Ni (II) REMOVAL BY BIO-SORPTION USING THE COCONUT HUSK

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ABSTRACT**:** *There are very few materials used for the removal of heavy metal with high removal capacity, but peanut husk has the tremendous ability to remove the number of heavy metal ions. It was clear from the experimental results that the time taken to develop the sorption equilibrium was 7 minutes, which means that the phenomenon of bio-sorption was very rapid and almost 90% of the bio-sorption was completed within first 3 minutes of the experiment. This study includes the investigation of the pollutant binding capacity of the coconut husk under varying conditions. An effect of the pH and the initial metal concentration on these absorbent was notable; the maximum sorption capacity was at the 4 pH. It was interesting to note the behavior of the dosage amount on the sorption capacity; from the experiments, it was clear that the sorption capacity and the dosage amount have almost direct relation till the contact time of 3 minutes. The pseudo-second-order kinetic model was used to analyze all the experimental results; it has proven its effectiveness as compared to the pseudo-first order and intra-particle diffusion kinetic models. All the experimental results were the healthy indication towards the low cost, hazardless alternative treatment of wastewaters with lower concentrations of Nickel.*

INTRODUCTION:

The rapid industrial growth is obvious due to increase in population across the Globe. This industrialization is not only facilitating the humans, but also causing some problems, like the discharge of various harmful chemicals; some of these chemicals are major environmental pollutants [1]. The leading share of these harmful chemicals is the heavy metals, which are the main threat to the bio life. The heavy metal characteristics like the bioaccumulation tendency and their persistent nature make them major apprehensive chemicals. There are some conventional techniques for the removal of these toxic heavy metal ions from the aqueous solutions, like the membrane separation technologies, adsorption, oxidation or reduction, precipitation and ion-exchange. These methods are effective, but on the large scale they are considered as expensive and time consuming. There are also some questions about their effectiveness if the concentrations are over the range of 1 to 100 $mgL^{-1.}$ Furthermore, these typical methods tend to produce toxic chemical sludge, and there is also a valid point of concern regarding their disposal; as the process to make them harmless is not eco-friendly and expensive. The disposal of theses chemical sludge is expensive and also not eco-friendly. Safe removal of catastrophic heavy metals is vital to promote a healthy environment and the method of removal should also be cost effective [2].

Bio-sorption for the removal of heavy metal from the water/wastewater is a new emerging technique and has proven its effectiveness for the various heavy metal ions. The term Bio-sorption is not limited to only one process, but includes the various numbers of passive, metabolisms independent accumulation processes and the processes like complexion, chemical or physical adsorption, chemical precipitation, ion exchange, and chelation may also include in this term. Bio-sorption is preferable over the conventional technique because of its low operating cost and highly effective in removing very dilute effluents [3]. The Bio-sorption techniques are relatively fast; at the cost of a few minutes it can bring marvelous results. However, these heavy metal ions removals are not widely used techniques, only the few treatment plants has introduced the bio-sorption/bioaccumulation-based processes [4].

Ni (II) is the one of the toxic environmental pollutants, and its concentration in the environment is increasing at the alarming rate over the last decade. Nickel compounds can cause skin allergy, asthma and also the deadly diseases like cancer. There are two major causes of the nickel release into the atmosphere, the mining and the industrial waste. Some of the industrial processes also cause the release of nickel into the atmosphere, like paint formulation, porcelain enameling, electroplating, the manufacturing process of copper sulphate, and the mineral processing. Many of the oil burning power plants are also releasing the nickel compounds above the authorized limits [5]. The concentration of the nickel ions in the waste is different for the different industry, solely depends on the quantity of the metal used in the process. Such as, in the plating rinse process the concentration of the nickel ion can range from the 2-900mg/L. On the other hand, the concentration in the porcelain enameling process can range over 0.25-67, in the manufacturing of the paint and ink it varies 0-40 and in copper sulphate manufacturing it can be around 22mg/L; which is quite in the alarming range [6]. The maximum discharge limits of the nickel in the wastewater set by the Environmental Protection Agency (EPA).Numerous agricultural waste materials with the nominal cost have proven their potential to remove heavy metal icons from the industrial sludge [7]**.** It has been reported that the removal capacities of biomass of terrestrial-plant materials for numerous heavy metal ions is very high. There are different forms of low cost, non living plant materials such as pith and peach, root, plant wood, leaves and bark, papaya wood, saw dust, Capsicum annuum seeds, cork biomass, dehydrated wheat bran, grape stalks waste, tea-industry waste are being used widely, and the newly investigated biomass coconut husk ,as capable adsorbents for the toxic heavy metals [8]. This research work is based on the evaluation the effectiveness of lower cost adsorbent material; coconut husk in Pakistan [9].

