

Zinc Adsorption Determination of H₂SO₄ Activated Pomegranate Peel

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Abstract—Active carbon can be obtained from agricultural sources. Due to the high surface area, the production of activated carbon from cheap resources is very important. Since the surface area of 1 g activated carbon is approximately between 300 and 2000 m², it can be used to remove both organic and inorganic impurities. In this study, the adsorption of Zn metal was studied with the product of activated carbon, which is obtained from pomegranate peel by microwave and chemical activation methods. The microwave process of pomegranate peel was carried out under constant microwave power of 800 W and 1 to 4 minutes. After the microwave process, samples were treated with H₂SO₄ for 3 h. Then prepared product was used in synthetic waste water including 40 ppm Zn metal. As a result, removal of waste Zn in waste water ranged from 91% to 93%.

Keywords—Activated carbon, chemical activation, H₂SO₄, microwave, pomegranate peel.

I. INTRODUCTION

ACTIVATED carbon which has highly developed porosity and surface area is a black solid charcoal [1]. Using physical method, chemical method or two methods together can be produced activated carbon from lots of raw materials such as coal, wood, industrial waste products and some agricultural products [2]. Physical activation has two steps: carbonization step (thermal decomposition of the raw material) and activation step (the activation of the carbonized structure) [3]. By the chemical activation, a raw material is impregnated with an activating reagent and the impregnated raw material is heated under an inert atmosphere. In industry, zinc chloride (ZnCl₂), phosphoric acid (H₃PO₄) and potassium hydroxide (KOH) are most commonly used chemicals [4]. Chemical activation is generally carried out at a lower temperature and shorter time comparing with physical activation. Chemical activation process is more effective for development of a porous structure [5].

In literature it is reported that microwave process can be used instead of pyrolysis [6]-[8]. Microwave heating has lots of advantages, such as high heating rates, controllable and selective heating; energy and time savings as compared with conventional heating [9]. Microwave processes in pilot scale

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and industrial scale is very important for the production with stability and purity of the extracts of plant materials [10], [11]. Several researchers studied the parameters such as; temperature of decomposition, heating rates and requirement for feedstock pre-processing (e.g. shredding or drying) with microwave and convection heating [12]-[16].

All living organisms at food chain are affected from heavy metals on industrial waste water which has severe toxicity. Before waste water is released to environment, heavy metals should be made to remove from waste water with aim of the regulatory safe discharge standards [17]. Removal of heavy metals from aqueous solution is performed with several methods such as membrane separation, chemical coagulation, adsorption, ion exchange, extraction, and chemical precipitation [18]. Initial cost, simple design, and easy operation are important for adsorption process [19]. Activated carbon (as powder, granular or fiber) is the most widely used adsorbent because of having large surface area, porous structure, high adsorption capacity and large reactive surface [20]. Among various heavy metals, Zn(II) is a common pollutant in different industrial applications such as natural ores, acid-mine drainage, galvanizing plants and municipal waste water treatment plants [21].

In this study, the effect of microwave process is investigated for the removal of Zn metals from aqueous solution. First of all, pomegranate peel was subjected to 800 W microwave power for 1 to 4 minutes. Then the chemical activation with H₂SO₄ is conducted. Finally removal of Zn(II) from waste water was measured by obtained activated carbons.

II. EXPERIMENTAL

A. Materials and Method

Pomegranate peel was obtained from local juice bar. The residual parts inside pomegranate peel in the end of juicing process are discharged. After pomegranate peel was washed with tap water, it was dried overnight at 70 °C. Then it was grinded and eliminated from 20 mesh sieve. Dry pomegranate peel was put into low density polyethylene bags.

The MW treatment of dry pomegranate peel was carried out using a Robert Bosch HMT72G420 Microwave Oven which has maximum power of 800 W with an operating microwave frequency of 2.45 GHz (wavelength 12.2 cm).

