

Turkish Journal of Engineering



Turkish Journal of Engineering (TUJE)
Vol. 3, Issue 2, pp. 102-105, April 2019
ISSN 2587-1366, Turkey
DOI: 10.31127/tuje.456741
Compilation Article

THE REMOVAL OF NICKEL IONS WITH WALNUT SHELL

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Received: 03/09/2018

Accepted: 25/10/2018

ABSTRACT

The present study was aimed at determining whether walnut shell would have acceptable adsorption efficiency for removing Ni (II) and thereby offer an effective and economical alternative to more expensive treatments. This paper describes the removal of Ni (II) ions from aqueous solutions containing 100 mg L⁻¹ of nickel using walnut shell. The effects of various parameters such as optimum adsorbent mass, contact time, pH of the medium were investigated. The maximum removal efficiency of 43.23% was obtained at a pH of 5.85 with a 5-min contact time for a 5 mg L⁻¹ solid-to-liquid ratio and an initial heavy metal concentration of 100 mg L⁻¹. It can be concluded that walnut shell could be used as a low-cost and abundant source for the removal of Ni (II), and as an alternative to more costly materials such as ion-exchange resins and activated carbon. It is thought that it will be possible to make walnut shell modification studies in order to obtain higher increases in recovery efficiency.

Keywords: Adsorption, Nickel Removal, Walnut Shell

1. INTRODUCTION

Heavy metal pollution in many parts of the world is an important economic and environmental problem (Whang *et al.*, 2009). Heavy metals are defined as metals with a density of 5 g cm^{-3} (Kobielska *et al.*, 2018). Heavy metals are transferred to the environment through many industrial activities such as mining, metal plating, painting, automobile production and metal processing. In order to meet water and food quality standards, heavy metals in the environment need to be monitored (Feizi and Jalali, 2015). In addition, it has been determined that high concentrations of heavy metals have negative effects on human, animal and plant health (Çelebi and Gök, 2015). Lead (Pb), Cadmium (Cd) and Nickel (Ni), which are among heavy metals, are considered important environmental contaminants.

Natural nickel is a mixture of five stable isotopes. Although it occurs in many oxidation cases, its common oxidation under environmental conditions is Ni (II). Ion radius of Ni (II) shows similarity with other cations (Ca, Mg). In contrast, Cd and Pb have high transportation and mobility (Amari *et al.*, 2017).

Although the World Health Organization (WHO) determined the maximum acceptable nickel concentration in drinking water as 0.02 mg L^{-1} , it has been determined that the nickel concentration in industrial wastewaters has reached 900 mg L^{-1} . If no treatment is made, these wastewaters may contaminate drinking water resources (Ong *et al.*, 2017). Harmful health effects of having high concentrations of Ni(II) ions in drinking water include anemia, diarrhea, encephalopathy, hepatitis, lung and kidney damage, gastrointestinal distress, pulmonary fibrosis, renal edema, skin dermatitis, and central nervous system dysfunction. Due to these adverse effects, it is important to take measures in removing nickel from contaminated wastewaters before discharge to the environment (Mangaleshwaran *et al.*, 2015)

It is typically used in processes like production of stainless steel, coins, metallic alloys, super alloys, nonferrous metals, batteries, copper sulfate, electroplating, forging, compound for coloring ceramics, mineral processing, paint formulation and team-electric power plants, and as a catalyst (Raval *et al.*, 2016; Ghaee *et al.*, 2012).

Related to the removal of heavy metals in the water, there are various methods such as chemical precipitation (Mauchauffee and Meux, 2007) reverse osmosis (Mohsen-Nia *et al.*, 2007), ion exchange (Verma *et al.*, 2008), coagulation (El Samrani *et al.*, 2008) and adsorption (Gupta *et al.*, 2003; Gupta and Ali, 2004; Gupta and Ali, 2000; Zabihi *et al.*, 2009).

