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Removal of Heavy Metals from Simulated Wastewater Using Physically and Chemically Modified Palm Shell Activated Carbon

Nur Azreen Fuadi, Ahmmed Saadi Ibrahem and Kamariah Noor Ismail
Chemical Engineering Faculty, Universiti Teknologi MARA, 40450, Shah Alam, Selangor, Malaysia

Abstract: The purpose of the present study is to investigate the adsorption efficiency of Activated Carbons (AC) derived from oil palm shell in an adsorption column for removal of beryllium, calcium, cadmium, cobalt, chromium, copper, iron, lithium, magnesium, manganese, molybdenum, nickel, lead, antimony, strontium, titanium, vanadium and zinc ions from aqueous solution. Three types of adsorbent were used for the metal removal, which undergoes physical and/or chemical treatment. In physical treatment, raw palm shell was burned at 600°C for 5 h. All the adsorbents undergo physical treatment, with only the first adsorbent unblended, while the second adsorbent was blended. The third adsorbent underwent physical and chemical treatments where the physically treated AC was mixed with solvents for 24 h, then washed and dried. The solvent used for the third adsorbent were acetone and benzene. The results indicated that removal of metal ions by adsorption spawned different activities for different adsorbents. It is indicated that for overall adsorption efficiency, AC derived by combining physical and chemical treatment showed a maximum adsorption capacity with the least area under graph; 1371, calculated using trapezoidal equation. The physical treatment produced high carbon content by carbonization and high surface area by size reduction, while the chemical treatment enhanced the development of carbon surface by generating more pores, thus increasing the number of adsorption sites.

Key words: Acetone, activated carbon, adsorption, benzene, heavy metals

INTRODUCTION

Concerns about environmental protection have increased due to the technical development which keeps changing, producing industrial product, as well as waste. Manufacturing industry has played an important role for economic growth in major countries. However, rapid changes in industrialization produce vast amounts of waste and will cause harm and deteriorate the environment and ecosystem if improperly managed. Pollutants from heavy metals are widely discharged in the wastewater from industries; such as cadmium, chromium, lead, copper, manganese, zinc as well as mercury are very toxic and harmful to living organisms by lowering the reproductive success, prevent proper growth and development and even causing death (Alturkmani, 2004) due to its non-biodegradable character and persistency in environment and it is reported that the most toxic heavy metals are Cd, Pb and Hg ions due to their high attraction for sulphur and will disturb enzyme function by forming bond with sulphur. The ions will hinder the transport process through the cell wall, therefore disturbing the cell function. Concern is raised about Malaysia where most of the rivers are polluted and cannot be used as drinking source. According to Department of Environment (DOE) 10% of rivers in Malaysia are heavily polluted or dead, 63% is polluted and only 27% is healthy. These figures show the need of wastewater treatment before discharging to rivers or water bodies.

Therefore, the problem has to be solved by treating the wastewater before discharging into waterways. There are many technologies that have been developed for purification and treatment of waste water including chemical precipitation, solvent extraction, oxidation, reduction, dialysis/electro dialysis, electrolytic extraction, reverse osmosis, ion-exchange, evaporation, cementation, dilution, adsorption, filtration, flotation, air stripping, steam stripping, flocculation, sedimentation and soil flushing/washing chelation (Mohan and Singh, 2002). Adsorption process is found to be the most suitable technique to remove pollutants from wastewater. It is mostly preferred due to its convenience, ease of operation and simplicity of design. Apart of removing many types of pollutants, it also has wide application in water pollution control. AC is widely used as adsorbent due to its high surface area and pore volume as well as inert properties.

Corresponding Author: Nur Azreen Fuadi, Chemical Engineering Faculty, Universiti Teknologi MARA, 40450, Shah Alam, Selangor, Malaysia Tel: +60122776351

Low cost precursor has seen strong interest by researchers to replace the conventional AC. The factors affecting substitution of raw material are: high in carbon content, low in inorganic content, high in density and sufficient in volatile content, stability of supply in the countries, the potential extent of activation and inexpensive material (Nurul'Ain, 2007). The AC mainly comprises of carbon with large surface area, large pore volume and high porosity where the adsorptions take place. As one of the successful and progressive leading country of palm oil industry, Malaysia produces large amount of waste from palm oil (*Elaeis guineensis*). Due to the abundant source of precursor, which is 0.4 million tons palm shells per million tons of crude palm oil produced, palm shell, high in volatile and carbon contents, is a suitable precursor to replace the conventional AC. Utilizing the palm shell for production of AC will reduce cost, compared to conventional AC. Moreover, it can be said to transform the waste to wealth. In this study, activated carbons derived from oil-palm shells were investigated. Effects of preparation in terms of raw, physical and chemical treatment of AC on the pore structures and heavy metal adsorption were investigated. The system involved removal of many types of heavy metal, including antimony, cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, vanadium and zinc.