Dry pomegranate peel (1 g) was put into two watch glasses and placed in microwave oven. Microwave process was done for 1 to 4 minutes. Process was carried out under constant MW power (800 W) and air condition. At the end of microwave process, samples were weighed and loss weight

was noted.

At this step, 3 ml of H_2SO_4 was added for each 1 g of pretreated samples. At the end of 3 h, it was rinsed with deionized distilled water several times until pH 5.5. Same chemical activation process was carried out for dry pomegranate peel without microwave treatment. Product dried over night at 105 °C.

Adsorption of Zn was examined by mixing 0.25 g of the product with 40 ppm of Zn solutions (50 ml) at room temperature (22 ± 0.5 °C). Stirring speed and time were selected as 500 rpm and 2 h, respectively. At the end of adsorption experiment, solution was separated from activated carbon by filter paper.

Characterization

Fourier Transform Infrared Spectroscopy (FTIR) spectra with Universal ATR sampling accessory – Diamond / ZnSe Crystal were recorded in the 1800–650 cm^{-1} region by a Perkin Elmer Spectrum One (Fig. 1 (b)).

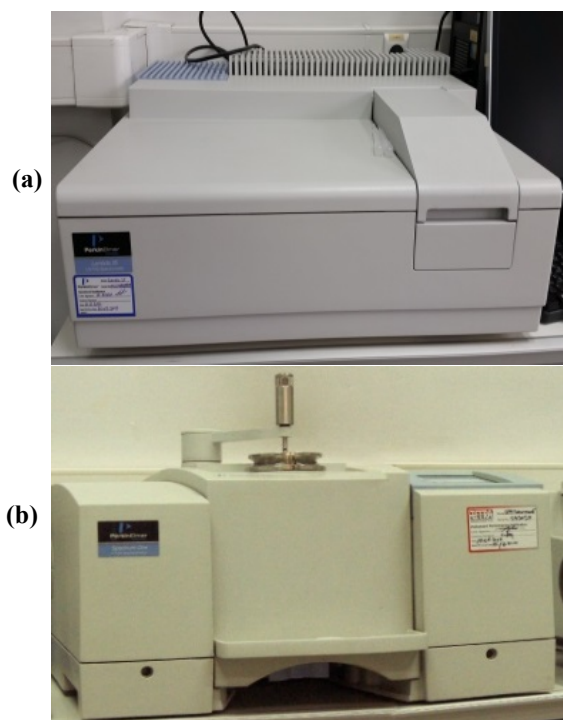


Fig. 1 (a) Perkin Elmer 35 Lambda UV/Vis Systems, (b) Perkin Elmer Spectrum One FT-IR

III. RESULTS AND DISCUSSION

For measurement of equilibrium concentrations of Zn, Perkin Elmer 35 Lambda UV/Vis Systems spectrophotometer (Fig. 1 (a)) was used at wavelength 300 nm.

Results of Microwave Pre-Treated Samples

After microwave process, loss weight results of samples are shown in Fig. 2.

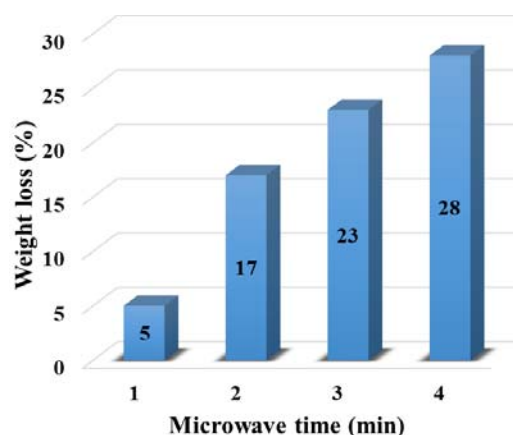


Fig. 2 Weight loss of the samples with increasing microwave treatment time

As shown in Fig. 2, loss weight depends on time of microwave. Because of volatilization of some volatile substances, loss weight can increase with increasing time.