MATERIALS AND METHODS:

Reagents:

The analytical grade chemicals were used in the present study. These chemicals are $Ni(NO_3)_2 \cdot 6H_2O$, 0.1 Mol L-1 NaOH, 0.1 Mol L-1 HNO_3(to adjust PH of solution) and Ni (II) atomic absorption spectrometry standard solution (1000 mg L-1) (Fluka Chemicals).

The Method of Bio-sorbent Preparation:

For this study, coconut husk a very low cost biomass was used for the bio-sorption and removal of Ni(11) from aqueous solution. The first step involved the collection and the preparation of the bio-sorbent coconut husk. After collection, the required amount of these materials was washed with the tap water and put to dry in the shadow. The next step involved the grounding and sieving the dried coconut husk to 60 mesh sizes [10]. Warring blender was used to bring the biomass to powder form and then sieved to a size of 60 mesh. From this sample certain portion and size were taken for experiments. Adsorbent particle size of 60 mesh was used for the adsorption experiment to carry out [11]. This biomass material has the capability of absorbed metals on their surface from the environment. There were not any other physical or the chemical treatments involved before the actual experiments. The air right glass bottle was used to store this processed material. It is cleared from the Fourier Transform infrared (FT-IR) spectroscopic studies that the coconut husk has the carboxylic, hydroxyl and carbonyl group; which is a clear indication of the good metal sorption [12].

Preparation and analysis of Ni (II) Solution

The preparation of the 1000 PPM/2L nickel stock solution was achieved by dissolving the suitable amount of Ni $(NO_3)_2$.6H2O in DDW, which is also known as de-ionized distilled water. Ni (II) solutions of different concentrations were required and these are called synthetic solutions, therefore, all the required synthetic solutions were prepared from the stock solution and kept them separate [13].

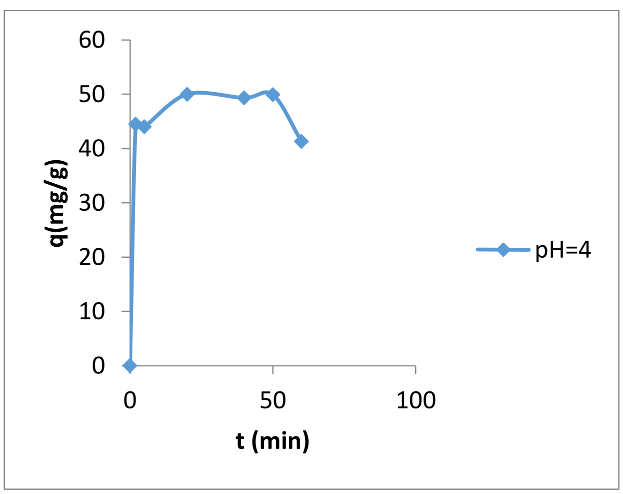

Fig. 1. Effect of contact time on the uptake of Ni (II) by coconut husk at pH=4, Con = 100 ppm, D = 0.2 g.

