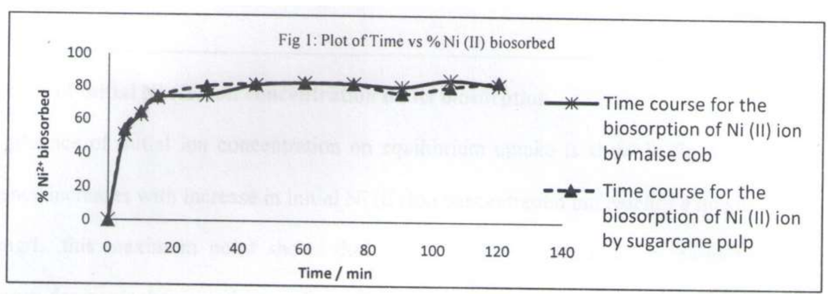

Fig 1

The reaction involved the biosorption of metal ion from the liquid phase to the soild phase. It is considered as a reversible reaction with equilibrium been made between the two phases and thus the pseudo-first order kinetic model by Lagergren was used to establish the rate of reaction. The pseudo-first order rate equation (Ahmed et al 2008, Goel et al 2005; Kavitha and Namasivayam 2007) is

$$\ln (q_e - q_t) = \ln q_e - k_1 t \text{ ----------------------------------- } (5)$$

Where q_e and q_t (mg/g) are the amounts of the metal ions biosorbed at equilibrium (mg/g) and t (min), respectivelt and k1 is the rate constant of the first-order equation (min-1).

The plot of ln ($q_e - q_t$) versus for the biosorption of Ni (II) ion by maize cob and sugarcane pulp at initial concentration of 100mg/L obey the pseudo-first order reversible kinetics. The overall rate constant of the biosorption (k1) was calculated from the slope of the curves. As could be seen in figs 2 and 3 the Lagergren first order rate constant obtained for this study are 0.0193 min^{-1} and 0.0192 min^{-1} for maize cob and sugarcane pulp respectively.

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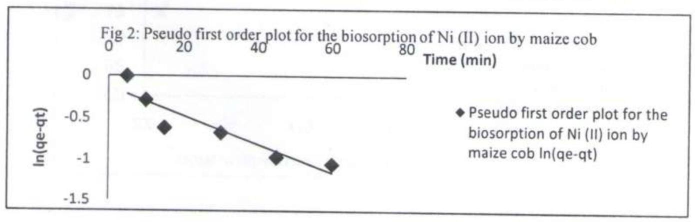

Fig 2

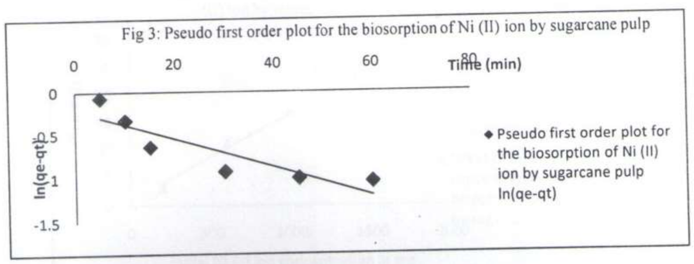

Fig 3

The effect of Initial Ni (II) ion concentration on its biosorption

The influence of initial ion concentration on equilibrium uptake is show in fig 4. The biosorption efficiency increases with increase in initial Ni (II) ion concentration but reaches a maximum at around 600 mg/L, this maximum point shows that as the metal/biomass ratio increases the biosorption efficiency decreases, because the no of metal ions competing for the fixed number of bonding sights increases. Thus the higher the concentration of the metal ion, the higher the amount of metal ion left in solution. For a biosorbent having carboxyl functional group, the reaction mechanism have been shown by (Goel et al, 2005) to be

$$2CxOH^{+} + M^{2+} \rightleftharpoons (CxO)_2M^{2+} + 2H^{+}$$

An increase in metal ion concentration will cause more H^{+} to be released thereby causing decrease in the pH. Invariably, this would lead to decrease in biosorption efficiency. The biosorption capacity of Ni (II) by the maize cob and sugarcane pulp is also plotted against initial concentration of Ni (II) ion and shown in fig 5