Characterization of Activated Carbons

FTIR spectra and spectroscopic assignment of synthesized activated carbons and raw material are shown in Fig. 3 (a). Also FTIR spectra of commercial activated carbon are given in Fig. 3 (b). The numbers used as symbol in Fig. 2 (a) are the microwave times as min.

In Fig. 3 (a), transmittance peaks are approximately 1715 and 1595 cm^{-1} of the wave number for activated carbon and 1014 cm^{-1} of the wave number for raw material. Also commercial activated carbon has peaks about 1580, 1100 and 790 cm^{-1} . Also due to C=C tensions, many carbonaceous materials make absorption in the region of approximately 1600 cm^{-1} peak. The small peak at about 1700 cm^{-1} results from C = O tensions. Kinonik groups (1550-1680 cm^{-1}), carboxylic acid (1665-1760 cm^{-1}) and lactones (1675-1790 cm^{-1}) show absorbance in this region. And in the FT-IR spectrum of raw material, C–O–C (1057 cm^{-1}) tension is observed.

In the FTIR spectra, all samples have similar bands. But observed peak around 1000 cm^{-1} in the band of raw and commercial material disappears in bands of the activated carbons.

Results of Adsorption of Zn (II) by Activated Carbon

In Fig. 4, the removal of zinc (II) solution with respect to microwave treatment time is given. Numbers using for synthesized activated carbon in Fig. 4 represent microwave times.

As seen from the results the maximum absorption was occurred at the 1 min microwave treated sample and the minimum absorption was occurred at the 3 min microwave treated sample.