Synthetic solutions were prepared by using the following formula

$M_1V_1=M_2V_2$

The treatment of all the glassware and polypropylene flasks was necessary to get the accurate reading; therefore, all the apparatuses were engrossed in 10% (v/v) HNO_3 solution for about 12hrs and then washed properly with de-ionized distilled water. Flame atomic absorption spectrometry (FAAS) was used to determine the Ni (II) contents in the dilution before and after performing every experiment [14].

Batch Bio-sorption experiments:

The batch experiments were selected to find out adsorption characteristics of the biomass for the Ni (II) ions. In all these experiments, the specific volume of synthetic solution of the Ni(II) (100mL) was taken and then mixed with the bio-sorbent 60 mesh sized dose (10g/L) at temperature of 25c at 120 rpm for 60 minutes.250mL glassware flasks were used in these experiments containing synthetic solution of known Ni(11) concentration. The experiment was carried out applying the different PH (PH 4 to PH 5), while the metal concentration was from 100 to 10 ppm, and 10 mg/L., and the contact time was 0 to 60 with the increment of 10 minutes. The PH regulation was carried out applying the 0.1mol L-1 NaOH and 0.1mol L-1 HNO_3.The solution was then placed on the shaker, and then set to the orbital rotation with the constant shaking rate for the period as written in above paragraph. The Watman 50 filter paper was used for the separation of the solution from the biomass. The one hour was enough for the Ni (II) uptake to achieve the equilibrium. The calculation of the Ni (II) uptake was of major importance, so it was calculated by the concentration difference.

$$q_e = \frac{(C_i - C_f)V}{W} \qquad (1)$$

RESULTS AND DISCUSSION

Effect of contact time and PH

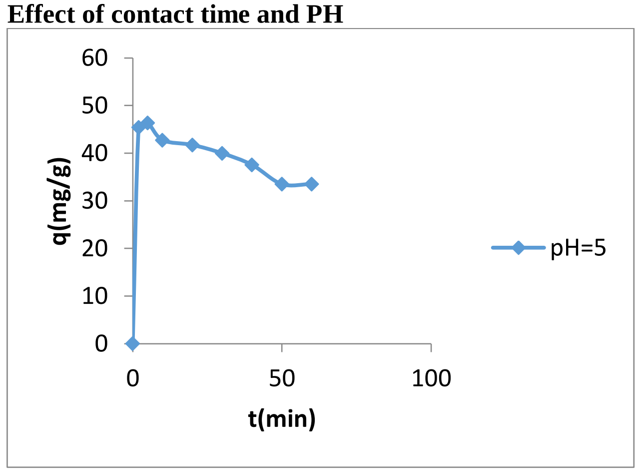

Fig.2. Effect of contact time on the uptake of Ni (II) by Coconut husk at pH = 5, Co = 100 ppm, D= 0.2 g.

From these experiments, the variables which affect the bio-sorption was the solution PH. Therefore, the batch experiments were carried out with the different solution PH (4 and 5) for the peanut husk. In the figure 1 and 2 the effect of PH on the intake of the metal is notable. At the PH 4 the intake of the metal ions was rapid and reached to 44.5 in less the 3 minutes, from the plot it is clear that the metal uptake is slow as compared to the figure 2 when the PH value was 5. Therefore, it is essential to mention the PH value close to 4 for an effective metal intake. The phenomenon which causes the diffusion of metal ions from the bulk solution to active sites is passive transport mechanism; which is defined as the metal ion diffusion from the solution to the active sites of the biomass. In this study the biomass was peanut husk, the active sites are where the various groups like carboxylate, hydroxyl, amino and phosphate; these chemical groups have the affinity for the metal ions. The presence of the groups like carboxylic, hydroxyl and amino bestow the sites a negative charge at the PH closer to 4, the PH affects the intensity of the induced charge, and intensity depends on the value of the PH. Therefore, the bio-sorbent attract the Ni (II) at this PH. At the end of the experiment, the ion exchange phenomenon was carried out between the Ni^{+2} and H^{+} ions, which caused the release of the proton, therefore the decrease in the PH value was observed. From the shift of the PH value it can be concluded that the major cause during the sorption process is the ion exchange.