MATERIALS AND METHODS

Preparation of palm shell activated carbon: Palm shell collected from Palm Oil Mill Technology Center (POMTEC), Malaysia, was used as adsorbent. The shell abundant material is used for heavy metal adsorption from wastewater. The palm shell is carbonized at 500°C in the furnace for 5 h and divided into three parts. The rest underwent physical treatment by grinding to reduce the size and sieved to desired mesh size (300-500 μm) for use and one part of them was used as adsorbent for chemical treatment, by mixing all the carbon with acetone for a day to improve uniformity of pores at the surface of activated carbon (Kiran, 2010), followed by treatment with benzene for 1 day to produce micropore surface (Fujiwara *et al*., 2012). The solvents were all carbonaceous solvents that will deposit on the surface to control the pore. All the carbon was filtered, washed and dried at 100°C after each chemical treatment to remove chemical residue. Three types of adsorbent were used for the removal of heavy metal.

Characterization of activated carbon: Elemental analysis for carbon, hydrogen, nitrogen, oxygen and sulfur was identified by CHNO/S Analyzer 2400, Perkin Elmer. Surface morphology was observed by a Supra 40VP Field Emission Scanning Electron Microscopy (FESEM).

Preparation of wastewater solution: The wastewater used for adsorption contains heavy metals which were beryllium, copper, molybdenum, manganese, magnesium, cadmium, zinc, nickel, chromium, vanadium, lead, lithium, antimony, titanium, iron and strontium that was simulated by dilution of 1 g chemicals each: iron (II) sulphate, cadmium chloride, iron (II) nitrate, copper (II) nitrate trihydrate, lead nitrate and chromium (VI) oxide, copper (II) sulphate anhydrous, magnesium chloride, manganese (IV) oxide, zinc sulphate, aluminum chloride and aluminum nitrate in 10 L distilled water. The adsorption of adsorbates was studied due to its harmfulness and it was adsorbed by several adsorbents preferentially to a very good extent. The concentration of elements in wastewater solution was determined by ICP-OES. The container of wastewater must be kept tightly closed to prevent changing of concentration due to other material addition or reduction. The initial concentration of each element is presented in Fig. 1.

Fixed bed adsorption study: A fixed bed column was used in the column adsorption study. Adsorption characteristics of heavy metals onto palm shell activated carbon in fixed-bed column were studied by varying the type of adsorbent: i. Unblended burned ii. Blended burned iii. Blended treated with acetone and benzene palm shell activated carbon.

All the adsorption tests were conducted in a continuous downward flow mode. 15 g activated carbon is filled by using filter paper, with the top uncovered in the column to prevent activated carbon dropping to the bottom of the column. For multiple fixed beds, the amount of activated carbon was 5 g for each three stages. The flow of feed solution was fixed. The treated wastewater solution was collected at regular time intervals for 360 min and the concentration was measured by ICP-OES. The experiments were carried out at room temperature without any pH adjustment. The evolution of

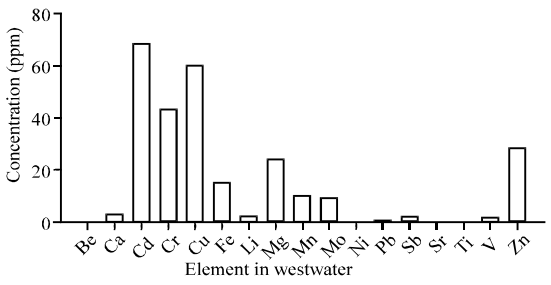

Fig. 1: Initial concentration of elements in wastewater

the adsorption is presented in terms of C/C_o (concentration/initial concentration) of elements over interval time.

RESULTS AND DISCUSSION

Elemental analysis: The result of elemental analysis of palm shell is listed in Table 1. The carbon percentage had been already high in the raw palm shell, treated AC was used to determine the adsorptivity of palm shell as adsorbent. The carbonized palm shell has a greater percentage of carbon due to the loss of moisture content and volatile compound through carbonization in the furnace.