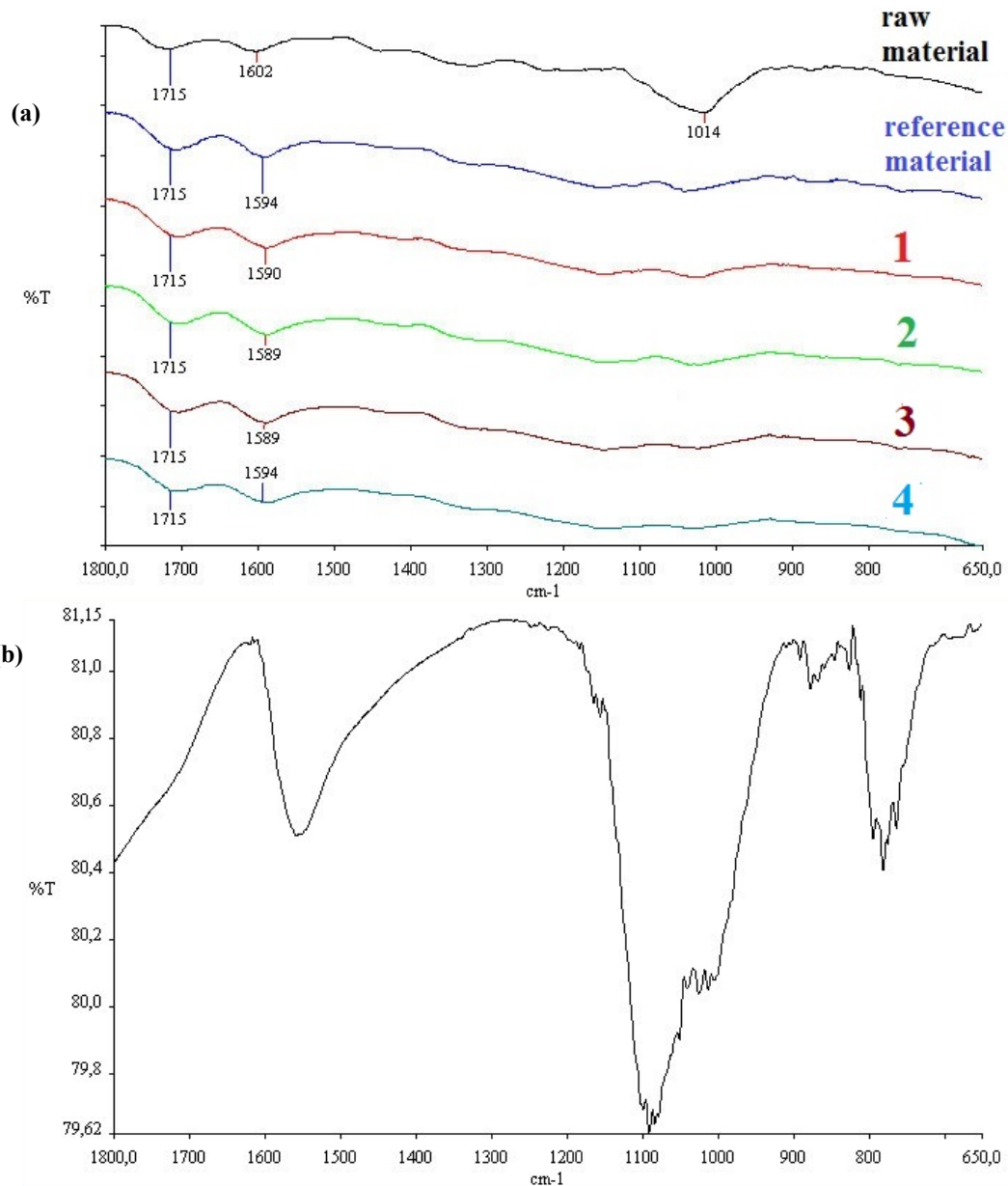


Fig. 3 FT-IR spectrum (a) synthesized activated carbon and raw material, (b) commercial activated carbon

IV. CONCLUSIONS

Activated carbon is most popular material for removal of heavy metals from waste water. For this reason, investigations oriented reducing cost are continued. In recent years, researchers have been directed towards production of activated carbon with microwave energy due to advantage saving energy and time.

In this study, H_2SO_4 was used as an activation agent after the microwave pretreatment for pomegranate peel. And obtained activated carbon was used for adsorption of Zn (II) ions in the Zn solution. Although significant weight loss is observed in the microwave process, there is substantially no effect on the zinc removal. Produced activated carbon by using only chemical activation is quite successfully for adsorption.

In the future studies, firstly chemical agent then microwave process will be used to produce activated carbon.

