

Adsorption Kinetics Of Nickel (II) Onto Activated Carbon Prepared From Natural Adsorbent Rice Husk.

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ABSTRACT: The batch adsorption of Ni(II) onto activated carbon prepared from an agriculture applies to analyze adsorption data and were found to be applicable to these adsorption process. The reaction was effect of initial concentrations, adsorption dose, contact time and pH dependent .The latter was found to control efficiency of nickel removal. The kinetics of adsorption and extent of adsorption at equilibrium are rice husk has been studied. Langmuir and Freundlich adsorption isotherm models were dependent on the physical and chemical characteristics of the adsorbent, adsorbate and experimental system. In comparison with other metals, nickel removal is poor, and possible reasons are discussed. The results show that the amount of adsorption of Ni⁺⁺ increases with initial metal ion concentration, contact time and solution PH but decreases with amount of adsorbent and temperatures. The adsorption process has fit pseudo-first order kinetic model. Thermodynamic parameters e.g. ΔG° , ΔS° and ΔH° of the adsorption process was found to be endothermic. Finally it can be seen that activated carbon was found to be effective for removal of Ni⁺⁺.

KEY WORDS: Natural adsorbent, Nickel, Activated carbon, Langmuir and Freundlich Isotherm.

INTRODUCTION

Heavy metal pollution is environmental problem of global concern [1]. Nickel is a non-biodegradable toxic heavy metal ion present in waste water. The main source of nickel pollution in the water derives from industrial production processes such as galvanization, smelting mining, dyeing operation, batteries manufacturing and metal finishing [2]. Trace amounts of nickel are beneficial to human organism as an activator of some enzyme system, but if it is beyond the scope of normal levels, different types of diseases occur such as lung cancer, renal edema, skin dermatitis and gastrointestinal disorder. For this reason, the Water Sanitation and Hygiene (WSH) under World Health Organization (WHO) established the toxic limits of permissible concentrations of nickel at a level of Ni (II) and insoluble compounds of 1.0 mg/m³, soluble compounds of 0.1mg/m³, nickel carbonyl of 0.05-0.12 mg/m³, and nickel sulphide of 1.0mg/m³, [3,4]. The conventional methods of Ni (II) removal from water include chemical oxidation or reduction, chemical precipitation, ion exchange, membrane separation, filtration, electrochemical treatment and adsorption, etc. As an economical and efficient method, adsorption technique has been widely applied to remove heavy metal ions from waste water. . Numerous materials have been used as adsorbents for the removal of Ni (II) processes including activated carbon, silica, ion- exchange resins, rock materials, activated slag, agricultural wastes, microbial and plant derived biomass and chitin, [5]. But it remains necessary to develop a low-cost, easily available, high adsorption capacity material for waste water treatment that might remediate the Ni (II) environmental problems. In recent years, a number of novel metallic oxides have gained a growing interest since they are especially useful in the removal of heavy metal ions from waste water effluents. Industrial waste water may contain a large number of heavy metals in it. Nickel, one of them, is a non biodegradable toxic heavy metal ion present in waste water. The main source of nickel pollution in the water derives from processes such as galvanization, smelting, mining, dyeing operations, batteries manufacturing and metal finishing [2].

Trace amounts of nickel are beneficial to human organism as an activator of some enzyme systems, but if it is beyond the scope of normal levels, different types of diseases occur such as lung cancer, renal edema and skin dermatitis and gastro intestinal disorder. The main objectives of this study were; **1)** to investigate the optimum condition for the removal of nickel using activated carbon **2)** to study nickel adsorption isotherm by the rice-husk **3)** to propose the adsorption kinetics based on the experimental data.

2. EXPERIMENTAL

2.1.- Materials and Methods

Activated carbon from an agriculture by-product (rice husk) was prepared by carbonization at 500°C (50°C/15 min) followed by activation at 850°C for 1 h. The adsorption of phenolic compounds onto this activated carbon was studied using batch adsorbed methods. The experimental results showed that the carbonization was carried out by heating the rice husk in a tubular furnace (a4cmi.d.stainless steel tube mounted inside calibrated tubular electric furnace). Thus, RH was heated gradually at a rate of 50⁰C/15 min in a limited supply of air. The activation step was carried out in an atmosphere of CO₂ with the temperature maintained at 850°C for 1 h.

2.2- The removal of nickel from battery manufacturing wastewater using activated carbon.