Effect of contact time and dosage amount:

The removal of Ni (11) from aqueous solution was investigated by varying adsorbent dosage because bio-sorption to a great extent dependent on the dosage amount. The specific surface area of the bio-mass, in this case coconut husk is proportional to the bio-sorption. The definition of specific surface area is as "part of the total area available for bio-sorption". Effect of the dosage of the biomass on the removal of Ni(11) was investigated by keeping PH constant at 4 and constant initial Ni(11) concentration at 100ppm. Following figures show that as we increase the concentration of adsorbent/ biomass i.e. coconut husk from to 0.2gm to 0.5gm the rate of bio-sorption also increases. It happens due to increase in the available active sites. It means that for the given initial concentration of N i(11) equilibrium concentration of Ni(11) decreases as we increase the amount of biomass(coconut husk). Result shows that as we increase the dosage of coconut husk from 0.2 to 0.5 gm the uptake increase from 58.2 to 85.5%.

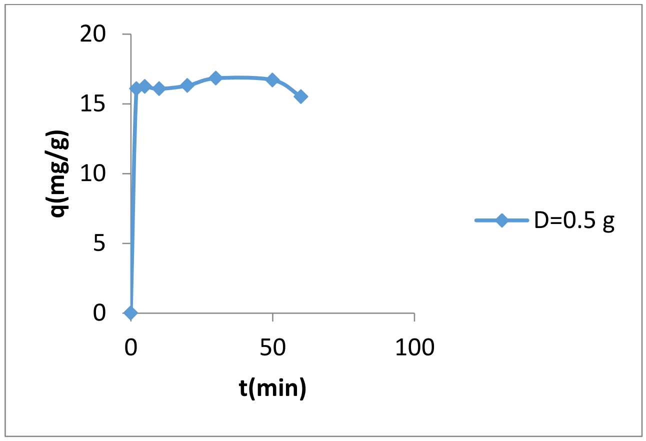

Fig.3. Effect of contact time on the uptake of Ni(II) by Coconut husk at pH 4 and Dosage D=0.5 g and Co=100 ppm.

Effect of contact time and initial metal concentration:

The initial metal ion concentrations taken were 50 ppm and 100 ppm. The effect of the initial metal ion concentration and the contact time is illustrated in the figure 1 and 4. These figures illustrate that there is a direct relation between the equilibrium concentration of Ni (II) and the adsorb-ate concentration. The initial concentration and the rate of sorption are closely linked together; therefore, it is important to consider it for the effective bio-sorption. The initial concentration helps to overcome a resistance in sorption called the mass transfer resistance of the metal ions between the solid phase and the aqueous solution. The results were closely observed while keeping all other parameters constant and the initial concentration was changed in the range of 50 to 100 ppm.

In the figure 1, the variables were set at pH=4, Co = 100 ppm, D = 0.2 g, this plot reveals that the value of q (mg/g) was reached at 44.5 in less than 3 minutes. At higher concentration the sorption intake was slow, as the active sites were few, and at that point the particles need to defuse in the biomass surface by the inter-particle diffusion phenomenon. The figure 4 illustrates the plot between the time (t) and the metal intake q (mg/g) at the initial metal concentrate Co = 50 ppm; the metal intake was only 18.81 in less than 3 minutes. Therefore, the higher was the sorption capacity at higher initial metal concentration.

