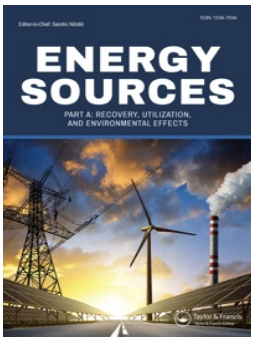

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Energy Sources, Part A

ISSN: 1556-7036 (Print) 1556-7230 (Online) Journal homepage: www.tandfonline.com/journals/ueso20

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To cite this article: N. Özbay (2009) Adsorption of Ni (II) Ions from Aqueous Solution by Pyrolytic Chars Derived from the Cottonseed Cake, Energy Sources, Part A, 31:14, 1271-1279, DOI: 10.1080/15567030802089557

To link to this article: https://doi.org/10.1080/15567030802089557

Energy Sources, Part A, 31:1271–1279, 2009

ISSN: 1556-7036 print/1556-7230 online
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Adsorption of Ni (II) Ions from Aqueous Solution by Pyrolytic Chars Derived from the Cottonseed Cake

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Abstract *The adsorption of Ni (II) ions from aqueous solution by pyrolytic char obtained from the cottonseed cake was studied in thisarticle. The sample was pyrolysed with a heating rate of 7°C min^{-1} up to select final pyrolysis temperatures of 400°C, 550°C, and 700°C under a steam atmosphere with sweep gas velocities of 2.7 cm sec^{-1}. Three pyrolytic char were used as adsorbent obtained at final pyrolysis temperatures. The influence of experimental parameters such as pyrolysis temperature, adsorbent dosage, condition time, and nickel (II) concentration were investigated. Optimal condition was determined as: 0.35 g/50 ml adsorbent dosage, 10 mg/l Ni (II) concentration, 60 min contact time for temperature 700°C of pyrolytic char. Adsorption parameters were determined by using Langmuir isotherm. The adsorption capacity of the pyrolytic char is 25 mg/g and the maximum surface area (47.98 m^2/g) was obtained at 700°C. According to the experimental results, the pyrolytic char can be used as carbon adsorbent for adsorption processes.*

Keywords BET surface area, cottonseed cake, Langmuir, Ni (II) adsorption, pyrolytic char

1. Introduction

Water pollution has become a serious problem nowadays. Both the environmental and human beings are exposed to hazards of different pollutants (organic pollutants, metal ions, etc) from waste and potable water. The enormous damage caused by water pollution have led to numerous investigations having as their objective the protection of the threatened environment and living creatures through new methods. Metals such as Ni, Hg, Cd, Pb, As, etc., have a harmful effect on human physiology and other biological systems (Yardim et al., 2003).

Nickel is a toxic metal, which may be present in wastewaters. Nickel salts are commonly used in metal plating and its concentration in industrial wastewaters range from 3.40 to 900 mg/l. Maximum contaminant limit for nickel in bottled water has been fixed at 50 μg/l by the European Economic Community. Different industries such as silver refineries, electroplating, zinc base casting, and storage battery industries discharge significant

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amounts of nickel in various forms to the environment. The recovery of heavy metals from wastewater is a major topic in water research and several methods are commonly used for this purpose: chemical precipitation, electrochemical reduction, evaporation, reverse osmosis, membrane filtration, co-precipitation, electro dialysis, adsorption, biosorption, etc. However, these techniques have certain disadvantages (cost and suitability) and, carbon adsorption is the most attractive process among these methods. Adsorption by activated carbon is widely used for the removal of toxic metal and has been studied extensively (Erdoğan et al., 2005).

Studies on the adsorption of heavy metals by activated carbon and various low-cost materials have been reported in the literature. Ekinci et al. (2002) have studied adsorption of Hg (II) from aqueous solution at 293 K by activated carbons obtained from apricot stones, furfural, and coals. Adsorption studies were performed under the varying conditions of time of treatment, metal ion concentration, and pH.

Christian Taty-Costodes et al. (2003) investigated the feasibility of metallic ions removal from aqueous solution by sawdust of *P. sylvestris.*

Grape stalk wastes have been investigated for removal of copper and nickel ions from aqueous solutions. The influence of pH, sodium chloride, and metal concentration on metal removal has been studied. Maximum sorption for both metals was found to occur at around pH 5.5–6.0 (Villaescusa et al., 2004).