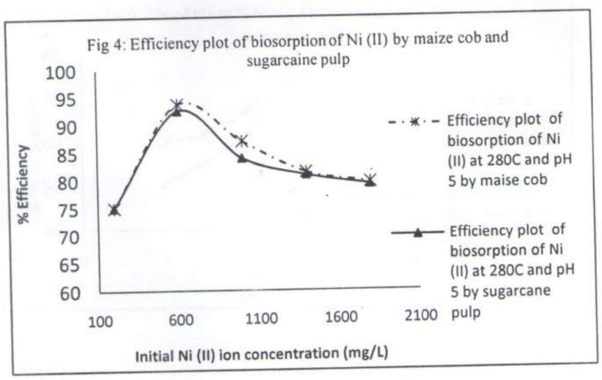

Fig 4

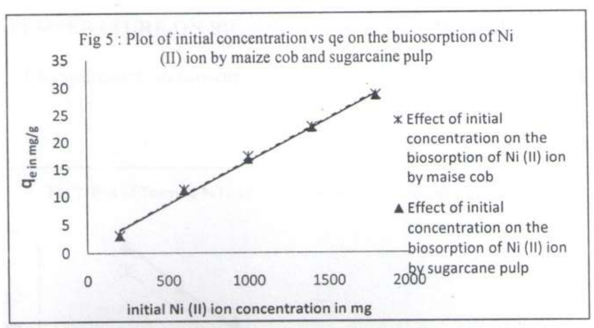

Fig 5

THE EFFECT OF Ph ON BIOSORPTION OF Ni (II) BY MAIZE COB AND BAGASSE

The pH of the solution is perhaps the most important parameter for biosorption as it was reported that biosorption capacities for heavy metals are strongly pH sensitive (Goel et al, 2005). Sorption of heavy metals from solution depends on properties of adsorbent and molecules adsorbed from the solution to the solid phase. There is an increase in biosorption capacity of biomass with increasing pH from 3 to 7 for Ni (II) ions are shown in fig 6. Under acidic condition, both the biosorbent and the metal ion are positively charged thereby causing electrostatic repulsion (Goel et al, 2005).

Increase in the concentration of H^+ through decrease in pH causes increase in competition with the positively charged metal ions. At pH values above the isoelectric point, there is a net negative charge on the sell wall components and the ionic state of ligands such as carboxyl, phosphate and amino groups will promote reaction with metal cations.

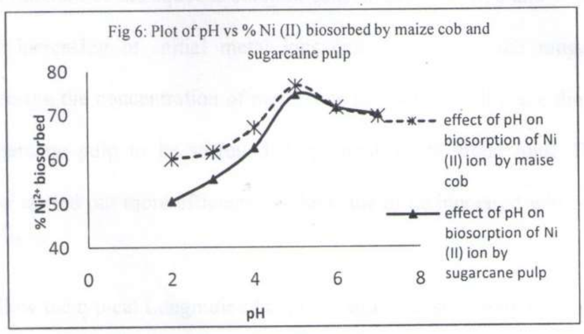

Fig 6

The Effect Of Temperature On Biosorption Of Ni (Ii) By Maize Cob And Bagasse

The effect of temperature on biosorption on Ni (II) by biomass is shown in fig 7.

For both biomasses, with the temperature rising, the adsorptive quantity of nickel was decreasing. This in agreement with the observation of R.P.Han, (2006), on the effect of temperature on biosorption of nickel (II) using cereal chaff. It shows that the process is exothermic.