Surface morphology: The scanning electron micrograph in Fig. 2, 3 and 4 show the pores on the surface of the oil palm shell with three conditions which are 1) raw palm shell, 2) carbonized palm shell and 3) carbonized and chemically treated palm shell respectively. The pores present in the AC surface provide sites of adsorption of heavy metals. In Fig. 2, the surface of the raw palm shell was covered with a thin layer over the carbon pores. The layer consists of volatile compound and moisture, which is why the pore could hardly be seen, but the adsorption is still occurring on the surface.

When the palm shell is burned, the layer was removed and the pore began to appear clearer (Fig. 3). The pore size diameter is identified from 340 nm to 760 nm. Deposits on the particles surface can be seen (Fig. 2) but none was observed (Fig. 3). The depth of the carbonized AC's pore is not deep enough. The depth is increased when the carbonized palm shell underwent chemical treatment by acetone and benzene as in Fig. 4. It exhibited well-developed porous structure with mainly regular pore sizes and the size ranged from 630 nm to 1µm. Combination of physically and chemically treated AC will adsorb more elements due to its high surface area. The pore will produce the hypothetical T-shirt shaped pore where more electrons can adsorb in the adsorption site. The T-shirt shaped theory can be proved by BET analysis of pore volume. The mechanism is of hypothetical T-shirt formed by multi solvent treatment, where the solvent is accumulated at the end of the pore. The solvent sipped through the adsorbent and at the same time forming channel looks like pore after the solvent is removed. The activity continues with further solvent treatment, thus forming more pore. Lastly, pore formed are hypothetically in T-shirt size pore model, where many pores are

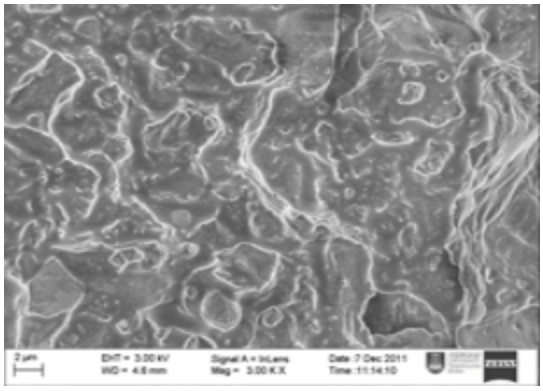

Fig. 2: Surface morphological of oil palm shell

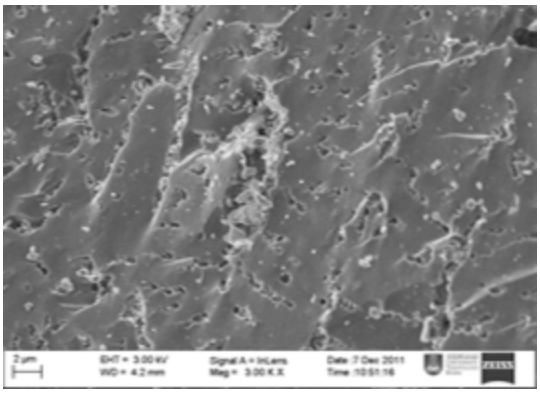

Fig. 3: Surface morphological of carbonized palm shell

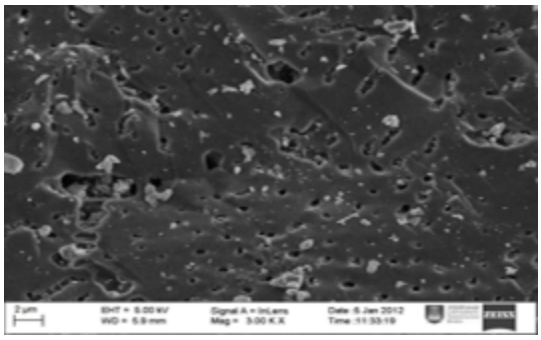

Fig. 4: Surface morphology of chemically treated activated carbon

Table 1: Elemental analysis of AC

Sample	%C	%H	%O	%N	%S
Raw palm shell	46.6	5.6	46.3	1.5	0
Palm shell AC (physical treatment)	57.5	1.1	38.5	2.9	0
Palm shell AC treated with acetone and benzene (physical and chemical treatment)	58.8	1.0	38.4	1.8	0