Hazelnut shell activated carbon (Demirbas et al., 2002; Kobya, 2004; Kobya et al., 2002), apricot stones (Kobya et al., 2005), coirpith (Kadirvelu et al., 2001), rice husks (Ajmal et al., 2003; Bishnoi et al., 2004), and various activated carbons (Chubar et al., 2004; Pardhan et al., 2005) have been also used for removal of heavy metals from aqueous solutions.

Utilization of pyrolysis char for adsorption purposes is an advantage and important when considering the ubiquitous need for a cheap source of carbon adsorbent for various small-scale industries for wastewater treatment. In this regard, the purpose of this study is to investigate the possibility of the removal Ni (II) ion by pyrolytic char from cottonseed cake obtained by pyrolysis in the presence of water vapor. Adsorption studies were performed under the varying contact time, metal ion concentration, adsorbent dosage, and pyrolysis temperature.

2. Experimental

2.1. Preparation of Adsorbent

The cottonseed cake sample, which has been produced at a cottonseed oil factory was used in this study. Prior to use, the sample was air-dried and ground in a high-speed rotary cutting mill. The pyrolysis of the sample was carried out in a fixed-bed reactor in the presence of steam atmosphere. The 316 stainless steel retort has a volume of 400 cm^3 (70 mm id.) and it is externally heated by an electric furnace in which the temperature is measured by a thermocouple inside the bed. In the pyrolysis processes, 20 g samples were placed into the reactor and pyrolysed under water vapor atmosphere with water vapor velocities of 2.7 cm sec^{-1} at a heating rate of 7°C min^{-1} up to select final pyrolysis temperatures of 400°C, 550°C, and 700°C. Experiment apparatus was held at this temperature either a minimum of 30 min or until no further significant release of gas was observed. Three pyrolytic char were used as adsorbent obtained at final pyrolysis temperatures.

2.2. Characterization of Adsorbent and Determination of Ni (II) Concentration

The surface area of chars was measured in automated volumetric gas adsorption apparatus (Quantochrome Co.) using nitrogen as an adsorbate at 77 K. Before adsorption measurement, the sample was out gassed at 270°C for 3 h.

In order to determine Ni (II) ion concentration, Philips PU 9100X Model Flame Atomic Absorption Spectrometer (FAAS) (Philip, England) was used with an air acetylene mixture. Wavelength 232 nm and 0.5 nm slit width were chosen for Ni (II) ion detection. Hallow cathode lamp current was 5 mA. The measurements were repeated three times and no result was accepted if standard deviation was greater than 0.1 mg/l.

A value of 1,000 ppm Ni (II) solution was prepared from Ni $(NO_3)_2.6H_2O$ (Merck) and this stock solution was used for Ni (II) stock during the adsorption experiments.

Langmuir isotherm study was carried out with four initial concentrations of Ni (II) concentration: 5, 10, 15, and 20 mg/l with adsorbent dosage of 0.35 g/50 ml, pyrolysis temperature of 400°C, 550°C, and 700°C.

3. Result and Discussion

3.1. Proximate Analyses

Proximate analysis of raw cottonseed cake (wt%, dry basis) gave 6.1% moisture, 78.7% volatile matter, 4.9% ash, and 10.3% fixed carbon. The result of the proximate analyses of the chars at various pyrolysis temperatures are given in Table 1. When compared to the proximate analyses, increasing pyrolysis temperatures from 400°C–700°C, the content of volatile matter of the pyrolytic char decreased, whereas the contents of fixed carbon and ash increased. Increasing pyrolysis temperature leads to an increasing conversion into gaseous product volatile matter. At pyrolysis temperature of 700°C, most volatile matter has been released. Increasing devolatilization steadily increases the content of fixed carbon and ash in the char and these results are consistent with the literature (Lua et al., 2004; Lua et al., 2006; Gua and Lua, 1998).

3.2. Properties of Adsorbent

The adsorptive properties of pyrolytic chars are related to its surface area. The BET surface areas of various char samples are presented in Table 1. These results indicate that

Table 1
Proximate analysis and specific surface area of pyrolytic chars obtained from different pyrolysis temperature

Temperature, °C	V,* %	Ash,[a] %	FC, %	S_{BET}, m^2/g
400	21.54	13.92	64.54	1.00
550	16.26	16.65	67.09	17.00
700	5.37	20.74	73.89	47.98

V: Volatile matter; FC: Fixed carbon.
[a] Moisture free.

increasing the pyrolysis temperature from 400°C to 700°C increases the BET surface area due to the increasing evolution of volatiles from cottonseed cake, resulting in enhanced pore development in the chars. The low surface area values suggested that the pores might be virtually closed at low temperatures, thus preventing any access to the gas adsorbing and large macropores contribute only slightly to the surface area. Maximum surface area (47.98 m^2/g) was obtained at pyrolysis temperature of 700°C. These results consistent with the literature (Duran-Valle et al., 2005; Sharma et al., 2001; Sharma et al., 2000).

