International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 9 Issue 07, July-2020

Adsorption of Lead and Iron from Industrial Wastewater using Melon (Citrullus Colocynthis) Husk Activated Carbon

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Abstract— The application of activated carbon as an adsorbent in remediating heavy metals from industrial wastewater is increasingly being embraced. Agro wastes activated carbon adsorbents have proven to be more suitable and cost effective than the conventional wastewater treatment methods for the remediation. In this work, the shell of melon (melon husk) were converted into activated carbon and applied for the adsorption removal of Iron (Fe^{2+}) and Lead (Fe^{2+}) ions. The melon husk carbon were activated using NaoH, H_2SO_4 and $CO(NH_2)_2$ (Urea) reactive agents. After which the adsorbent were then characterized using Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). An adsorption study was then conducted; the wastewater were treated with activated adsorbent at a dosage interval of 0.2g, between 0 and 1.0g with a reaction time of 0 to 100 minutes at 10 minutes intervals and at constant speed of 150 rpm. The characterization study indicates that the melon husk ask is suitable for use as an adsorbent and the adsorption study indicate that the removal rate of these heavy metals varies with changes in activation method, contact time and adsorbent dosage. On the effect of dosage, the Melon husk activated carbon (MHAC) removed Iron (Fe^{2+}) ions between 6.39 - 22.81% for all activation agents at optimum dosage of 0.8g. While, 0-100% of Lead (Pb^{4+}) ions were adsorbed at dosage of 0.8g for all activation agent except for H_2SO_4.On the effect of contact time, equilibrium for removal of Iron (Fe^{2+}) and Lead (Pb^{4+}) was reached at an average contact time of 70minutes and 20minutes respectively for all activation agent. It was thus concluded that the Melon Husk Activated Carbon (MHAC) was more effective for removal of Lead (Pb^{4+}) ions compare to removal of Iron (Fe^{2+})ions.

Keywords—Activated carbon; adsorbent; waste water; heavy metals; melon husk.

I. INTRODUCTION

Availability of portable water is vital to the human race because it is essential for all life forms and energy (Emenike, et al., 2016; Nwankwo and Mogbo, 2014; Bhatnagar and Sillanpaa, 2010). Water also being a universal solvent has made it important for industrial usage. Due to the aforementioned reason there is a tremendous increase in demand for portable water, but there is limited supply due to drought, over exploitation and contaminations.(Emenike, et al., 2016; Bhatnagar and Sillanpaa, 2010; Abdel-Raouf and Abdul-Raheim, 2017).

Contaminations of these portable water is ascribed to discharge of industrial effluent (Nwankwo and Mogbo, 2014), discharge of untreated domestic sewage and Lethal industrial wastes, and runoff from agricultural fields (Bhatnagar and Sillanpaa, 2010).

Industrial effluent discharged from metal industries are sources of high concentration of heavy metal ions such as Mercury, Lead, Tin, Cadmium and Iron (Corral-Bobadilla, et al.,2019). The release of heavy metal ions in water streams poses a risk of affecting the ecosystems because of their non-biodegradability and bioaccumulation (Ojedokun and Bello, 2016; Asuquo and Martin, 2016). One of the heavy metal ions in our ecosystem that has raised serious concern is Lead and Iron. High accumulation of these metals has been identified to cause slight deficits in mental development, kidney problems and high blood pressure (Ojedokun and Bello, 2016; Igwe, 2007). Thus there is a necessity for removal of these metals from our sources of portable water.

A great deal of effort has been dedicated to the efficient removal of heavy metal ions. The commonly used methods for removal of metal ions from industrial effluents are chemical precipation, coagulation, ultra-filtration, chemical oxidation, ion exchange, filtration, electrolysis activated sludge etc. (Ujile and Okwakwam, 2018; Giwa, et al., 2013; Radaideh, et al., 2017). However, some of these methods cannot effect complete removal of the heavy metal ions, are too expensive, are selective of metal for removal, requires high energy, requires high concentration of reagents and generate very toxic sludge (Sulyman, et al.,2017).

