Thursday, January 21, 2016
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Jr. of Industrial Pollution Control 31(1)(2015) pp 129-134

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ISOTHERMS STUDIES OF EQUILIBRIUM SORPTION OF NI (II) ION ON *VIGNAUNGUICULATA* HUSK

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(Received ; accepted , 2014)

Key words: Ni (II) metal ion, Isotherms, Sorption and *Vignaunguiculata* husk.

ABSTRACT

Equilibrium sorption of Nickel on *Vignaunguiculata* husk was studied using batch adsorption method. The applicability of Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin equations was investigated. Of the four adsorption isotherms, the R^2 value of Temkin isotherm model was the highest and exhibited the best fit with the experimental data. The maximum monolayer coverage (Q_0) from Langmuir isotherm model was determined to be 2000.00 mg/g, the separation factor indicating a favorable sorption experiment is 0.594. According to Freundlich isotherm model the sorption intensity (n) which is indication of favorable sorption is 0.692 with correlation coefficient 0.945. The heat of adsorption process was determined from Temkin isotherm model (1626.009 J/mole) and the mean free energy was estimated from Dubinin-Radushkevich isotherm model (8.558 x 10-4 J/mol). Which indicate that adsorption experiment followed a physical process.

INTRODUCTION

Inorganic effluents from the industries contain toxic metal ions which tend to accumulate in the food chain. The toxic heavy metal ions have high solubility in the aquatic environments and thus they can be absorbed by living organisms. Once they enter the food chain, large concentrations of heavy metal ions may accumulate in the human body. If the metal ions are ingested beyond the permitted concentration, they can cause serious health disorders (Dadhaniya and Patel, 2009). Existence of heavy metal ion pollutants in water results in ecological problems even at very low concentration which increased the need for materials that can provide efficient complexing potential toward these metal ions (Essawy and Ibrahim, 2004).

Nickel is a toxic metal, which may present in wastewater. Nickel salts are commonly used in metal plating and its concentration in industrial waste waters range from 3.40 to 900 mg L^{-1}. Maximum permissible limit for Nickel in bottled water has been fixed as 50 mg L^{-1} by European Economic Community (D em irbas *et al.*, 2002). The chronic toxicity of Nickel to humans and the environment is well known and high Nickel concentration causes lungs and bone cancers. Considerable research has been carried out

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in developing Nickel removal techniques. Conventional method such as chemical precipitation, chemical oxidation or reduction, filtration, electrochemical treatment, ion exchange, adsorption, membrane processing and electrolytic methods, have been traditionally employed for heavy metal removal from industrial wastewater (Dar *et al.*, 2011). However, the shortcomings of most of these methods are of high operational and maintenance costs, generation of toxic sludge and complicated procedure involved in the treatment. Comparatively, adsorption process is considered better in water treatment because of convenience, ease of operation and simplicity of design (Jirekar *et al.*, 2013). Furthermore, this process can remove/minimize different type of pollutants and thus it has a wider applicability in water pollution control. Activated carbon is undoubtedly considered as universal adsorbent for effluent treatment and is commonly used for the removal of various pollutants from water . However, its widespread use in wastewater treatment is sometimes restricted due to its higher cost. A large variety of nonconventional adsorbents have been examined for their ability to remove various types of pollutants from water and wastewater. It has been found that various low-cost adsorbents developed from different origins show little or poor sorption potential for the removal of aquatic pollutants as compared to commercial activated carbon. Therefore, the search to develop efficient sorbents is still going on. From last few decades, bio-sorption process has emerged as a cost effective and efficient alternative for water and wastewater treatment utilizing naturally occurring and agricultural waste materials as bio-sorbents as these are cheaper, renewable and abundantly available. At present, biosorption field has been enriched by a vast amount of studies published in different journals.

Agricultural materials contain proteins, polysaccharides and lignin which are associated with functional groups responsible for metal ion adsorption (Wase and Forster, 1997). The abundant natural occurrence and presence of large amount of surface functional groups make various agricultural wastes good alternatives to expensive synthetic adsorbents (Bulut *et al.*, 2007). In recent years, agricultural byproducts have been widely studied for metal removal from water. These include peat, wood, pine bark, banana pith, soybean and cottonseed hulls, peanut, shells, hazelnut shell, rice husk, sawdust, wool, orange peel, and compost and leaves (Hasar, 2003). The use of orange peel as a bio-sorbent material presents strong potential due to its high content of cellulose, pectin (galacturonic acid), hemicellulose and lignin. As a low cost, orange peel is an attractive and inexpensive option for the bio-sorption removal of dissolved metals. (Ajmal *et al.*, 2000) employed orange peel for metal ions removal from simulated waste water (Wan Ngah *et al.*, 2007; Ajmal *et al.*, 2000). Some authors reported the use of orange waste as a precursor material for the preparation of an adsorbent by common chemical modifications such as alkaline, acid, ethanol and acetone treatment (Li *et al.*, 2007; Liang *et al.*, 2009). Other low cost material is also used for the removal of metals and dyes from aqueous system (Abdo Taher, *et al.*, 2011; Hussain *et al.*, 2010; Hussain *et al.*, 2011; Jirekar *et al.*, 2014)

