BIOSORPTION OF NICKEL(II) FROM AQUEOUS SOLUTION ONTO ACTIVATED CARBON PREPARED FROM COW HOOVES

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ABSTRACT

Heavy metals present in waste waters which were released into the environment by various industries have become a serious problem to man and his environment. This research focused on the use of Activated Carbon from Cow Hooves (ACCH) for removal of Ni(II) ions from aqueous solution. Fourier Transform Infrared (FTIR) analysis was carried out on ACCH to reveal the functional groups for the adsorption of the ions. The optimization factors such as ACCH dosage, pH, and contact time were investigated at ambient temperature. The optimum biosorption condition was found at pH 7.0, 1.2 g biomass dosage and at 80 minutes equilibrium time. The experimental data obtained for Ni^{2+} sorption were treated using pseudo first order and second order kinetic models. The adsorption behavior was found to follow pseudo second order kinetics.

Key words: Adsorption, cow hoof, kinetics.

INTRODUCTION

Heavy metals are widely distributed in the environment and are ecologically important due to their high toxicity to living organisms including human beings [1]. Industrial activities such as mining, electroplating, tanning, metallurgical operation and manufacturing have led to the release of these metals into the environment [2]. Adsorption onto activated carbon is by far the most versatile and extensively used process as a result of its ability to remove a wide range of adsorbates, low cost of operation and capability of removing trace level of toxic metals from waste water [3].

Nickel is one of the potentially toxic elements that are not biodegradable in nature. Due to frequent handling of nickel in developing countries during industrial processes, their fume is released into the atmosphere and may also be discharged into water bodies. Its high concentration in humans can cause gastro intestinal irritation. Ni(II) ion is a chronic toxic metal

ion that can cause cancer of the lungs, nose and bones [4]. Therefore, in order to maintain the acceptable concentration for these toxic metals in waste water, there is need to adopt simple, efficient, inexpensive and economical methods for removing them from wastewater [5]. In the present research work, Activated Carbon from Cow Hooves was used for the removal of Ni(II) ion from aqueous solution and the kinetics involved in adsorption process were examined.

MATERIALS AND METHODS

Collection of Cow hooves

Cow hooves were randomly collected from the local abattoirs in Zaria Local Government Area, Kaduna State, Nigeria.

Sample Pre-Treatment and preparation

The Cow hooves were washed thoroughly with detergent and rinsed with deionized water to remove the debris. The cow hooves were later sun dried for two months after which they were ground to powder with mortar and pestle. The ground Cow hooves were then sieved using 300 and 350 μm mesh sizes. The sample retained after using the 350 μm mesh sized sieve was used for sorption studies [6]. The fine powdered cow hooves obtained was then soaked in chloroform for about 72 hours to remove the fat, after which it was sun dried and washed with deionized water to remove the color [6]. The sample obtained was then modified with 1M H_3PO_4 in 1:1 weight ratio. The sample was finally carbonized using a tubular furnace with temperature set at 400 ºC for 2 hours. The sample obtained was then left to cool to ambient temperature.

Reagents

All chemicals, supplied by Merck Company, Canada were of analytical grade. Stock solution of Ni(II) was prepared by dissolving 4.48 grams of Nickel chloride hexahydrate ($NiCl_2.6H_2O$) in deionized water and then the desired concentrations were provided by diluting the stock solution.

Experimental plan [7]

This study investigated some factors such as adsorbent dose (0.4, 0.6, 0.8, 1.0, 1.2 and 1.4 g), pH (2, 3, 5, 7, 9, 11) and contact time (20, 40, 60, 80, 100, 120 min) using batch adsorption technique. The nitric acid and NaOH 0.1N were used to adjust the pH of the solution.

The amount of metal ion adsorbed at equilibrium qe, (mg/g) was calculated by Equation:

$$q_e = \frac{V(Ci - Cf)}{S} \text{--(1)}$$

Where q_e= Metal ion uptake capacity (mgg-1), Ci = Initial concentration of metal in solution (ppm),

C_f= Final concentration of metal in solution (ppm), S = weight of biosorbent (g), and V = Solution volume (cm^3).

The difference between the initial metal ion concentration and final metal ion concentration was assumed to be bound to the biosorbent.

The Biosorption efficiency, A %, of the metal ion was calculated using

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

where C_0 and C_e are the initial and equilibrium metal ion concentrations (ppm), respectively [8].