Activated Carbon in adsorption of heavy metal ions has been gaining attention of researchers due to affordability and availability, simplicity in design and operation, high effectiveness in removal of heavy metals, generation of low toxic sludge and it's adaptability for domestic and industrial waste water (Madu and Lajide, 2013). Activated carbon is produced from burning agricultural wastes material like rice husks, coconut shells, melon husk, and palm oil shell, which are activated either by pyrolysis, chemical or physical process (Tadda, et al., 2017). Activated Carbon effectiveness in removal of heavy metal ion depends on its surface area, pore space and volume of ash content present (Mutegoa, et al., 2014).

Melon Husk is an agricultural by-product which is readily available in abundance at no or low cost. The melon husk don't have an immediate use, they are either disposed as waste causing nuisance to the environment, feed to livestock or burnt as a form of disposal. This work aim to use the shell of melon (melon husk), which were converted into activated carbon and applied for the adsorption removal of lead (Pb^{4+}) and iron (Fe^{2+}) ions.

II. MATERIAL AND METHODS

A. Adsorbent and Waste water

Melon husks were collected from the melon sellers at the Wazo Market in Ogbomosho, Oyo State, Nigeria. The materials were left and open sun drying for 3- 4 days. Then, the material was washed with double distilled water several times to remove impurities. After that the material was again dried in oven at 105^0C up to 24 hours. The raw material was crushed into small pieces and prepared to fine grind powder by use of mixing grinder. After grinding the material they was sieved (75-150 µm) to achieve uniform particle size before it was used for characterization without any prior chemical treatment.

The wastewater was collected from a Blacksmith workshop at Ile – Ijesha, Ojuekun off Adangba road, Ilorin, Kwara State.

B. Fourier Transform Infrared Spectrometer (FTIR) Analysis

The Fourier Transform Infrared (FTIR) spectrometer to determine the functional groups on adsorbent was performed at the quality control Laboratory of the Chemistry Department of University of Ilorin. In order to study the functional group of the adsorbent, an IR analysis was performed with a FTIR spectrometer (Nicolet Avator 330, England). One milligram of dried, finely divided adsorbent was mixed with 200 mg of KBr and pressed using hydraulic press and mould. The mixture obtained was immediately analyzed with a spectrophotometer in the range 3500 to 500 cm^{-1} with a resolution of 1 cm^{-1}. The influence of atmospheric water and CO_2 were subtracted.

C. Scanning Electron Microscopy (SEM)

The surface texture and morphology of the carbonized melon (*Citrullus colocynthis*) husk was determined using scanning electron micro-graph. The availability of pores and internal surface is a requisite for a potential adsorbent. To observe the surface pore structure of the activated carbons, SEM studies was carried out using Electron Probe Micro Analyzer (Model Jeol-JXA 840 A, Japan). For char samples, the foremost requirement was that they must be moisture free. The pulverized sample was mounted onto a substrate with a conductive adhesive. Coating with a thin film of conducting material was the primary requisite for all non-conducting specimens to be examined in SEM. In the present study, conducting material coating of specimen was done with gold medal by vacuum evaporation to get uniform thickness of specimen study during analysis

D. Melon Husk Carbon Activated by H_2SO_4

Saiful Azhar *et al.*, (2005) and Raghuvanshi *et al.*, (2004) acidic activation method was used. The carbonized husk was treated with H_2SO_4 in the ratio 1:1(w/v), and was dried, after which it was soaked in 1% $NaHCO_3$ overnight to remove residual acid. It was then oven dried at 150ºC for 24 hours.

E. Melon Husk Carbon Activated by NaOH

Raghuvanshi *et al.*, (2004) base activation method was used. The carbonized husk was soaked in 0.5m NaOH for 12 hours. After which it was soaked in 1% formaldehyde (HCHO) at 50º C for 4 hours to prevent any further color interference during activation and then dried at 60ºC for 2 hours. The NaOH activated melon husk was stored in an air tight container ready for use.

F. Melon Husk Activated by Urea

Nwankwo and Mogbo (2014) activation method was used. 100g of carbonized melon husks was soaked in 0.6 g/cm^3 urea solution for 6 hours, drained and dried overnight at 50ºC and was further activated at 120ºC for 4 hours using Memmert oven. The urea activated melon husk carbon was stored in an air tight container ready for use.

G. Heavy Metal Analysis

Flame Atomic Absorption Spectrometry (FAAS) is a simple and well available technique for the determinations of heavy metals in the natural water samples. A Perkin–Elmer and HACH DR890 colorimeter was used in this study. Atomic absorption measurements were carried out using air: acetylene flame while HACH colorimeter measurement test kits provided was used. The operating parameters for working elements were set of a recommended by the manufacturer.