The optimum pH value analysis

- The pH values of wastewater were controlled at 4,5 and6 by using 1M. NaOH.
- 200ml of sample was added into Erlenmeyer flask and Nickel concentration was analyzed. Then 0.05g of activated carbon was added in each sample and the rotary shaker was adjusted at 200rpm, 90 minutes.
- reated wastewater was filtered through filter paper No.4, and then the nickel concentration was determined.

2.3--The optimum contact time analysis

- 0.1 g of activated carbon was added into optimum pH wastewater (from step 1) and the magnetic stirrer was adjusted at 250 rpm with 30, 60, 90, 120 and 150 minutes.
- Treated wastewater was filtered through filter paper No.4, and then the nickel concentration was determined.

2. 4-The optimum dose of activated carbon analysis

- 200 of optimum pH wastewater was added into Erlenmeyer flask, and then nickel concentration was analyzed.
- 0.1, 0.3, 0.5, 0.7, and 1.0 g of activated carbon was added into each sample and the rotary shaker was adjusted at 200 rpm with optimum contact time (from step 2).
- Treated wastewater was filtered through filter paper NO.4, and then the nickel concentration was determined.

2.4- Study of adsorption isotherm

Data from step 3 were used to study adsorption isotherm for determining the best adsorbent. Langmuir, and Freundlich, adsorption isotherms are the most commonly used for the description data [6].

2.5-Statistical analysis

The removal efficiency (%) = $(A - B) / A \times 100$ [7]. Then, A = Initial concentration (mg/L), B = Final concentration (mg/L). The results were investigated by using the least significant differ.

3. RESULTS AND DISCUSSION

Adsorption kinetics

The kinetics study for the adsorption of Ni²⁺ was completed in 2 h for the concentrations (50, 100, 150, 200 and 300 mg/L) Ni²⁺ ions on to (0.1, 0.3, 0.5, 0.7 and 1.0 g/200 mL) doses of natural activated carbon at 25°C. The experimental results for the adsorption of Ni²⁺ ions rice husk (RH) showed rapid initial adsorption rate followed by a slower rate. Initially, the adsorption sites are open and the metal ions interact easily with the sites and hence a higher rate of adsorption is observed. Further, the driving force for adsorption (the concentration difference between the bulk solution and the solid-liquid interface) is higher initially and this leads to a higher adsorption rate. However, after the initial period, slow adsorption may be due to slower diffusion of solute into the interior of the adsorbent. Several adsorption kinetics models have been developed to understand the adsorption kinetics and rate limiting step [17-20]. Two kinetic models were considered to investigate the mechanism of nickel adsorption, as follows: Lagergren proposed a pseudo-first order kinetic model, the integral form of the model is:

$$dq/dt = k_1(q_e - q) \quad (1)$$

$$\ln(q_e - q) = \ln q_e - k_1 t \quad (2)$$

where *q* is the amount of nickel sorbed (mg/g) at time *t* (min), *q_e* is the amount of nickel sorbed at equilibrium

(mg/g), *K₁* is the equilibrium rate constant of pseudo-first order adsorption (min⁻¹). This model was successfully applied to describe the kinetics of many adsorption systems. The adsorption kinetics may also be described by a pseudo-second order reaction. The linearized-integral form of the model is:

$$dq/dt = k_2(q_e - q)^2 \quad (3)$$

$$t/q = t/q_e + 1/k_2 q_e^2 \quad (4)$$

where *K₂* is the pseudo-second order rate constant of adsorption. The applicability of the above two models can be examined by each linear plot of *ln(q_e-q)* vs. *t*, and (*t/q*) vs. *t*, respectively and are represented in **Figs. (1)** of rice husk. To quantify the applicability of each model, the correlation coefficient, *R²*, was calculated from these plots. The linearity of these plots indicates the applicability of the two models. However, the correlation, *R²*, showed that the pseudo-second order model, fits better the experimental data (*R²* > 0.990) than the pseudo-first order model (*R²* in the range of 0.9108 – 0.986), the kinetic parameters calculated are shown in Table 1. The kinetic parameters calculated are shown in **Table (1)**. It has been found that, the equilibrium sorption capacities determined using pseudo-second order model were in agreement with the experimentally determined equilibrium sorption capacities. The applicability of the above two models can be examined by each linear plot of *ln(q_e-q)* vs. *t*, and (*t/q*) vs. *t*, respectively and are represented in **Figs. (1) and (2)**, respectively. To quantify the applicability of each model, the correlation coefficient, *R²*, was calculated from these plots. Also, the rate constant decreased with the solution concentration increasing. In general, the adsorption reaction is known to proceed through the following three steps: **(1)** transfer of adsorbate from bulk solution to adsorbent surface, which is usually mentioned as diffusion, **(2)** migration of adsorbate into pores and **(3)** interaction of adsorbate with available sites on the interior surface of pores.