Among these methods, adsorption process offers an attractive alternative because it can provide treatment with cheap adsorbents (Cao *et al.*, 2014). Sorption process by using biosorbents is based on use of organic sorbents such as agricultural residues. The application of different sorbents such as sugar beet pulp, rice husk, carrot residue, bagasse, corn stalk, bacterial biomass, rice straw, green tomato husk, sugarcane bagasse, banana pee and sunflower residues have been recently investigated (Feizi and Jalali, 2015). Walnut shells, which are used as solid fuel in Turkey, are agricultural wastes that can be found in large amount. When the structural analysis of walnut shell was examined, it was determined that it had a lignocellulosic structure containing 17.74% cellulose,

36.06% hemicellulose and 36.90% lignin (Altun and Pehlivan, 2012).

Due to its wide surface area, high mechanical strength, chemical stability and easy regeneration, the walnut shell has been successfully used to remove heavy metals such as Cesium, Copper, Chromium (IV), Zinc and Mercury from wastewaters (Cao *et al.*, 2014).

The main purposes of this study are to remove Ni (II) from aqueous solution by using walnut shells that can be found cheap and in a large amount in our country and to investigate the beneficial usage of the walnut shell that is seen as agricultural waste.

The effects of factors such as contact time, pH, adsorb concentration on the studies of Ni (II) adsorption were investigated.

2. MATERIAL AND METHOD

2.1. Adsorbents and chemicals

Walnut shells were obtained from walnut trees grown in Usakpinar, a village in Silifke County of Mersin Province in the Mediterranean Region of Turkey. Walnut shells were shredded with grinders (Arnica, GH21520), the particles were sifted through a series of sieves, and only the samples passing from the pore diameter of $212 \mu\text{m}$ were used in this study. Walnut shells were washed 3 times with distilled water and the effects that could emerge due to the foreign substances in their structures were prevented. Then, they were dried in a drying oven (Memmert, UNB-400) at $70 \text{ }^\circ\text{C}$ for 24 hours.

In this study, Ni^{+2} having 100 mg L^{-1} concentration was used. The stock Ni (II) (1000 mg L^{-1}) solution was prepared by using $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ chemical compound. The pH value of each solution was set to the desired values by adding 0.1 M NaOH or 0.1 M HNO_3 . All chemical compounds used to prepare reactive solutions were prepared in analytical quality (Merck)

2.2. Measurements

All batch experiments were carried out in series of 250 mL Erlenmeyer flasks Adsorption studies were carried out in the specific period at the temperature of 25°C in the thermal mixer (ZHWY-200B, ZHICHENG Analytical Co., Ltd). After adsorption process, samples were filtered from $0.45 \mu\text{m}$ membrane filters. Ni^{+2} concentrations of the filtered samples were analyzed by using an inductively coupled plasma mass spectrometry (Optima 2100DV ICP, Perkin-Elmer, Boston, MA) (SM: 3120 B). pH measurements (SM: 4500- H^+ B) were performed using multi- electrode digital ion analyzer (Hach, HQ440d Multi) (APHA, 2005).

2.3. Experimental procedure

The effects of adsorbent mass, operating time and pH on the adsorption were examined by using the experimental conditions shown in Table 1. Experimental adsorption studies were carried out within 250 mL erlenmeyer flask.

Table 1. Adsorption process was carried experimental conditions

	Agitating speed (rpm)	Adsorbent content (mg L ⁻¹)	Time (min)	pH	Initial solution of nickel
Effect of adsorbent mass, Ms (g)	150	0,5-5,0	60	5,8 5	100,6
Effect of contact time, t (min)	150	5,0	0-120	5,8 5	103,2
Effect of pH	150	5,0	5,0	2-6	104,3

Each study was performed in 3 repetitions and the results were given as mean values. In the study, tests were repeated to check for errors in cases where standard errors are greater than 0.01.