In the present study *Vignaunguiculata* husk is an agricultural waste material, a hard protecting covering of seeds obtained from the wet seeds of *Vigna unguiculata*. It has many applications in household, industries, animal food and even in the treatment of direct dyes. It is used as adsorbent for the removal of Nickel from wastewater.

MATERIALS AND METHODOLOGY

Preparation of the adsorbent

Vigna unguiculata seeds were purchased from a local market. The mature and fresh seeds of purchased biomaterial were extensively washed under tap water to remove any particulate then to soak the beans overnight. The husk of soaked beans are separated from their pulses, then washed with distilled water and dried in shadow (Selvaraju and Pushpavanum, 2009). The dried husks were grinded to fine powder. The homogeneous powder was obtained by passing through mesh of desired particle size (44-60 µm). The homogeneous fine powder adsorbent was stored in an air tight container for the adsorption study for further experiments.

Materials

All the chemicals used were of analytical grade. Ammonium Nickel sulphate [$NiSO_4 (NH_4)_2.6H_2O$] was purchased from Sd. Fine Chemicals Pvt. Ltd. Mumbai (India). All solutions were prepared in double distilled water. The concentration of Nickel (II) metal ion solutions were determined by using UV-Visible single beam Spectrophotometer, (Bio Era: Cal No.BI/CI/SP/SB-S-03). Stock solution of Nickel metal ion (100 ppm) was prepared by weighing and dissolving

0.675 g of ammonium Nickel sulphate [$NiSO_4 (NH_4)_2.6H_2O$] in one liter of double distilled water in graduated volumetric flask and used to prepare solutions in different concentrations. The concentration of solution was determined from calibration curve spectrophotometrically. The absorbance was determined at 366 nm against blank.

Sorption Experiments

Batch adsorption experiments were carried out at temperature 304.5 K in 250 mL glass stoppered Erlenmeyer Flasks by adding 0.5 g of the *Vignaunguiculata* husk adsorbent in 50 mL Nickel (II) metal ion solution of the 5 ppm -20ppm initial concentration and 6.0 pH. The residual amount of the Nickel (II) metal ion in each flask was studied by using UV/VIS spectrophotometer. The amount of adsorbed (mg/g) was calculated using the formulae,

$$q_e=(V(Co-Ce))/M \qquad (1)$$

where, q_e is the adsorption capacity equal to the amount of Nickel (II) metal ion adsorbed at equilibrium (mg/g), *V* is the volume of the solution (mL), *M* is the mass of the adsorbent (g), *Co* and *Ce* are the initial and the equilibrium solution concentrations, respectively. The data was fitted into the following Isotherms: Langmuir, Freundlich, Temkin and Dubinin-Radushkevich. The percent removal (%) of Nickel (II) metal ion was calculated by using the following equation:

The percentage adsorption was calculated by following equation;

$$\text{Percentage adsorption} = \frac{(C_o)-C_e)}{C_o} *100 \qquad (2)$$

Where, C_0 and C_e are the initial and equilibrium concentrations respectively.

RESULTS AND DISCUSSION

Sorption Isotherms of Nickel (II) metal ion

The equilibrium sorption of the Nickel (II) metal ion was carried out by containing 0.5g. of the *Vignaunguiculata* husk with 50 mL. of 100 mg/L of different concentrations from 5 mg/L - 20 mg/L in conical flasks shaking intermittently for 24 hrs. The mixture was filtered and filtrate analyzed for Nickel (II) metal ion concentration using UV-Visible single beam Spectrophotometer, (BioEra: Cal No.BI/CI/SP/SB-S-03). The data was fitted into the following isotherms

Isotherm Studies

The equilibrium adsorption isotherm is important in the design of adsorption systems (Bulut and Aydin, 2006). In general, the adsorption isotherm describes how adsorbate interact with adsorbents and this is critical in optimizing the use of adsorbents, The relationship between the amount of a substance adsorbed at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm.