RESULTS AND DISCUSSION

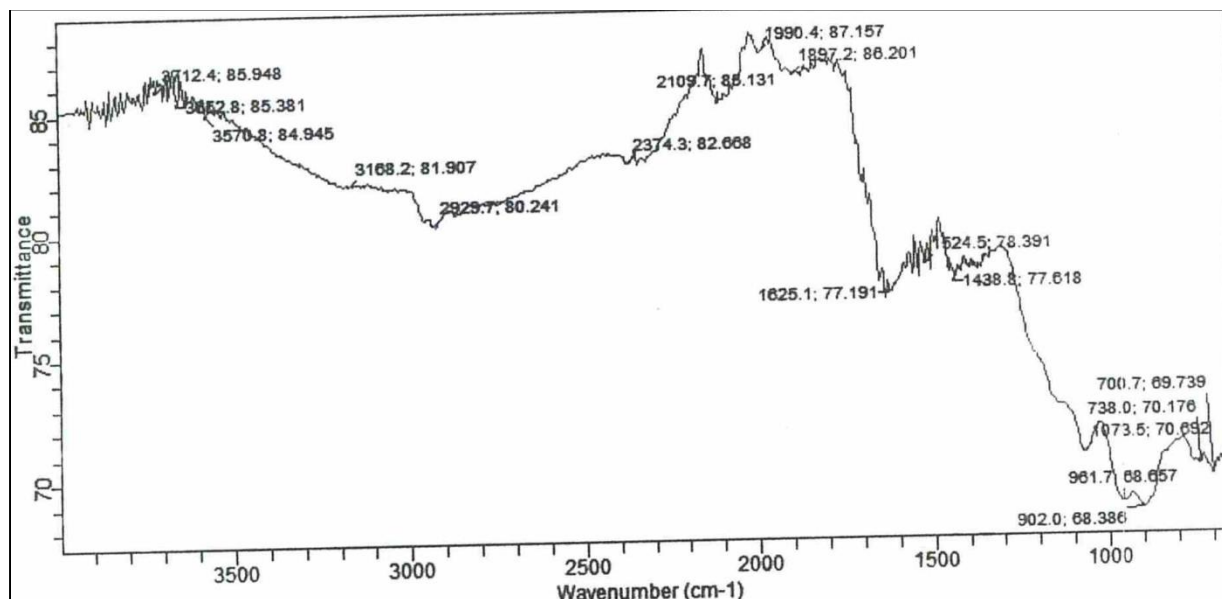### *Characteristics of the Activated Carbon*

Fig.1: Fourier Transform Infrared Spectroscopy of ACCH

Fourier transform infrared spectroscopy was used to measure the carbon of the adsorbent within the range of 650-4000 cm^{-1} wave number. The technique is an important tool to identify functional groups, which are capable of adsorbing heavy metal ions.

The spectrum of ACCH (Fig.1) showed that the most prominent peaks in the spectrum originate from H-C-H asymmetric and symmetric stretching vibrations from alkanes 2929.7 cm^{-1}. Sharp peaks was observed in the region of 2109 cm^{-1} which originated from C≡C or C≡N. Intense peaks in the region of 2374.3 cm^{-1} is a stretching S-H mode which originates from Thiol. In the region of 1625.1 cm^{-1} is a stretching mode of carbonyls, mainly ketones of C=O. Finally, intense peaks in the FTIR spectrum of ACCH in the region (1438.8 cm^{-1}) originates from secondary Amines N-H, while stretching at 1073.5 cm^{-1} for C-O come from ethers.
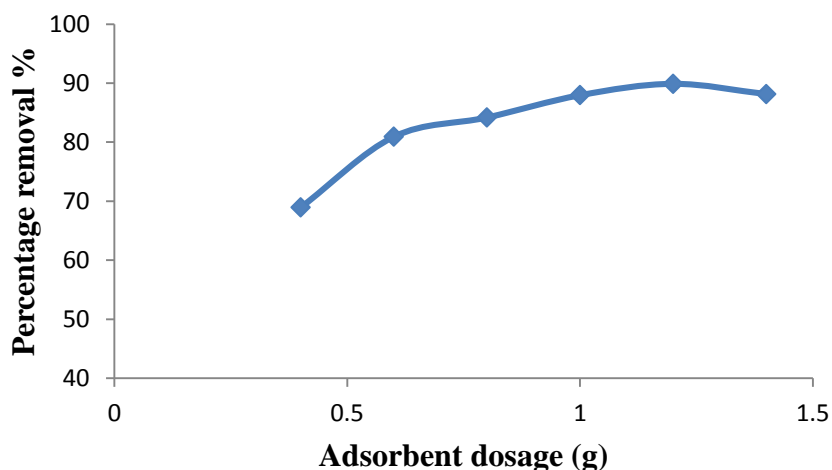
Effect of ACCH Dosage