H. Treatment of Waste Water using the Adsorbent

Batch adsorbent experiments was conducted to determine the effects of parameters such as adsorbent dosage (0.2 g to 1.0 g at 0.2 g interval) and contact time (0 to 100 minutes at interval of 10 minutes) on the sorption of Lead (Pb^{4+}) and Iron (Fe^{2+}) from aqueous solution using melon husk activated carbon. The batch experiment was conducted at room temperature and stirred with 20ml waste water sample in a 100ml Erlenmeyer flask. After stirring, the suspension was filtered using Whatman filter paper and sample adsorbed was measured spectrophotometrically by using standard method of (Sun and Shi, 1998) to determine Lead (Pb^{4+}) and Iron (Fe^{2+}) ions content. The amount of the Lead (Pb^{4+}) and Iron (Fe^{2+}) ions adsorbed, qt (mg/l) at time (t) was calculate by using equation 1

$$q_t(mg/l) = (C_o - C_e)*V/m \quad (1)$$

Where q_t(mg/l) is the adsorption capacity of the Melon husk activated carbon, C_o and C_e are the initial and equilibrium adsorbates concentration at a given time, t respectively, V (l), is the volume of the adsorbates and m(g) is the mass of the adsorbent.

III. RESULTS AND DISCUSSIONS

A. Structural Composition

Fourier Transform Infrared (FTIR) spectrometer analysis of the adsorbent was performed, and the percentage transmissions of various wave numbers were presented in

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Fig. 1. The FTIR spectra of the adsorbent, showed the presence of amine $R\text{-}NH_2$ (amino acids, protein, glycoprotein), carboxylic acids (fatty acids, lipopoly, saccharides) and phosphates. The characteristic adsorption bands of hydroxyl and amines of 3354.09 cm^{-1}, indicating the presence of exchangeable OH^- and NH^+ group respectively; alkyl chain at 2920.32 cm^{-1}; amides and phosphate groups at 1026.91 cm^{-1} and between 900.26 cm^{-1} and 773.61 cm^{-1} respectively and P-O vibration of moiety at 675.46 cm^{-1}. The adsorption bands identified in the spectra and their assignment to the corresponding functional group in the adsorbent could enhance the surface to which adsorption could take place.

Fig. 2(a) to Fig. 2(d) show the Scanning electron microscopy (SEM) image of melon husk carbon without any modification, with H_2SO_4 activation, with NaOH activation, and Urea activation respectively.

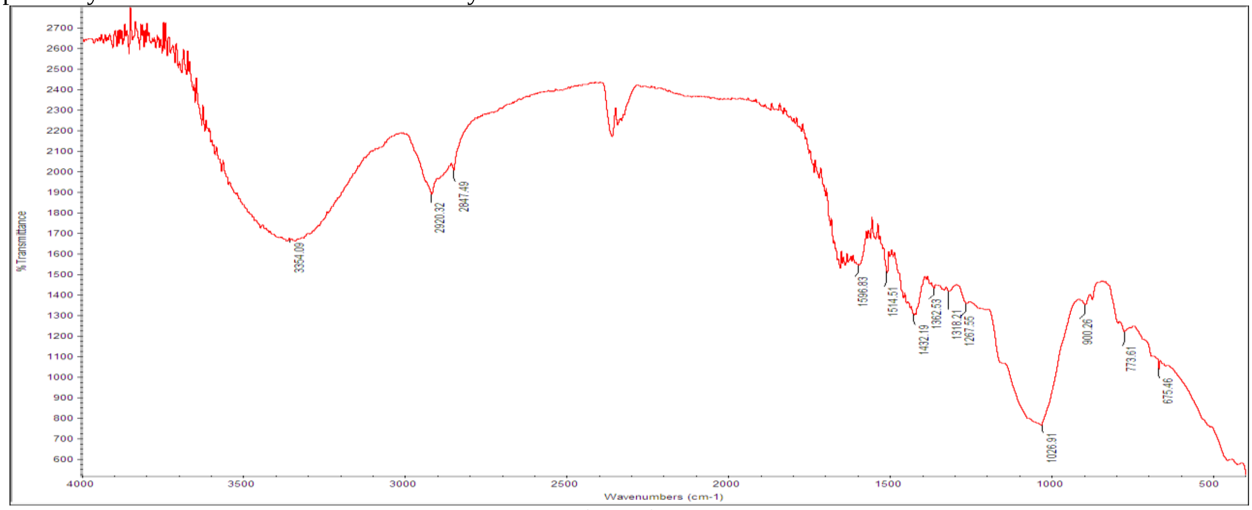

Fig. 1. Fourier transform infrared spectroscopy (FTIR) image.