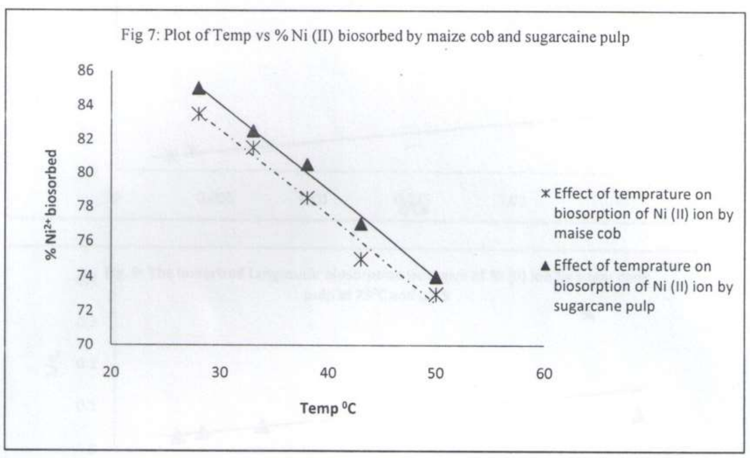

Fig 7

Adsorption Isotherms

Sorption isotherm represents the concentration dependent equilibrium distribution of metal ions between aqueous and solid phase. The metal ion equilibrium levels of maize cob and sugarcane pulp are represented as a function of the aqueous solution concentration in fig 8 and 9. Equilibrium uptake increase with the increasing of initial metal ions concentration at the range of experimental concentration. Increasing the concentration of metal ions in solution will make the active sites of the maize cob and sugarcane pulp to be surrounded by much more metal ions.

The process of the adsorption would be carried out more efficient. So the value of q_e increased with increasing of metal ion concentrations.

These isotherms follow the typical Langmuir adoption pattern as shown by the linear transformation in equation 4. The Langmuir model is based on the assumption of a single layer adsorption on a complete homogeneous surface. P.Y in et al, in (2000) did observe that the inspite of this; it has often been used as a model for metal adsorption on various types of biosorbents even though the metal uptake may not exactly follow the single layer adsorption mechanism.

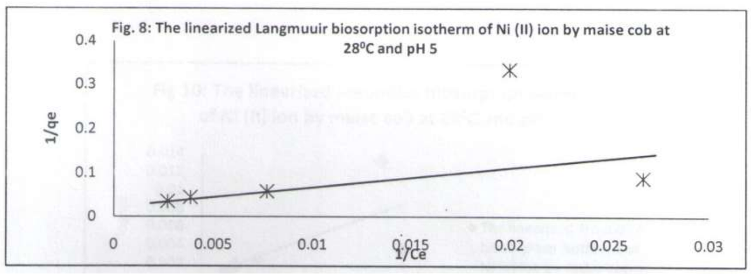

Fig 8

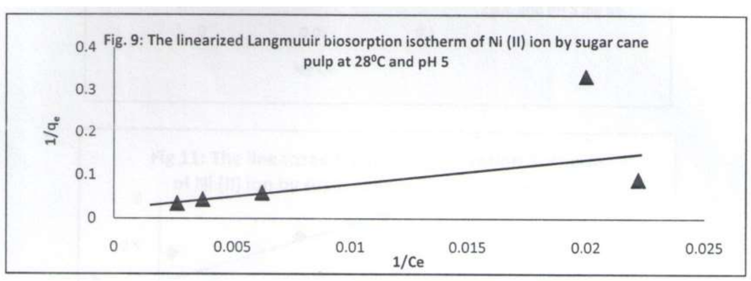

Fig 9

The equilibrium established between the adsorbed metal ions q_e and that remaining free in the solution C_e was also represented by the Freundlich adsorption isotherms, (equation 3).

The equilibrium data of nickel (II) ion adsorption by cob and pulp obtained at 301k was applied to Langmuir and Freundlich models. The related parameters and correlation coefficients (R) were listed in table 1.

Table 1: Parameters for the application of Langmuir and Freundlich model to the biosorption of Ni (II) ion on maize cob and sugarcane pulp.

Metal/Biomass	Langmuir Constants				Freundlich Constacts		
	K_1(l/mg)	b_m	q_{max}	R	K_1	n	R
Ni (II) ion on maize cob	.00203	0.166	57.1	0.900	1.001	0.084	0.910
Ni (II) ion on sugarcane pulp	.00134	0.112	83.3	0.901	25.119	0.737	0.900

Greater values of $1/K_L$ mean higher affinity of biosorbent to the investigated metals. Consequently, the preference of investigated biosorbent for metal ions is as follows: Ni on pulp > Ni on cob.