Fig. 2: Effect of Adsorbent dosage on the removal of Ni (II) using ACCH

Figure 2 is a graphical illustration of the optimized biosorbent dosage for Ni(II) ions removal. The uptake of Ni(II) by ACCH from aqueous solution increased from 68.952 to 89.897 % as the adsorbent dose was increased from 0.4 to 1.2 g. This is due to the availability of more binding sites with increase in biosorbent dose [9]. It was however observed that during the interval of 1.2 g to 1.4 g, the percentage removal decreased. This could be as a result of the aggregation of adsorption sites resulting in a decrease in total adsorbent surface area of particles available to adsorbates and an increase in diffusion path length [10].

Effect of pH On ACCH

The pH level of the aqueous solution is an important variable for the adsorption of metals on the adsorbent. The effect of pH on the removal of nickel ion using ACCH as an adsorbent was studied with initial pH range from 2 to 11. The relationship between the initial pH of the solution and percentage removal of nickel ion is depicted in Table 1. It was observed that increasing the pH from 2.0 to 7.0 resulted in an increase in percentage removal of Ni (II) ion from 56.44 to 98.135 % is due to the reduction in number of hydrogen ions available which compete with the Ni(II) ions for the available vacant sites on the biosorbent [11]. Optimum pH of 7 was therefore observed for the removal of Ni(II) ions using ACCH. Further increase in pH resulted in a decrease in removal efficiency. This could be due to the weakening of electrostatic force of attraction between the oppositely charged biosorbate and biosorbent that ultimately led to the reduction in percentage removal of Ni(II) ion [12].

Table. 1: Effect of pH on the Removal of Ni (II) using ACCH

pH	Percentage removal of Nickel (%)
2	56.44
3	93.24
5	96.92
7	98.135
9	97.989
11	97.131

Effect of Contact time

The effect of contact time on Ni(II) removal by the sorbent is illustrated in Fig 3. It is evident that percentage removal of Ni(II) ion increased from 85.0 to 98.58 % as contact timewas increased from 20.0 to 80.0 minutes until it reached saturation level after 80.0 minutes indicating the equilibrium time. The progressive increase in the removal efficiency with time is due to the availability of uncovered surface area of biosorbent [13]. After the adsorption equilibrium had

reached on 80 minutes, a decrease in the metal uptake was observed with further increase in contact time as theavailable binding sites were used up and clogged by metal ions. Therefore, optimum contact time for adsorption of Ni (II) using ACCH is 80 minutes.
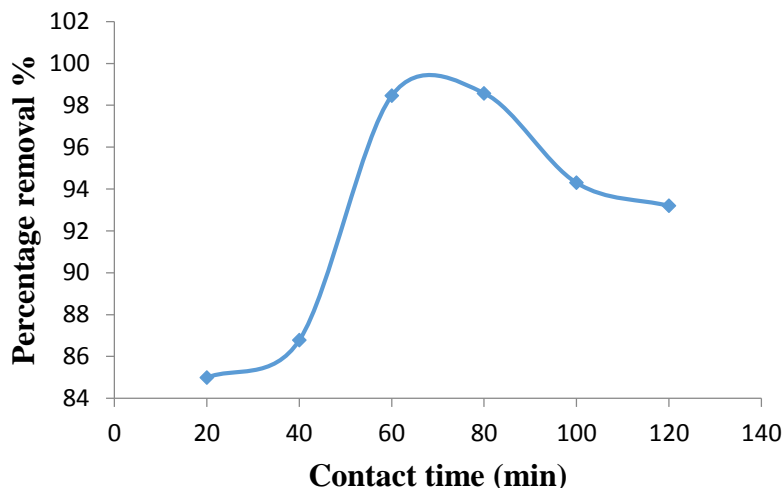

Fig. 3: Effect of Contact time on the Removal of Ni (II) using ACCH

Adsorption kinetics

Adsorption kinetics was used to explain the adsorption mechanism and characteristics. Pseudo-first order and pseudo-second order kinetic models were applied to the experimental data in order to investigate the kinetics of sorption of N (II) ions onto ACCH. Kinetic studies were conducted in optimum conditions determined in preliminary experiments (ACCH dosage of 1.2 g, temperature of 298 K and pH of 7).