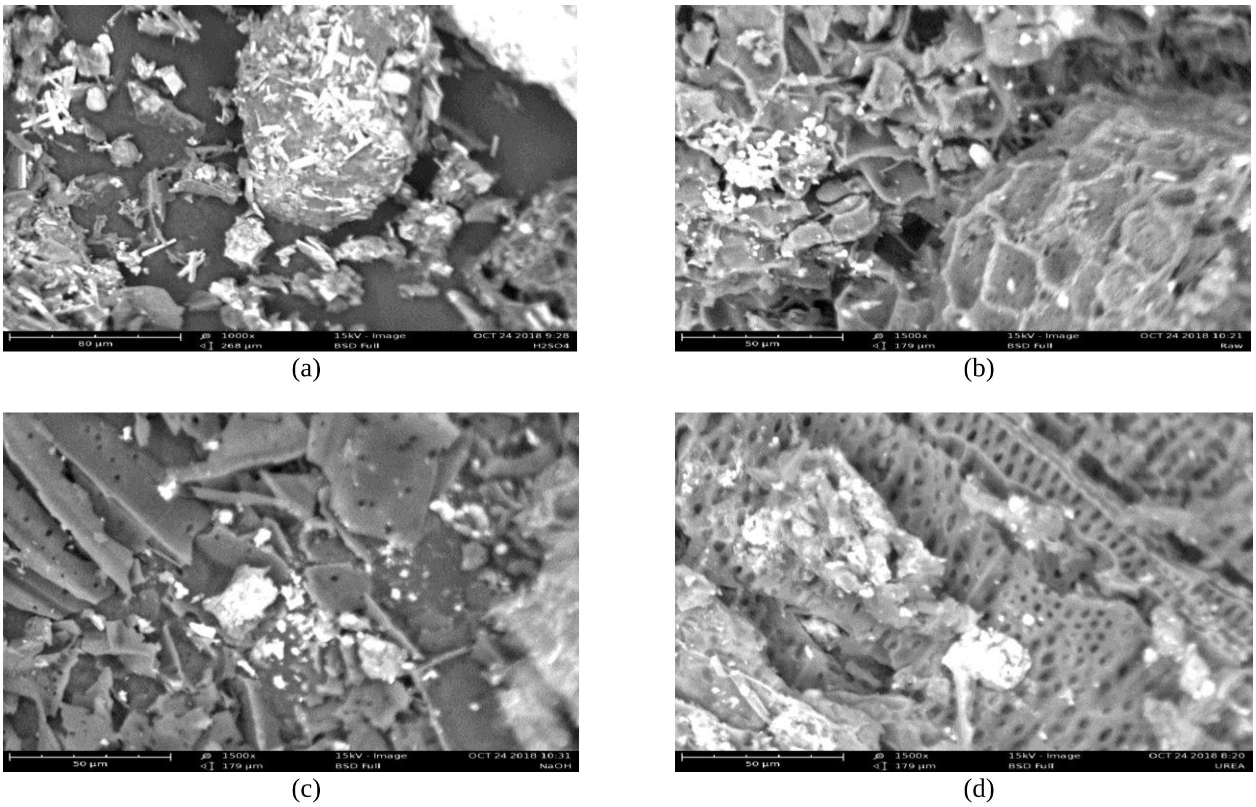

Fig. 2. Scanning electron microscopy (SEM) images of melon husk. (a) without any modification (b) with H_2SO_4 activation (c) with NaOH activation (d) with Urea activation.

It was observed from Fig. 2(a) that the structural composition of the melon husk carbon is densely packed and has some voids which indicate its ability to absorbed metal ions from the wastewater. It was observed in Fig. 2(b) that the structural composition of the activated melon husk with H_2SO_4 have large voids compare to that in Fig. 2(a), thus indicating a more likely effectiveness in adsorption. It was also observed in Fig. 2(c) and Fig. 2(d) that their structural composition has many smaller voids compare to Fig. 2(a), thus indicating more effectiveness in adsorption. The seeming

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rough surface of all the adsorbent is an indication of high surface area.