3.3. *Optimization of Ni (II) Adsorption*

Adsorption of Ni (II) onto adsorbent was systematically investigated by parameters such as varying conditions of treatment time, metal ion concentration, adsorbent dosage and pyrolysis temperature.

Figure 1 shows the effect of the adsorbent amount. As it can be seen, the optimum amount of adsorbent 0.35 g was found to be sufficient to reach the equilibrium for 10 mg/l of Ni (II) solutions, condition time was 60 min. Adsorption percentage increases from 54 to 76% while the amount of used adsorbent increases from 0.025 g to 0.25 g at 400°C. At the same temperature, adsorption percentage decreases after using 0.25 g adsorbent but there was no significant effect on adsorption percentage after using 0.35 g adsorbent at 550°C and 700°C.

The effect of the initial Ni (II) ion concentration (in the range of 5–20 mg/l) on the adsorption of Ni (II) is given in Figure 2. Adsorption of Ni (II) was very high remaining ca 99.4% at 700°C and 95.0% at 550°C. At 400°C, Ni concentration is changed from 5 mg to 15 mg/l, adsorption percentage increased from 25.0 to 85.7%; after using 15 mg/l Ni concentration, adsorption percentage decreases 62.0%. Removal of 5–20 mg/l Ni (II) by adsorbing onto pyrolytic char obtained at 700°C is very suitable for Ni (II) removal from waste waters and 10 mg/l of Ni (II) solutions was selected optimum and this value was used to optimize the other conditions.

Figure 3 indicates the effect of contact time on Ni (II) adsorption. There was no observed significant change to adsorption; percentage was stable as 99% at 700°C and 95.0% at 550°C. On the other hand, for 400°C, when condition time is changed from

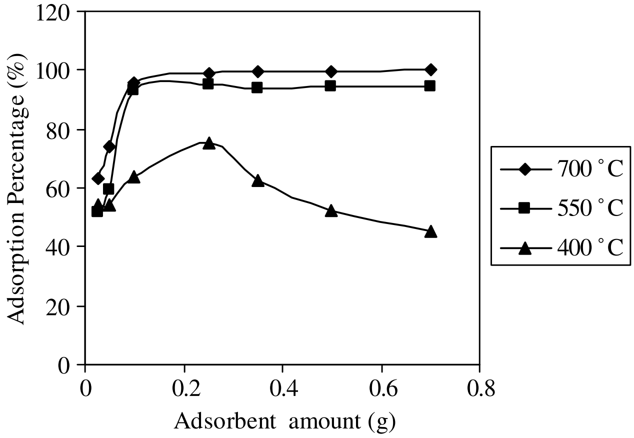

Figure 1. Effect of amount adsorbent concentration on adsorption percentage of Ni (II). Conditions: Ni (II), 10 mg/l; T, 25°C; contact time, 60 min.

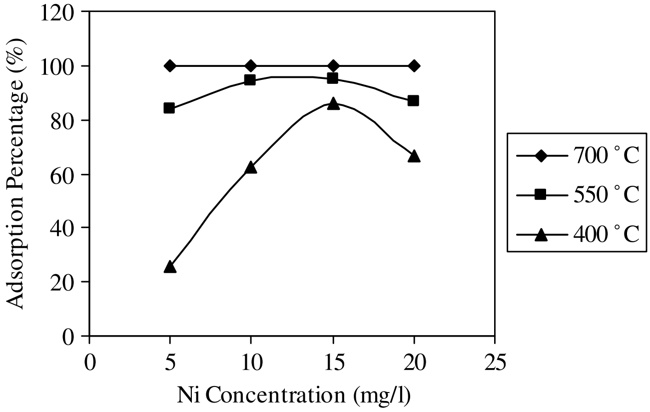

Figure 2. Effect of initial Ni (II) concentration on adsorption percentage of Ni (II). Conditions: Amount of adsorbent, 0.35 g/50 ml T, 25°C; contact time, 60 min.

15 to 60 min, adsorption percentage is decreased from 82% to 63% and at 120 min it reached a value of 83%.