The pseudo first order kinetic model was applied by plotting log (qe-qt) vs t. The regression coefficient (R^2) obtained from the pseudo first order kinetic graph was low (0.017) as shown in fig 4. This implies none applicability of the pseudo first order kinetic model to the experimental data on the adsorption of Ni(II) onto ACCH.

The pseudo second order kinetic model was applied by plotting $\frac{t}{qt}$ vs t. The regression coefficient (R^2) obtained from the pseudo second order kinetic graph was high (0.995) as seen in Fig 5. This implies that the mechanism of adsorption of Ni(II) ions onto ACCH followed second order kinetics, thus indicating an inclination towards chemisorption.
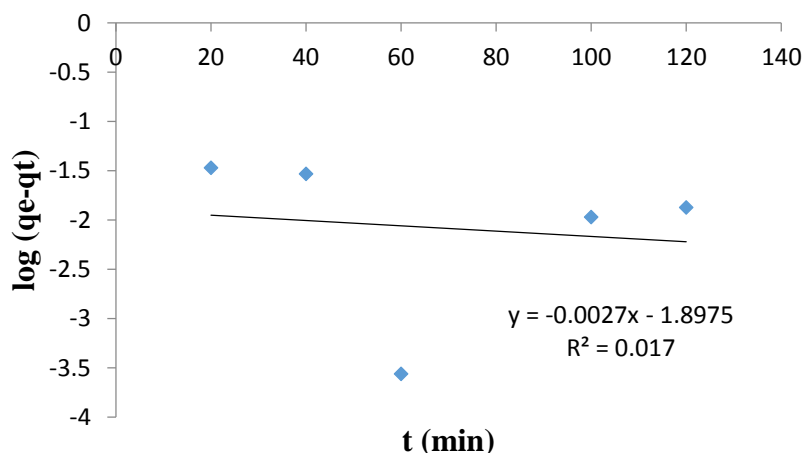
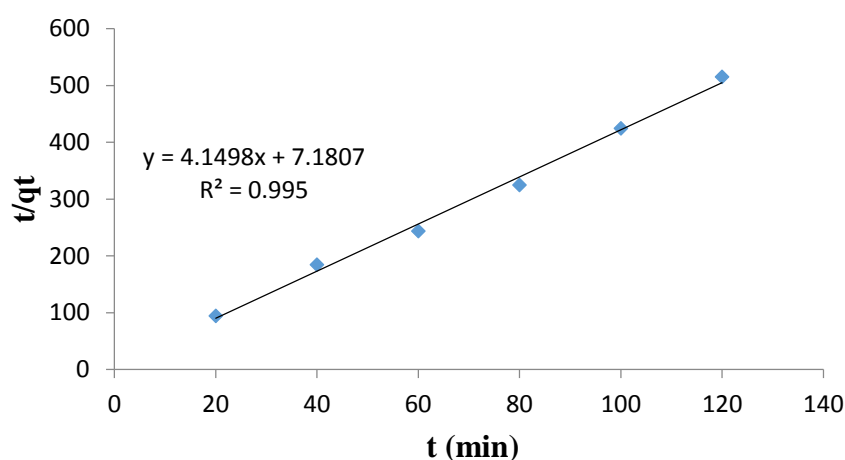Fig. 4: Pseudo first order model for Ni(II) removal using ACCH

Fig. 5: Pseudo second order model for Ni(II) removal using ACCH

CONCLUSION

The present work investigated the potentials of activated carbon from cow hooves as adsorbent for nickel ions from aqueous solution as an alternative to costly adsorbents. The main advantages include its availability, low cost (inexpensive), effectiveness and sorption capability.

The biosorption process was affected by contact time, pH and ACCH dosage. Adsorption kinetics was found to follow only pseudo second-order rate expression thus an indication that the adsorption process occurred via chemisorption.

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