World Academy of Science, Engineering and Technology
International Journal of Materials and Metallurgical Engineering
Vol:9, No:5, 2015

The Adsorption of Zinc Metal in Waste Water Using $ZnCl_2$ Activated Pomegranate Peel

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Open Science Index, Materials and Metallurgical Engineering Vol:9, No:5, 2015 publications.waset.org/10001226/pdf

***Abstract*—**Activated carbon is an amorphous carbon chain which has extremely extended surface area. High surface area of activated carbon is due to the porous structure. Activated carbon, using a variety of materials such as coal and cellulosic materials; can be obtained by both physical and chemical methods. The prepared activated carbon can be used for decolorize, deodorize and also can be used for removal of organic and non-organic pollution. In this study, pomegranate peel was subjected to 800W microwave power for 1 to 4 minutes. Also fresh pomegranate peel was used for the reference material. Then $ZnCl_2$ was used for the chemical activation purpose. After the activation process, activated pomegranate peels were used for the adsorption of Zn metal (40 ppm) in the waste water. As a result of the adsorption experiments, removal of heavy metals ranged from 89% to 85%.

***Keywords*—**Activated carbon, chemical activation, microwave, pomegranate peel.

I. Introduction

THERE are effective method as adsorption which is relatively useful and economical for quickly lowering the concentration of pollutants such as organic compounds, metal ions and dissolved dyes in an effluent [1]. Because of their mechanical stability, low specificity, fast adsorption kinetics and high adsorption capacities, activated carbon is accepted as one of the most popular material for adsorption [2], [3].

Activated carbon which has great capacity of adsorbing for various organic compounds such as dyes, heavy metals, pharmaceutical and surfactants are the most commonly used adsorbent. But price of activated carbon is relatively high. For this reason initiative have been started to study reduced cost and made of natural sorbents to remove impurity from wastewater. About production of activated carbon using lower cost methods and materials from renewable resources have been searched by many researchers. In some of this research, activated carbon using agricultural and industrial waste materials was produced. [4]–[10]. Activated carbon can be produced from all carbon-containing lignocellulosic agricultural waste as lignin [11], macro-algal [12], defective coffee press cake [13], palm shell [14], rice husk [15] wastes of vegetable origin (e.g. nut shells and fruit stones) [16].

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Solid waste of peel/skin, stones or seeds obtained from processing of fruits can be used production of activated carbon. One of these fruits is pomegranate (*Punica granatum* L.) and the total production of pomegranate in the world is about 1 million tonnes [17]. Turkey which the annual production of pomegranate in is about 60,000 tons is one of the world's largest producers [18].

Activated carbons are produced by physical or chemical activation. Chemical activation can be carried out by thermal decomposition of raw material with chemical reagents. Chemicals as zinc chloride ($ZnCl_2$), phosphoric acid (H_3PO_4), and potassium hydroxide/carbonate (KOH/K_2CO_3) is used commonly. An example of chemical activation with $ZnCl_2$ is that Olivares-Marin et al. prepared activated carbon from cherry stones [19]. In another study, Angin et al. produced activated carbons were from biochar of safflower seed press cake by chemical activation with $ZnCl_2$. It was reported that activation temperature and impregnation ratios are more influence on the porosity, surface area and adsorption capacity of activated carbons [20].

As the investigations, used microwave process instead of pyrolysis [21]-[23] provide lots of advantage as high heating rates, controllable and selective heating; energy and time savings [24].

In this study, pomegranate peel was subjected to pretreatment with microwave power for different times. As the reference material fresh pomegranate peel was used. Activated carbons were prepared by chemical activation with $ZnCl_2$ of the biochar obtained through microwave of pomegranate peel. After the activation process, adsorption capacities of the activated carbons were investigated.

II. Experimental Method

Pomegranate peels (Fig. 1) were collected from local juice bar. The residual dreg after juicing process is separated from pomegranate peel. Then pomegranate peel was washed with tap water to remove dusts and dried over night at 70ºC. It was granulated and then sieved through a 20 mesh sieve. Dry pomegranate peel powder was stored in food storage bag at room temperature. Pomegranate peel powder is shown in Fig. 2.

The MW treatment was carried out using a Robert Bosch HMT72G420 Microwave Oven (Fig. 3). Sample was exposed to a maximum power of 800 W with an operating microwave frequency of 2.45 GHz (wavelength 12.2 cm).

A gram of sample of dry pomegranate peel was placed in each of watch glass. Two watch glasses so as to opposite with each other were placed in microwave oven. Microwave oven was started under constant MW power (800 W) and air

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atmosphere. Process was carried out for 1 to 4 minutes.

Samples which had exposed to microwave, were added into $ZnCl_2$ solution (weight ratio=1:3) and stirred at 500 rpm. This process is shown in Fig. 4. After 2 h, mixture was decanted and then solid phase was added to HCl. After 1 h stirring, rinsed with deionized distilled water several times until pH 5.5. Product was dried over night at 105ºC. Dry pomegranate peels without microwave pretreatment was implemented same chemical activation. It was used as a reference material.