Langmuir Isotherm Model

The Langmuir adsorption model is given by:

$$\frac{bC_e}{q_e=Q_0\ 1+bC_e)} \qquad (3)$$

The Langmuir equation can be described by the linearized form

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0\, b\, C_e} \qquad (4)$$

Where C_e is the equilibrium concentration of the adsorbate, the amount of adsorbate per unit mass of adsorbent (mg/g), and Q_0 and b are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. The Langmuir constants, Q_0 and b were evaluated from the intercept and the slope of the linear plot of experimental data of 1/qe versus $1/C_e$ and presented in Table 2. The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless separation factor, R_L, defined as .

$$\frac{1}{R_L=1+bC_0} \qquad (5)$$

Where, C_o is the initial ion concentration, b the Langmuir's adsorption constant (L/mg). The R_L value implies the adsorption to be unfavourable ($R_L > 1$), Linear ($R_L = 1$), favourable ($O<R_L<1$), or irreversible ($R_L=0$) R_L values for Ni^{2+} on the adsorbents were less than 1 and greater than zero indicating favourable adsorption under conditions used in this study. However, the values of R_L for Ni^{+2} adsorption on *Vignaunguiculata* husk ranges from 0.7698 to 0.4553 (5ppm to 20 ppm) indicating favourable adsorption. The correlation coefficients showed that Ni^{2+} adsorption on adsorbents follow Langmuir.

A

Freundlich Isotherm Model

The Freundlich adsorption isotherm can be written as,

$$q_e = K_f C_e^{1/n} \qquad (6)$$

A linear form of this expression is,

$$\log q_e = \log K_f + 1/n \ \log C_e \qquad (7)$$

Where K_f and n are Freundlich constants, *n* giving an indication of how favorable the adsorption process is and K_f is the adsorption capacity of the adsorbent. K_f and n are determined from the linear plot of log qe versus log C_e. From the linear plots of Inqe versus In C_e, values of Freundlich constants K_f and n were calculated from the intercept and slope, respectively, and are presented in Table 2. The K_f which is a measure of adsorption capacity, decreased with temperature. The magnitude of the exponent, n gives an indication of the favourability and capacity of the adsorbent/adsorbate system. Halnor *et al.*, (2012) has reported that n values between 1 and 10 represent favourable adsorption conditions. The exponent is $n<1$, showing, adsorption conditions are not favourable for the system. The correlation coefficient, R^2 (0.945) indicating that Ni^{2+} adsorption not followed Freundlich model.

Temkin Isotherm

The Temkin isotherm has been used in the following form,

$$q_e = \frac{RT}{b} \ln(AC_e) \qquad (8)$$

A linear form of the Temkin isotherm can be expressed as

$$q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e \qquad (9)$$

Where $RT/b = B$ and A is Temkin constant, *l/g*. The adsorption data can be analyzed according to equation 9 and the constant *B* determines the heat of adsorption. The values of Temkin constants *A* and *b* as well as the correlation coefficients are listed in Table 2. The correlation coefficient was 0.9996. Generally, data fairly conformed to Temkin isotherm model.

Dubinin-Radushkevich Isotherm Model

The Dubinin – Radushkevich equation has the following form:

$$q_e = q_m^{\,e} - \beta\varepsilon^2 \qquad (10)$$

A linear form of Dubnin – Radushkevich equation isotherm is

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \qquad (11)$$

Where is the Dubinin– Radushkevich monolayer capacity (*mmol / g*), β a constant related to sorption energy, and e is the Polanyi potential which is related to the equilibrium concentration as follows,

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \qquad (12)$$

Where, *R* is the gas constant (8.314J/molK) and *T* is the absolute temperature. The constant gives the mean free energy, *E* of sorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using relationship.

$$E = \frac{1}{\sqrt{2B}} \qquad (13)$$

The Dubinin-Radushkevich constants were evaluated and given in Table 2. The correlation coefficient was 0.945, indicates that the adsorption of Ni^{2+} on *Vigna unguiculata* husk follows the Dubinin-Radushkevich isotherm. If the mean free energy, *E* is <8KJ/mol, the adsorption is physisorption and if the energy of activation is 8-16KJ/mol, the adsorption is

Table 1. Parameters for plotting Langmuir, Freundlich, Temkin and Dubinin-Radushkevich Adsrption Isotherms of Ni (II) metal ion on *Vigna unguiculata* husk.