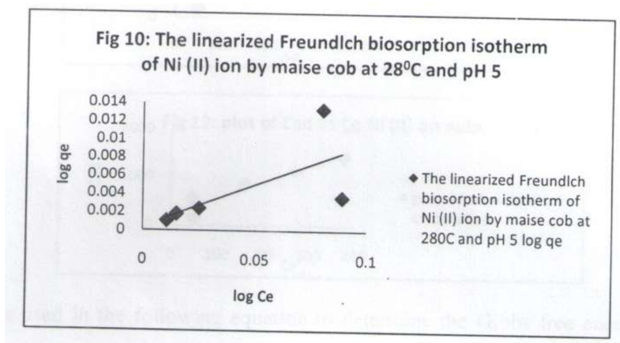

Fig 10

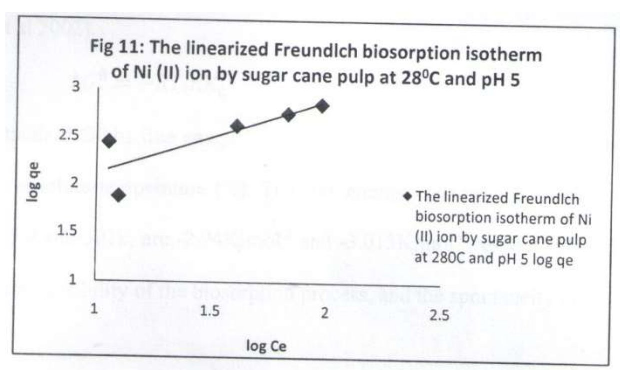

Fig 11

The Freundlich and Langmuir parameters obtained compare well with those of other biosorbents that have been reported (Akar and Tunali 2006, Kavitha and Namasivayam, 2007). The values of the parameters show that maize cob bagasse is a good biosorbent for the removal of Ni (II) ions from waste water.

Thermodynamics Of The Biosorption Process

The biosorption process of metal ions can be summarized by the following reversible process which represents a heterogeneous equilibrium. The apparent equilibrium constant (K_c) of the biosorption is defined as (R.P HAN 2006).

$$K_c = C_{ad}/C_e \text{ ------------------------------------ } (6)$$

Where C_{ad} is the concentration of metal ion on the adsorbent at equilibrium. The slope of the plot (figs 12 and 13) of C_{ad} versus C_e gives K_c value.

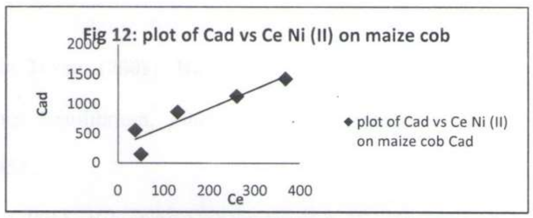

Fig 12

The K_c value is used in the following equation to determine the Gibbs free energy of biosorption (ΔG^0) (Z Aku et al 2002).

$$\Delta G^0 = -RTlnKc \text{ -------------------------------- } (7)$$

Where ΔG^0 is standard Gibbs free energy change ($Kjmol^{-1}$), R the universal gas constant $8.314jmol^{-1}k^{-1}$ and T is the absolute temperature (K). The free energy changes for Ni (II) on to cob and pulp determine at pH 5.0 and 301k, are $-2.94Kjmol^{-1}$ and $-3.013Kjmol^{-1}$ respectively the negative values of ΔG^0 validate the feasibility of the biosorption process, and the spontaneity of biosorption.

5. CONCLUSION

The results of experiment showed that the maize cob and sugarcane pulp (bagasse) has come ability to adsorb Ni (II) from solution. Different variables such as contact time, adsorbent dose, solution pH and temperate influenced the adsorptive quantity. The process of biosorption has nearly reached equilibrium in 40min and the optimum pH is near 5.0 increasing the initial concentration of Ni (II) results in higher adsorptive quantity. The experimental data of adsorbing Ni (II) fit well to Langmuir and Freundlich model and the maximum adsorptive quantity of cob and pulp are in accordance to Langmuir model. Maize cob and sugarcane pulp can adsorp Ni (II) from solution.

Acknowledgements

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