Fig. 1 Pomegranate peel



Fig. 2 Pomegranate peel powder



Fig. 3 Robert Bosch HMT72G420 Microwave Oven



Fig. 4 Mixture of sample and $ZnCl_2$



Fig. 5 Perkin Elmer Spectrum One FT-IR

Then samples were characterized with Perkin Elmer Spectrum One Fourier Transform Infrared Spectroscopy (FT-IR), (Fig. 5) with Universal ATR sampling accessory – Diamond / ZnSe Crystal. Working region of FTIR spectra was selected between 1800 and 650 cm^{-1}.

For the adsorption process (Fig. 6), 0.25g of the activated carbon products was mixed with 40 ppm of Zn solutions (50 ml). The mixture was stirred at 500rpm for 2h at room temperature (22±0.5 °C). Zn solution and activated carbon was separated from each other by using filter paper. The equilibrium concentrations of Zn were measured by using Perkin Elmer 35 Lambda UV/Vis Spectrophotometer (Fig. 7) at wavelength 300 nm.



Fig. 6 Adsorption process



Fig. 7 Perkin Elmer 35 Lambda UV/Vis Spectrophotometer

III. Results and Discussion

A. Results of Microwave Pre-Treated Samples

After microwave process, results of loss weight of samples shown in Table I.

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TABLE I
RESULTS OF LOSS WEIGHT OF SAMPLES

Time of Microwave	Weight Loss (%)
1	8
2	17
3	23
4	28

As a result, weight loss of the samples increased with increasing time. This situation may be due to volatilization of certain volatile component.

B. Characterizations of the Activated Carbons

FT-IR spectra of prepared activated carbons and raw materials are shown in Fig. 8. In Fig. 8 the numbers at the right hand side represents the exposure time of samples in the microwave. Fig. 9 represents the FT-IR spectrum of commercial activated carbon.

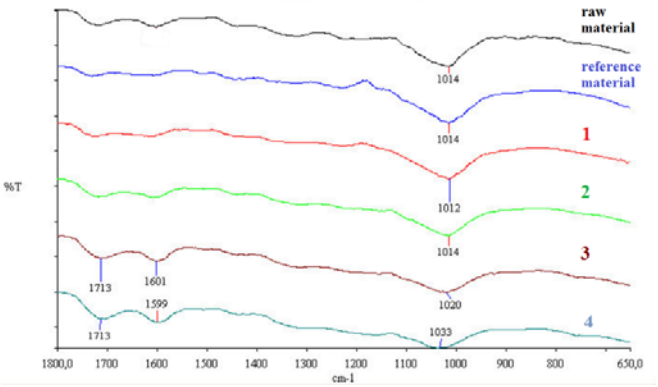


Fig. 8 FT-IR spectra of synthesized activated carbons and raw material

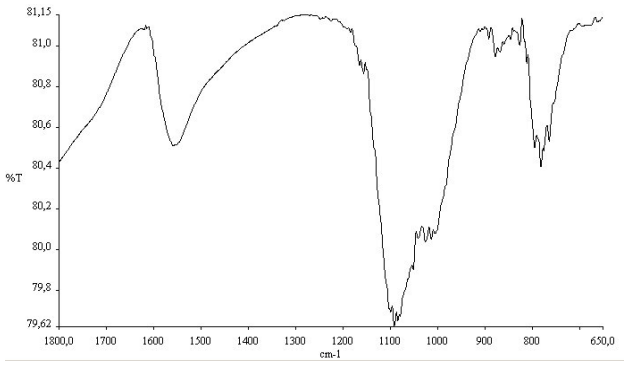


Fig. 9 FT-IR spectrum of commercial activated carbon

In all of spectra placed Figs. 8 and 9; vibration of C–O–C (1000-1100 cm^{-1}) is observed. Different from the prepared activated carbon samples, in activated carbon, ester C=O (1713 cm^{-1}) and aromatic C=C and C=O (about 1600 cm^{-1}) were seen.

C. Results of Adsorption of Zn (II) by Activated Carbon

Adsorption of Zn (II) by activated carbons is presented in Table II.

TABLE II
RESULTS OF LOSS WEIGHT OF SAMPLES

Synthesized Activated Carbon	Remaining Zn (II) in Solution (ppm)
Reference material	6.06
1	5.73
2	5.34
3	5.31
4	4.63

From the results it is seen that the increase in the microwave exposure time leads to better adsorption of Zn (II).

IV. CONCLUSIONS

Because of used activated carbon as most commonly adsorbent, investigation about reducing cost of activated carbon has been the major objective. For this reason, especially as alternative method and raw materials has been focused on a microwave energy and bio-waste. While microwave process has advantages like saving energy and time; bio-waste is low cost raw material.

In this study, the adsorption capacities of activated carbon obtained by exposure microwave energy at different times were investigated. When reference material is compared with activated carbons, the capacity of adsorption of Zn is increased with the increasing microwave exposure time.

In the future studies, activated carbon will be obtained by changing the sequence of process and ratio of chemical agents and raw materials.

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