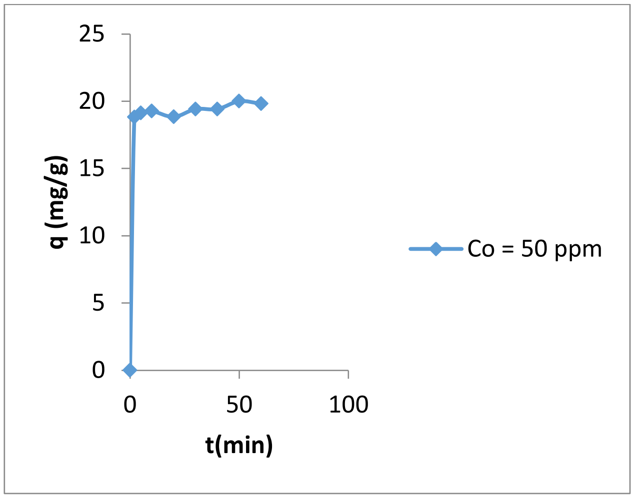

Fig. 4 Effect of contact time on the uptake of Ni(II) by Coconut husk at pH= 4, Co = 50 ppm, D = 0.2 g.

Variation in the Ni (II) sorption capacity with different contact time, metal concentration (initial), different PH was investigated. The accuracy of the results was of the major concern, therefore experiments were repeated thrice.

Kinetic Modeling:

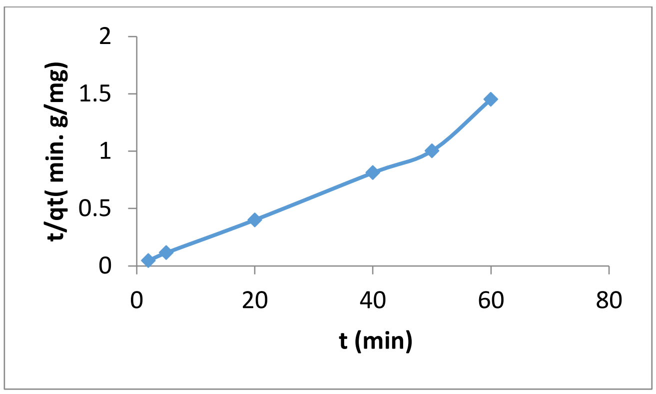

Fig.5. Application of Pseudo 2nd order kinetic model for the uptake of Ni (II) by Coconut husk at pH=4, Co = 100 ppm, D = 0.2 g

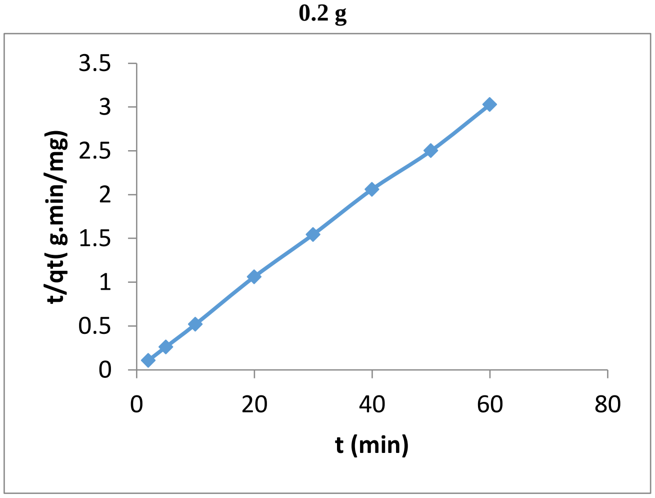

Fig.6. Application of Pseudo 2nd order kinetic model for the uptake of Ni(II) by Coconut husk at pH 4 and Dosage D=0.5 g and Co=100 ppm