Effect of contact time.

The effect of contact time on the adsorption of Ni(II) ions onto natural activated carbon was performed by contacting of (50, 100, 150, 200, and 300 mg/L) of Ni (II) concentration at initial pH 5.5 onto (0.1, 0.3, 0.5, 0.7 and 1.0 g/200 mL) of adsorbent dose. The results are depicted in **Fig. (3)**. It is easily seen from the figure that the percentage removal of Ni (II) metal ions increased with increasing the contact time. The Ni(II) adsorption rate is high at the beginning of the adsorption because the adsorption sites are open and Ni(II) interacts easily with these sites. A larger amount of Ni(II) was removed in the first 1 h of contact time, and after that Ni(II) increased slowly till equilibrium time (2 h). The relation between the amount of adsorbed Ni(II) ions per gram of adsorbent in presence of different amounts of natural activated carbon is illustrated in **Fig (4)**. It can be seen that, *q_e* increased rapidly with increasing time till the maximum adsorption.

Effect of initial Nickel(II) ions concentration

Fig. (4) Shows the effect of varying initial concentration of Ni(II) ions from 50 to 300 mg/L on the adsorption under the optimized conditions of pH 5.5 at 25°C and (0.1, 0.3, 0.5, 0.7 and 1.0 g/200 mL) of natural activated carbon. It can be seen from the figure that, with increased Ni(II) initial concentration, there was decreases in % removal of Ni(II) for adsorbent. However, amount of metal adsorbed per unit weight of adsorbent, q , is higher at high concentration for natural activated carbon as shown in **Fig. (5)**. According to the adsorption capacity and percentage of removal are equally important in adsorption experiments because both factors usually take part in deciding the adsorption performance of given adsorbent[21].

Effect of adsorbent dose

The effect of adsorbent dosage (0.1, 0.3, 0.5, 0.7 and 1.0 g/200 mL) for natural activated carbon on % removal of (50, 100, 150, 200 and 300 mg/L) of Ni(II) ions concentrations at 25°C is shown in **Figs. (5)**. It is apparent that by increasing the dosage, % removal increased till reached maximum at 1.0 g dosage of natural activated carbon. . Increasing the percentage of adsorption with adsorbent dose may be due to the increase in adsorbent surface area and availability of more adsorption sites [22- 25] therefore, more nickel ions were able to be adsorbed. But adsorption was decreased with increasing in adsorbent dose, **Figs. (5)**. this is may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles [26]. Another possible reason could be due to note that the concentration of nickel was fixed while the adsorbent dosage was increased. Therefore, as the dosage increased, the ratio of number of adsorption sites to the number of heavy metal ions would increase and there would be plenty of unabsorbed adsorption sites.

Effect of pH on the uptake of Ni²⁺

The pH value of the solution is an important variable which controls the adsorption of the metal ions at the solid-water interface. Hence, the influence of pH on the adsorption of Ni²⁺ ions onto rise husk was examined in the pH range of (1-6). The experiment of adsorption as a function of pH was conducted at known initial concentration of 1 mg/L Ni²⁺, dose of 0.05 g/200 mL for rise husk at 25°C. These results were represented in **Fig. (6)**, it showed that the adsorption capacities of Ni²⁺ ions on to adsorbents increased significantly with increasing pH value .At low pH , the higher concentration of H⁺ ion in the solution which compete with Ni²⁺ for the adsorption site of adsorbents. Generally the positive charges of adsorbent surface decreases with increasing pH to value 6 leading to the decrease in the repulsion between adsorbent and Ni²⁺ , thus improving the adsorption capacity