3. RESULTS AND DISCUSSIONS

3.1. Effect of the adsorbent amount

The effect of adsorbent mass on adsorption of Ni (II) was examined by using 100 ml of 100 mg L⁻¹ Ni (II) solution during 60-minute operation process of 0.5-5.0 mg walnut shell samples.



Fig. 1. Effect of the adsorbent amount

As seen in Figure 1, the adsorption of Ni (II) increased gradually with the increasing adsorbent amount and it was determined that the optimum walnut shell concentration was 5 mg L⁻¹. It was shown that the proportional increase between adsorbent concentration and removal efficiency was associated with the increase in the amount of adsorbent per unit contaminant.

3.2. Effect of contact time

The effect of contact time was studied by using Ni (II) solution that had constant concentration at room temperature. The adsorption of Ni (II) heavy metal was examined at 1-120 min time intervals. The effect of contact time on adsorption is given in Figure 2.

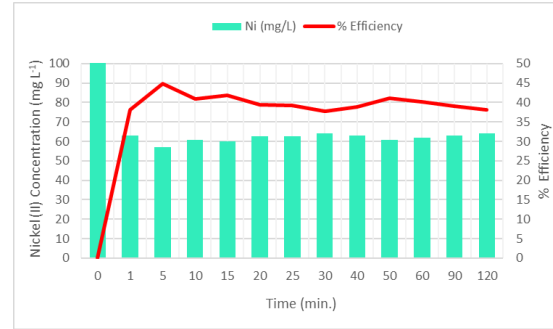


Fig. 2. Effect of contact time

Because increasing of the contact time in adsorption studies significantly increases the costs, time optimization needs to be done. As shown in Figure 2, the highest adsorption efficiency was obtained in 5 minute contact time (44.90%). In different contact times, decreases and increases in removal efficiency were observed. It is thought that the main reason for this situation is the desorption process, which occurs at the end of the saturation of heavy metals that hold onto the surfaces of walnut shells.

Based on these results, the optimum contact time was determined to be 5 minutes.

3.3. pH Effect

The effect of pH on walnut shells and Ni (II) heavy metals that have 100 mg L⁻¹ initial concentration was investigated in pH 2-6 range. The effect of Ni (II) on adsorption in determined pH values was shown in Figure 3.

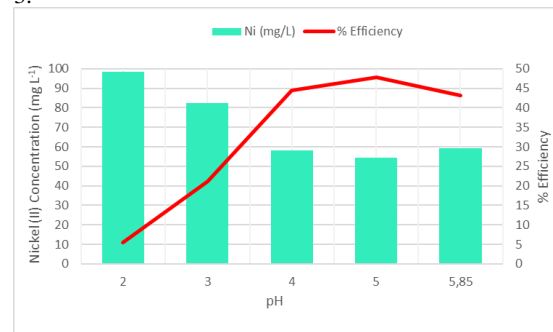


Fig. 3. Effect of pH

Because of the coating of the surface of the walnut shell due to the increase in H⁺ ion concentration at low pH values, Ni (II) ions were not able to hold on to the surface. As a result of this, the removal efficiency was determined as 5.53%. Depending on the increases in pH values, increases in removal efficiency were obtained.

Although the highest removal efficiency was obtained in pH 5 with 47.82%, the solution's own pH value (5.85) was determined as the most appropriate pH value. In pH 5.85, the removal efficiency of 43.23% was obtained. Given the economic factors, the effect of the use of chemical substances to change pH value on the adsorption efficiency has been neglected.

4. CONCLUSIONS

In this study, it was determined that by using the walnut shell found as common agricultural waste, removing of the heavy metal Ni (II) with aqueous adsorption process was possible. The removal efficiency of 43.23% was obtained in 5 mg L⁻¹ adsorbent concentration at 5 minute contact time and pH 5.85. It was concluded that the walnut shell can be used as a low-cost and abundant source for the removal of Ni (II) from water and it can be also used as an alternative to expensive materials such as ion exchange resins and active carbon. It is thought that obtaining higher increases in removal efficiency can be possible by making modification studies of walnut shell.

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