Figure 4 shows that adsorption percentage of pyrolytic char prepared at the range of 400°C–700°C, adsorption percentage does not change for 0.025 and 0.05 g adsorbent dosage but adsorption percentages of same pyrolytic char increases for 0.25, 0.50, and 0.70 g adsorbent dosages. The cause of observing same adsorption percentage for pyrolytic chars prepared at the range of 400°C–700°C can be explained by the pores occupied with Ni (II). Maximum adsorption percentage was seen for all adsorbent dosages of pyrolytic char at 700°C. This situation can be explained by the increase of pyrolytic chars surface area.

3.4. Langmuir Adsorption Isotherm

The adsorption data have been analyzed with two adsorption methods, which are Langmuir and Freundlich (Nasser and El-Hendawy, 2005; Ggregg and Siny, 1982). The data

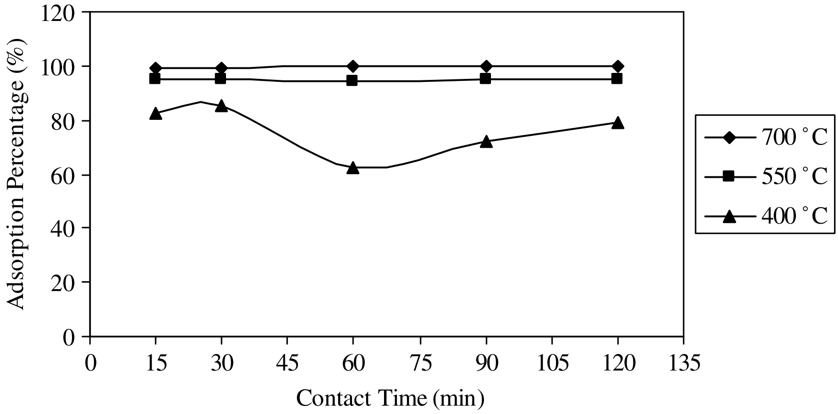

Figure 3. Effect of contact time on adsorption percentage. Conditions: Amount of adsorbent, 0.35 g/50 ml T, 25°C; Ni (II), 10 mg/l.

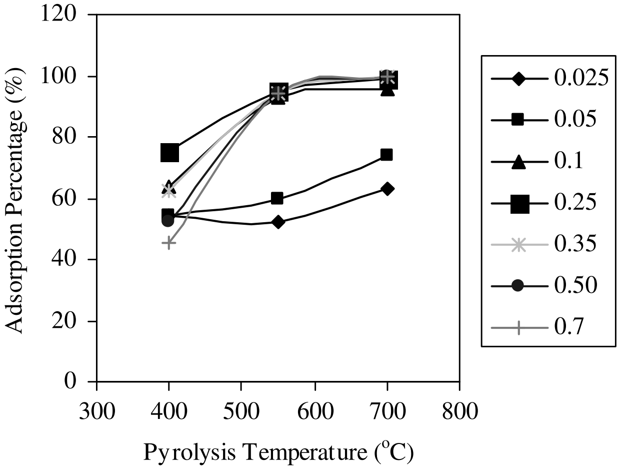

Figure 4. Effect of pyrolysis temperature on adsorption percentage for different adsorbent dosage. Conditions: Ni (II), 10 mg/l; T, 25°C; contact time, 60 min.

for adsorption of Ni (II) on pyrolytic chars were fitted to the Langmuir isotherm well. The Langmuir model was commonly used in literature for liquid phase adsorption. Langmuir model assumes that the uptake metal ions occur on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions.

The Langmuir equation is defined as:

$$C_e/q_e = 1/Q_o b + C_e/Q_o \tag{1}$$

where C_e is the equilibrium concentration (mg/l), q_e is the amount adsorbed at equilibrium (mg/g), and Q_o and b is Langmuir constants related to adsorption capacity and energy of adsorption, respectively. The linear plot C_e/q_e versus C_e shows that the adsorption obeys Langmuir isotherm Q_o and b were determined from slope and intercept. Langmuir isotherm can be expressed by equilibrium parameter $R_1 = 1/1 + bC_o$, where C_o is the initial ion concentration (mg/l) and b is the Langmuir constant (l/mg). R_1 indicates the shape of the isotherm as follows: $R_1 > 1$—unfavorable isotherm; $R_1 = 1$—linear isotherm; $0 < R_1 < 1$—favorable isotherm, $R_1 = 0$—irreversible isotherm.

Figure 5 indicates that Langmuir adsorption isotherm for Ni (II) on pyrolytic chars was prepared at a different temperature. The values of Q_o and b are given in Table 2.