Adsorption isotherm

The equilibrium adsorption isotherms are one of the promising data to understand the mechanism of the adsorption. Various isotherm equation are well known and two different isotherms are selected in this study, which are the Langmuir and Freundlich isotherms. The Langmuir adsorption isotherm assumes that adsorption takes place at specific homogeneous sites within the adsorbent and has

found successful applications in many adsorption processes of monolayer adsorption. The linearized Langmuir isotherm equation is represented by the following:

$$C_e/q_e = 1/(q_{max}b) + (1/q_{max}) C_e \quad (5)$$

Where q_{max} is the maximum metal ions uptake per unit mass of adsorbent (mg/g), which is related to the adsorption capacity and b is Langmuir constant (L/mol) which is exponentially proportional to the heat of adsorption and related to the adsorption intensity. Therefore, a plot of C_e/q_e versus C_e for the adsorption of nickel(II) ions onto natural activated carbon gives a straight line of the slope $1/q_{max}$ and intercept $1/q_{max}b$ as shown in **Fig.(7)**.

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The linearized form of the Freundlich isotherm equation(6) is:

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (6)$$

where the Freundlich constants K_F and n , which respectively indicating the adsorption capacity and the adsorption intensity, were calculated from the intercept and slope of the plot of $\ln q_e$ versus $\ln C_e$ for the adsorption of nickel²⁺ ions onto natural activated carbon as shown in **Fig. (8)**. The Langmuir and Freundlich parameters for the adsorption of (50, 100 ,150, 200 and 300 mg/L) initial concentrations of nickel(II) on (0.1, 0.3, 0.5, 0.7 and 1.0 g/200 mL) for activated carbon at 25°C are listed in Table 11. In other words, the Freundlich isotherm model fits very well than that of Langmuir isotherm model when the R^2 values are compared in Table 11 (R^2 values of Freundlich plot > 0.99 was close to unity, indicating isotherm data fitted well to Freundlich model). The Freundlich constant n is the measure of the deviation from linearity of the adsorption. If a value for n is blew to unity, this implies that adsorption process is govern by a chemical mechanism, but a value for n is above to unity, adsorption is favorable a physical process. The values of n at equilibrium are between (1.70-1.87), representing favorable adsorption at studied temperatures and therefore this would seem to suggest that a physical mechanism, which is referred the adsorption bond weak [27,28] and conducted with Vander Waals forces. Plots of (q_e) versus (C_e) are represented in **Fig. (8)**, from figures (q_e) increased by increasing (C_e) suggesting a very strong surface interaction between the metal ions Ni²⁺ and both adsorbents (natural activated carbon). This Freundlich type behavior is indicative of surface heterogeneity of the adsorbents, i.e. the adsorptive sites (rise husk) are made up of small heterogeneous adsorption patches that are homogeneous in themselves. The activation of adsorption sites takes place, leading to increased adsorption probably through the surface exchange mechanism.

Thermodynamic parameters

The determination of thermodynamic parameters has a great importance to evaluate spontaneity and heat change for the adsorption reactions. Thermodynamic parameters such as free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) changes of adsorption can be evaluated from the following equations (7 , 8):

$$\ln K_c = -\Delta H^\circ/RT + \Delta S^\circ/R \quad (7)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (8)$$

to determine the ΔG° , ΔH° and ΔS° , the K_c may be expressed in terms of the ΔH° (kJ mol^{-1}) and ΔS° ($\text{kJ mol}^{-1}\text{K}^{-1}$) as a function of temperature, Eq. (8). Thermodynamic parameters such as free energy of sorption (ΔG°), the heat of sorption (ΔH°) and standard entropy (ΔS°) changes during the sorption process were calculated using Eqs. (7) and (8) on a temperatures range of 25-40°C at initial concentrations (50, 100, 150, 200, and 300 mg/L) of Ni^{2+} ions and dose 0.5 g/200 mL for natural activated carbon. The values of these parameters were recorded in **Table 3**. The positive values of ΔG° confirm the feasibility of the process and the no spontaneous nature of the adsorption of Ni^{2+} onto natural activated carbon. On the other hand, the value with increase of temperature indicates that a better adsorption is actually obtained at higher temperatures. The positive values of ΔH° confirmed the endothermic nature of adsorption which was also supported by the increase in value of Ni^{2+} uptake of the adsorbent with the rise in temperature. The negative values of ΔS° showed the increased ordering at solid/solution interfaces during the adsorption of metal ions onto both adsorbents and also reflected the affinity of natural activated carbon toward Ni^{2+} ions under consideration.

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