B. *Contact Time Effect*

The effects of contact time on Iron (Fe^{2+}) and Lead (Pb^{4+}) ions sorption using different melon husk activated carbon were presented in Fig. 3 and Fig. 4 respectively. It is evident from Fig. 3 and Fig. 4 that the removal of Iron (Fe^{2+}) and Lead (Pb^{4+}) ions increases with increase in contact time, until equilibrium was attained, after which the sorption capacity started fluctuating below the maximum capacity.

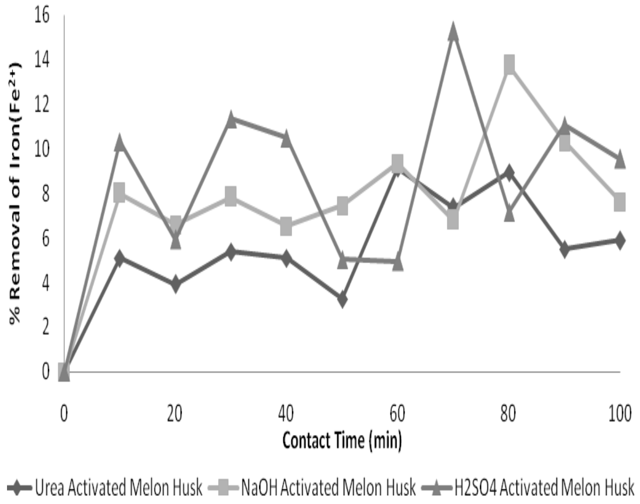

Fig. 3. Effect of contact time on Iron ions adsorption using different activated melon Husk.

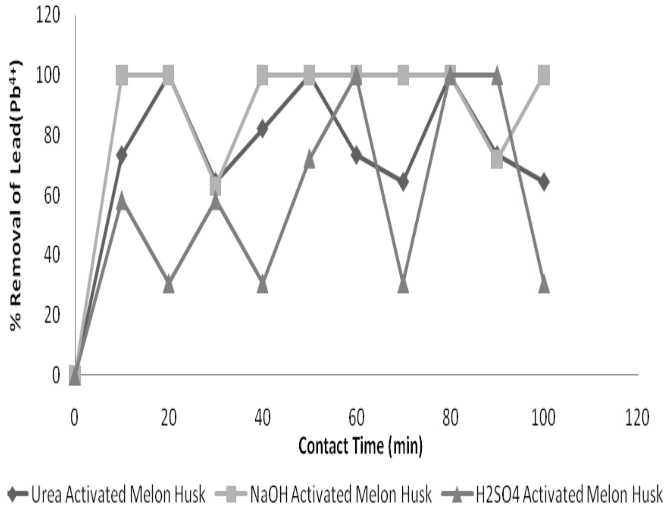

Fig. 4. Effect of contact time on Lead ions adsorption using different activated melon Husk.

The adsorption of Iron (Fe^{2+}) in Fig. 3, shows that equilibrium were attained at 60 mins for Urea activated melon husk, 80 mins for NaOH activated melon husk and 70 mins for H_2SO_4 activated melon husk, while for the Lead (Pb^{4+}) ions adsorption as shown in Fig. 4, equilibrium were attained within the first 10 mins for NaOH and H_2SO_4 activated melon husk and 20 mins for Urea activated melon husk. Therefore contact time can be optimized to 70min (i.e. 1hour, 10min).

C. *Adsorbent Dosage Effect*

The effects of adsorbent dosage on Iron (Fe^{2+}) and Lead (Pb^{4+}) ions sorption using different melon husk activated carbon were presented in Fig. 5 and Fig. 6 respectively.