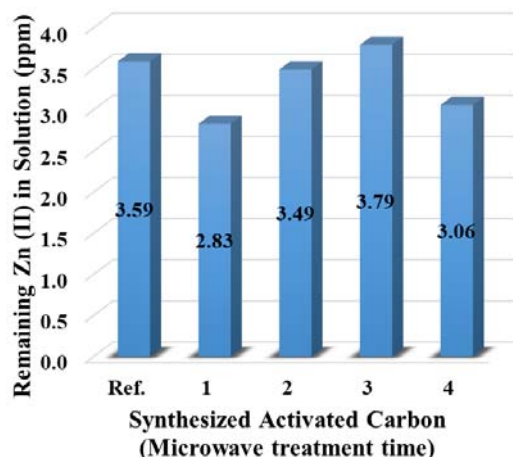


Fig. 4 Removal of Zinc (II) solution with respect to microwave treatment time

REFERENCES

- [1] J. N. Sahu, J. Acharya, B.C. Meicap, Optimization of production conditions for activated carbons from tamarind wood by zinc chloride using response surface methodology, *Bioresour. Technol.*, vol. 101 1974–1982, 2010.
- [2] J. Guo, A. C. Lua, Characterization of chars pyrolyzed from oil palm stones for the preparation of activated carbons, *J. Anal. Appl. Pyrol.*, vol. 46, 113–125, 1998.
- [3] B. S. Girgis, L. B. Khalil, T. A. M. Tawfik, Porosity development in carbons derived from olive oil mill residue under steam pyrolysis, *Journal of Porous Materials*, vol. 9, 105–113, 2002.
- [4] J. W. Patrick, *Porosity in carbons: characterization and applications*, Edward Arnold, 331 p, 1995.
- [5] S. Yorgun, N. Vural, H. Demiral, Preparation of high-surface area activated carbon from Paulownia by $ZnCl_2$ activation, *Micropor. Mesopor. Mater.*, vol.122, 189–194, 2009.
- [6] M. Miura, H. Kaga, A. Sakurai, T. Kakuchi, K. Takahashi, Rapid pyrolysis of wood block by microwave heating, *J. Anal. Appl. Pyrolysis*, vol. 71, 187–199, 2004.
- [7] H. Akitoshi, N. Yosuke, N. Toshio, C. Saika, K. Hisanori, K. Shunsaku Manufacturing method of activated carbon by microwave heating and its device, Patent of Japan, JP 2004-352595, 2004.
- [8] K. Setsuhi, A. Seiichi, K. Shiro, O. Masaharu, Carbonization and production of activated carbon, Patent of Japan, JP 2000-034114, 2000.
- [9] D.A. Jones, T. P. Lelyveld, S. D. Mavrofidis, S. W. Kingman, N. J. Miles, Microwave heating applications in environmental engineering-a review, *Resources, Conservation and Recycling.*, vol.34, 75-90, 2002.
- [10] D.E. Clark, W.H. Sutton, Microwave processing of materials, *Annual Review of Materials Research*, vol. 26 299–33, 1996.
- [11] "Crodarom production facilities," 2015. (Online). Available: <http://www.crodarom.com/home.aspx?s=110&r=124&p=896>
- [12] V. L. Budarin, J. H. Clark, B. A. Lanigan, P. Shuttleworth, D. J. Macquarrie, Microwave assisted decomposition of cellulose: a new thermochemical route for biomass exploitation, *Bioresour. Technol.*, vol. 101, 3776–3779, 2010.
- [13] L.G. Da Silv, A. Domínguez, J. A. Menéndez, M. Inguanzo, J. J. Pis, Production of bio-fuels by high temperature pyrolysis of sewage sludge using conventional and microwave heating, *Bioresour. Technol.*, vol. 97, 1185–1193, 2006.
- [14] X. Zhao, Z. Song, H. Liu, Z. Li, L. Li, C. Ma, Microwave pyrolysis of corn stalk bale: a promising method for direct utilization of large-sized biomass and syngas production, *Journal of Analytical and Applied Pyrolysis*, vol. 89, 87–94, 2010.
- [15] F. Yu, P. H. Steele, R. Ruan, Microwave pyrolysis of corn cob and characteristics of the pyrolytic chars, *Energy Sources, Part A: Recovery Utilization, and Environmental Effects*, vol. 32, 475–484, 2010.
- [16] E. Yagmur, M. Ozmak, Z. Aktas, A novel method for production of activated carbon from waste tea by chemical activation with microwave energy, *Fuel*, vol. 87 3278–3285, 2008.
- [17] A. K. Meena, C. Rajagopal, Kiran, G. K. Mishra, Removal of heavy metal ions from aqueous solutions using chemically (Na_2S) treated

- granular activated carbon as an adsorbent, *J. Sci. Ind. Res.*, vol. 69, 449–453, 2010.
- [18] S. H. Lin, S. L. Lai, H. G., Leu, Removal of heavy metals from aqueous solution by chelating resin in a multistage adsorption process, *J. Hazard. Mater.*, vol. 76(15), 139–153, 2000.
- [19] V. Meshko, L. Markovska, M. Minceva, A. Rodrigues, Adsorption of basic dyes on granular activated carbon and natural zeolite, *Water Res.*, vol. 35(14), 3357–3366, 2001.
- [20] C. C. Bansal, J. B. Donnet, F. Stoeckli, *Active Carbon*. Marcel Decker, New York, 1988.
- [21] L. Norton, K. Baskaran, S. T. McKenzie, Biosorption of zinc from aqueous solutions using biosolids, *Adv. Environ. Res.*, vol. 8, 629–635, 2004.