Sr. No.	C_0 (mg/L)	C_e (mg/L)	$1/C_e$	Log C_e	Ln C_e	q_e (mg/L)	$1/q_e$	Log q_e	Ln q_e	C_e/q_e (g/L)	ε2
1.	5	1.574	0.635	0.197	0.453	342.62	0.0029	2.534	5.837	0.0046	1550712
2.	10	2.109	0.474	0.324	0.746	789.07	0.0012	2.897	6.671	0.0026	965052
3.	15	2.612	0.383	0.417	0.960	1238.79	0.0008	3.093	7.122	0.0021	673402
4.	20	3.514	0.284	0.546	1.257	1648.63	0.0006	3.217	7.408	0.0021	402002

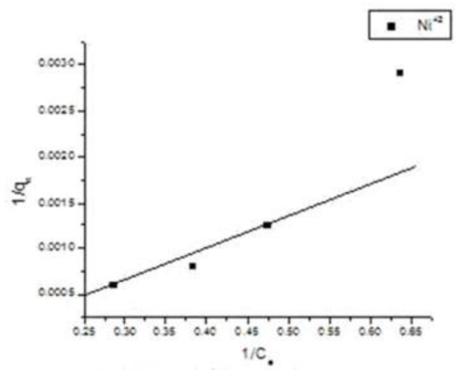

Fig1:Langmuir Adsorption Isotherm

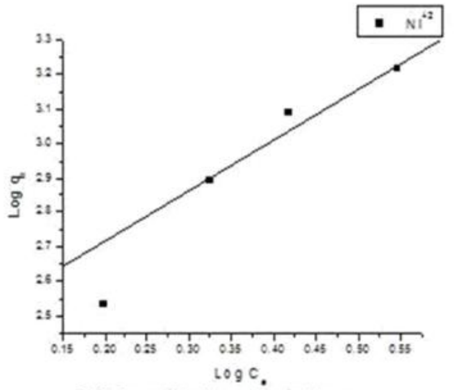

Fig2:Freundlich Adsorption Isotherm

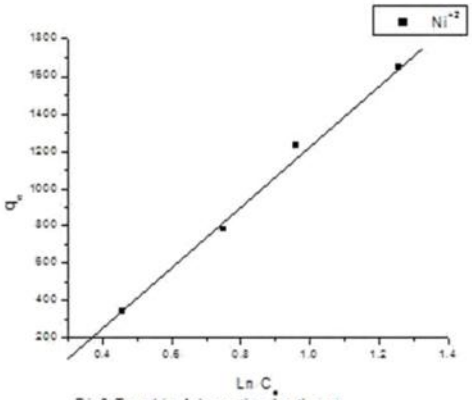

Fig3:Temkin Adsorption Isotherm

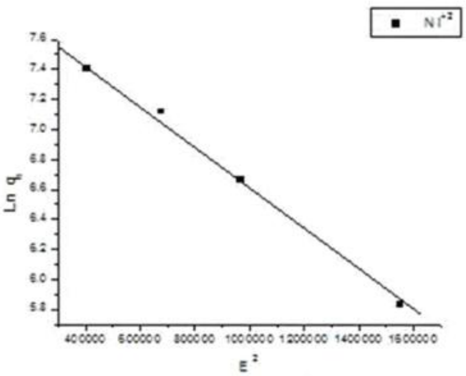

Fig4:Dubinin-Radusnkevich Adsorption Isotherm

Table 2. Parameters for plotting Langmuir, Freundlich, Temkin and Dubinin-Radushkevich Isotherms constants for the adsorption of Ni (II) metal ion on *Vigna unguiculata* husk.

	Langmuir Isotherms				Freundlich Isotherms		
Q_0 (mg/g)	b(L/mg)	RL	R^2	1/n	n	K_f(mg/g)	R^2
2000.0	0.0598	0.5945	0.827	1.444	0.692	446.68	0.945
	Temkin Isotherms				Dubinin-Radushkevich Isotherms		
AT(L/mg)	b_T	B	R^2	q_s(mg/g)	K_{ad}(mol^2/kJ)	E(kJ/mol)	R^2
1.057	1.557	1626.009	0.987	1844.57	682588.1	$8.56*10^{-4}$	0.945

chemisorptions in nature. Results of *E* obtained indicate that adsorption of Ni^{2+} on *Vignaunguiculata* husk was physisorption.

CONCLUSION

In this paper, investigation of the equilibrium sorption was carried out at 304.5K and 6.0 pH. The sorption data fitted into Langmuir, Freundlich, Temkin and Dubunin-Radushkevich isotherms out of which Temkin adsorption model was found to have the highest regression value and hence best fit. It could be concluded that *Vigna unguiculata* husk is a potential and active bio-sorbent for removal of Ni (II) metal ion from its aqueous solution and industrial waste water remediation.

ACKNOWLEDGEMENTS

One of the authors (D.B.Jirekar) is thank-ful to UGC (WRO) Pune for financial support .F.No.47-2031/ 11(WRO),Date.22 Feb 2012.

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