Table 2
Isotherm constant of Langmuir models for Ni (II) ions uptake by pyrolytic char obtained from the cotton seed cake

Sample	Q_o, mg/g	b, l/mg	r	R_1 5, mg/l	R_1 10, mg/l	R_1 15, mg/l	R_1 20, mg/l
400	17.85	5.60	0.999	0.034	0.017	0.011	0.0084
550	20.08	2.49	0.985	0.074	0.038	0.026	0.019
700	25	13.35	0.979	0.014	0.0074	0.0049	0.0037

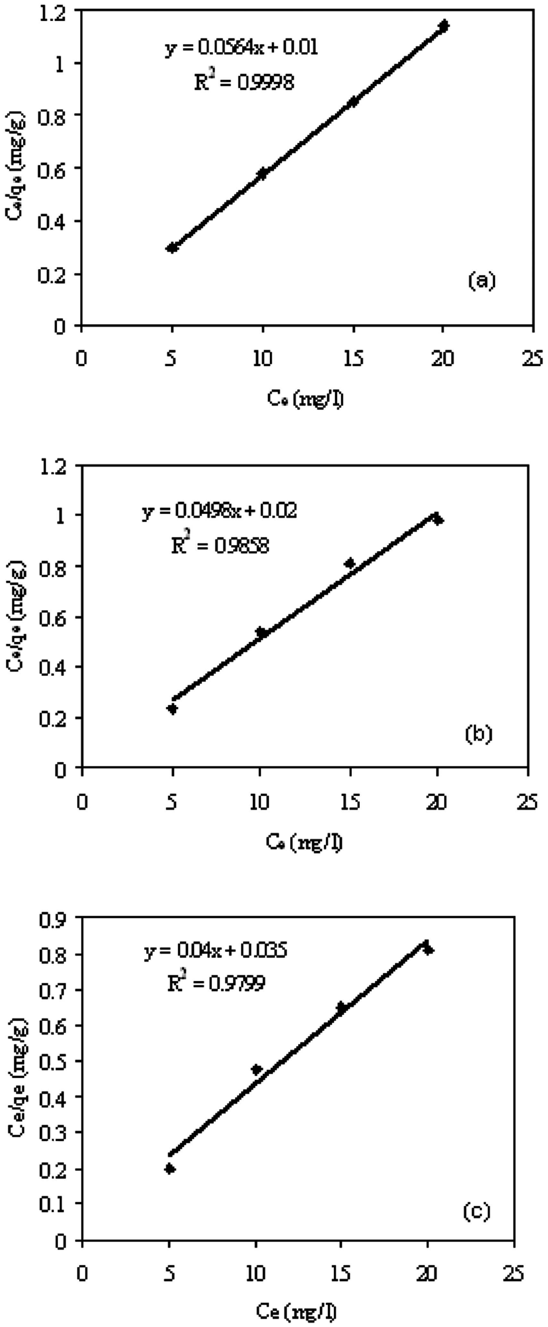

Figure 5. The Langmuir isotherm for pyrolytic char obtained from the cotton seed cake at different pyrolysis temperatures: (a) 400°C, (b) 550°C, and (c) 700°C.

It can be seen from Table 2 that there was increasing trend in Q_o values with increase in pyrolytic temperature and in surface area. Maximum Q_o value was obtained 25 mg/g for pyrolytic chars prepared at 700°C. The adsorption capacity of high temperature is higher than the low temperature. The results show that Ni^{+2} removal correlates with BET surface area. Obtained R_1 values between 0 and 1 shows favorable adsorption (Table 2).

4. Conclusions

- In this study, pyrolytic chars obtained from cottonseed cake by pyrolysis in the presence of water vapor at different temperatures were identified as adsorbent.
- The maximum surface area of pyrolytic char 47.98 m^2/g was determined at 700°C.
- The adsorbent prepared at 700°C was more effective (99%) for removal of Ni (II) from aqueous solution for 0.35 g adsorbent concentration. Adsorption percentage of all pyrolytic chars samples was determined in the range of 50–99%.
- Maximum adsorption percentage was determined in the experiments carried out with pyrolytic char prepared at 700°C sample by using different adsorbent dosage.
- The adsorption data fit reasonably well and the Langmuir isotherm for pyrolytic chars samples was obtained from different pyrolysis temperatures. Maximum Langmuir adsorption capacities were 25 mg/g for 700°C adsorbent.
- R_1 values were determined between 0 and 1, which indicate favorable adsorption.
- According to the experimental results, the pyrolytic char obtained from cottonseed cake can be used as carbon adsorbent for adsorption processes. It is important to produce cheaper carbon adsorbent, which are essential for small scale industries, through a simple and energy-efficient one stage pyrolysis process by choosing low-cost raw materials.

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