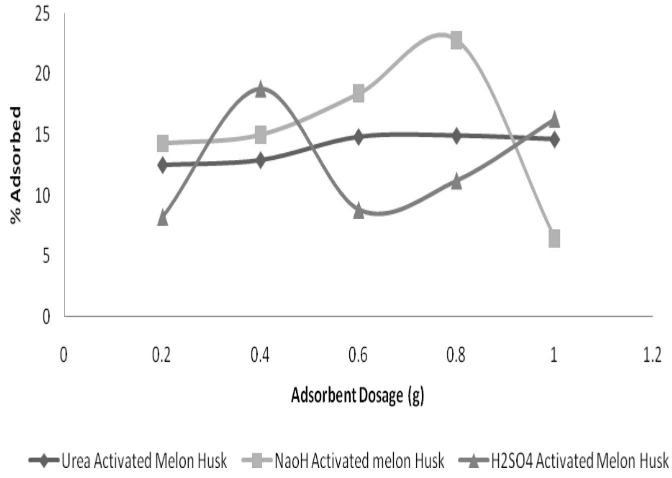

Fig. 5. Effect adsorbent dosage on Iron ions adsorption using different activated melon Husk (20ml/70min).

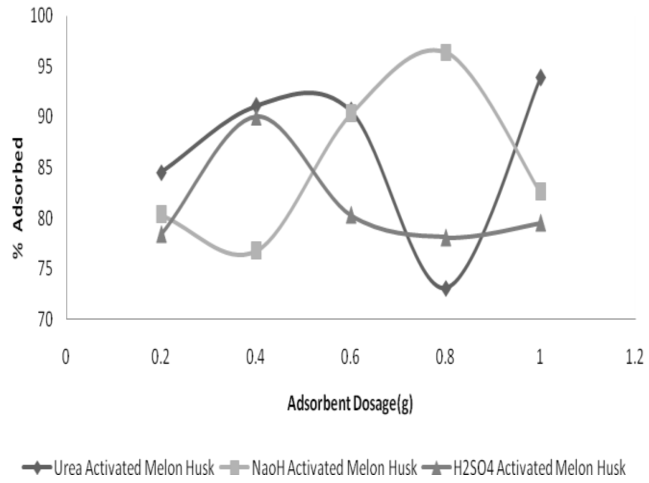

Fig. 6. Effect adsorbent dosage on Lead ions adsorption using different activated melon Husk (20ml/70min).

In Fig. 5, it was observed that increase in adsorbent mass of each melon husk activated carbon leads to an increase in Iron (Fe^{2+}) ions removal until it reach an optimum adsorption point, after which further increase in adsorbent dosage leads to a decrease in Iron (Fe^{2+}) ions removal. The optimum adsorbent mass of 0.4g was observed for H_2SO_4 activated melon husk carbon and 0.8g for both Urea and NaOH activated melon husk carbon. The optimum adsorption of Iron (Fe^{2+}) ions was 22.81% observed at 0.8g adsorbent dosage of NaOH activated melon husk carbon.

In Fig. 6, it was observed the removal of Lead (Pb^{4+}) ions did not show consistent increase in adsorption process with increased adsorbent dosage as observed for Iron (Fe^{2+}) ions removal except for H_2SO_4 activated melon husk. There was fluctuation in the rate of adsorption of Lead (Pb^{4+}) ions with increase in adsorbent dosage for Urea and NaOH activated melon husks. For H_2SO_4 activated melon husks, increase in adsorbent dosage increased the percentage adsorption of Lead

(Pb^{4+}) ions until optimum adsorption point of 4g adsorbent dosage was reached. The amount of ions bound to the adsorbent and the amount of free ions remained almost constant even with further addition of dose of the adsorbent. Khan, et al., (2004) reported that the sorption capacity is dependent on the type of adsorbent investigated and the nature of the wastewater treated. This could be possible reason Lead (Pb^{4+}) did not show strict dependency on the adsorbent dosage especially with Urea and NaOH modified melon husks carbon. The optimum adsorption of Lead ions was 96.4% observed at 0.8g adsorbent dosage of NaOH activated melon husk. Thus, activated melon husk is more effective in adsorbing Lead ions.

IV. CONCLUSION

From the above discussed results, a few important conclusions were drawn concerning the structural composition and effectiveness in sorption of melon husk activated carbon. The structural composition analysis indicates a spectra band of potential sites for adsorption of iron and lead ions. Also, the rough surfaces and voids observed from scanning electron microscopy (SEM) images indicate the potentiality of melon husk activated carbon in treatment process of heavy metals. The sorption capacity is dependent on activation method, contact time and adsorbent dosage. The Melon husk activated carbon is more effective for removal of Lead (Pb^{4+}) ions than for removal of Iron (Fe^{2+}) ions.

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