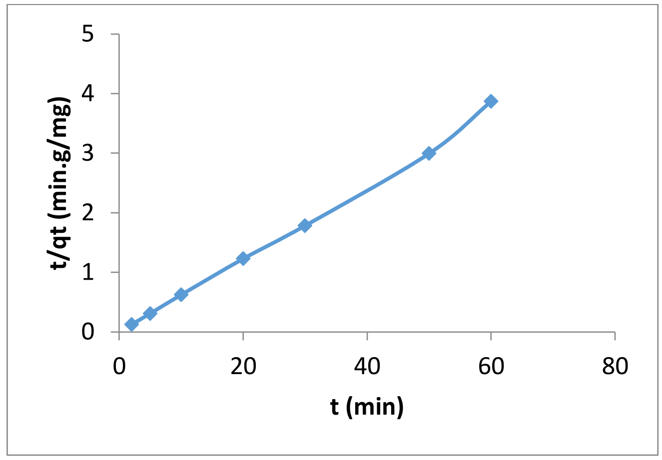

Fig.7 Application of Pseudo 2nd order kinetic model for the uptake of Ni(II) by Coconut husk at pH= 4, Co = 50 ppm, D = 0.2 g.

Investigating the bio-sorption mechanism is the crucial phase, Kinetic model helps to explain the bio-sorption mechanism and also find out the potential rate controlling step. The second-order kinetic model was used to determine the transient behavior of the batch bio-sorption process. The pseudo second-order model considers the relation between the rate of occupation of bio-sorption sites and the number of unoccupied sites; it explains that there is a proportional relation between the rate of occupation of bio-sorption sites and the square of the number of unoccupied sites.

$$\frac{dq_t}{dt} = \mathrm{k}\,(q_{eq} - q_t)^2$$

t = time (min)

q_t = uptake capacity (mg/g)at t

k = the equilibrium rate constant (g mg-1 min-1) of pseudo-second order adsorption.

Rearranging the equation:

$$\frac{t}{dt} = \frac{1}{kq_{eq}^2} + \frac{t}{q_e}$$

The figure 7 shows the linear plot between the t/qt and the t, from this plot the value of ‘k’ and the ‘q_{eq}’ can be determined. The figure 5 and 6 also illustrates the plot between the t/qt and the t, but these are not the straight lines. In the figure 5 the variables were set as pH=4, Co = 100 ppm, D = 0.2 g. After 50 minutes, the major variation from the straight line was sensed. In the second experiment, the Dosage D=0.5 g was taken, and all the other variable were same as the previous experiment. The plot between the t/qt and the t is shown in the figure 6; once again, this is not the straight line. In the third experiment, the initial concentration was set at 50 ppm, pH at 4, and the dosage D at 0.2 g; the figure 7 illustrates the plot between the t/qt and the t at these conditions, which is a straight line.

The approximated value of the coefficient of correlation was used for the kinetic model, which was one at given value of temperature, and value of q_e which justified the experimental values was (q_e = 6.63 mg/g). From all these facts, it is clear that the sorption of Ni (II) ions follows the second order kinetic model. The kinetic modeling makes the process equipment design process easier, as it replaces the material and the time consuming experimental work; from this fact, it is clear that those obtained kinetic result has major practical worth for solving the technological problem and developing the useful technological applications.

CONCLUSION:

The focus of this study was to determine the effect of different factors on the sorption capacity of an inexpensive agro-based material (coconut husk). The coconut husk caused litter and visual pollution impact on the environment after being thrown in the gardens and parks. Therefore the bio-sorption of Ni(11) from aqueous solution by using coconut husk can be regarded as eco-friendly efficient economic experiment.

From all the experimental work following conclusion can be drawn.

1. Coconut husk is an inexpensive agro based waste material, which has characteristics to effectively remove Ni (II) ions.
2. The variables which highly affect the sorption capacity of the following material are the contact time, PH of the solution, bio-sorbent dosage and the initial metal concentration. The suitable values of all these variables can bring the marvelous results regarding the sorption capacity.
3. The variable which affect the sorption capacity the most is the PH; the sorption capacity and the PH have the direct relation, but only for the specific PH range. Ion exchange is a force involved in removal of metal ions between the available active sites and the metal cat-ions.

ACKOWLEDGEMENT:

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