Table 2: Area under graph for heavy metal removal

	Area under curve		
Element	Unblended AC	Blended AC	Carbonized+acetone+benzene treated AC
Beryllium (Be)	1838.628	1074.604	97.52083
Calcium (Ca)	97.91667	96.45833	65.44637
Cadmium (Cd)	42.67854	79.40638	78.65069
Chromium (Cr)	47.30917	69.86294	91.96096
Copper (Cu)	17.27019	90.67208	92.77847
Iron (Fe)	96.40643	92.80267	96.68039
Lithium (Li)	61.10542	59.95746	88.6645
Magnesium (Mg)	41.6625	41.81644	13.98492
Manganese (Mn)	38.07519	61.18611	84.27926
Molybdenum (Mo)	63.73064	9.109542	83.55271
Nickel (Ni)	35.89894	37.42571	71.10525
Lead (Pb)	93.42484	92.42307	94.02685
Antimony (Sb)	95.05013	92.34303	96.94901
Titanium (Ti)	87.51796	67.32875	92.36306
Vanadium (V)	48.21144	72.81275	48.08236
Zinc (Zn)	45.23853	77.65583	78.24723
Strontium (Sr)	97.91667	92.91667	97.52083
Total	2848.041	2208.782	1371.814

generated at the end of previous pore, therefore increasing the surface area and pore. Narrow-middle pore was generated, which enhance adsorption and inhibit desorption. However, the mechanism is hardly proven by current existing instrumentation, due to the size factor of adsorbent. Therefore, it is hypothetically proven with result of metal adsorptions by adsorbent.

Adsorptivity evaluation: The concentration of elements in wastewater was determined after adsorption experiment using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). The concentration of the treated wastewater was plotted by graph within an interval time. After plotting the graph, area under curve was determined by trapezoidal rule and is arranged in Table 2 according to the elements in an interval. From the table, the highest efficiency of all the systems is shown by carbonized+acetone+benzene treated AC, with the lowest area under graph, followed by blended carbonized AC and lastly unblended AC. Areas under graph represented the area left for adsorption. The result is proven from the scanning electron micrograph. The heavy metal in wastewater was removed due to interaction of ions into the pore that inhibit desorption. Blended AC exhibited higher surface area contact with wastewater, compared to unblended AC due to the presence of void volume throughout the bed and its size.

As discussed earlier, the system involved many elements (adsorbate) to be removed. Comparing the adsorbents, only several elements were better removed by carbonized AC while the rest were better removed by carbonized+acetone+benzene treated AC. This is due to the availability of each element to be adsorbed at AC in terms of adsorption site. Throughout the study, desorption do occur where the elements that were previously adsorbed were released from the AC. As it was a complex system, determination of the place of adsorption was not a concern, however and which element desorped could be identified through ICP-OES. The factors for high performance of adsorption are: void space between adsorbent, pore size and particle size. The use of fixed bed column adsorption had enhanced the removal compared to many other studies by batch adsorption (Jumasiah *et al*., 2005). Adsorbent that is impregnated with acetone and benzene has the best removal rate probably due to chemisorption mechanism, where bonds are formed between molecules used for impregnation and wastewater. The bond is much stronger than the attractive force of physical adsorption and can prevent the volatile compound from desorbing. However, it is not the objective of the study.

CONCLUSION

Two types of activated carbons were produced from physical treatment at 600°C and another type by combination of physical and chemical treatment using acetone and benzene. The results showed that the activated carbon by the combination of physical and chemical treatment at thermal activation exhibited a good adsorption capacity with the lowest area under graph, 1371 in 6 h, which represented the least amount of heavy metals left after adsorption. It was supported by scanning electron micrograph that the combination treatment had more and deeper pores compared to raw and carbonized palm shell. The activated carbon produced by a combination of physical and chemical treatment was identified to be promising for the application of heavy metals removal from industrial wastewaters.

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REFERENCES

Alturkmani, A., 2004. Industrial wastewater. http://www.4enveng.com/.

Fujiwara, M., T. Kitabayashi, K. Shiokawa and T.K. Moriuchi, 2012. Surface modification of zeolites using benzene-1,4-diboronic acid to form gated micropores with mild and photo responsive pore reopening. Chem. Eng. J., 146: 520-526.

Jumasiah, A., T.G. Chuah, J. Gimbon, T.S.Y. Choong and I. Azani, 2005. Adsorption of basic dye onto palm kernel shell activated carbon: Sorption equilibrium and kinetics studies. Desalination, 186: 57-64.

Kiran, E., 2010. Foaming strategies for bioabsorbable polymers in supercritical fluid mixtures. Part II. Foaming of poly (?-caprolactone-co-lactide) in carbon dioxide and carbon dioxide + acetone fluid mixtures and formation of tubular foams via solution extrusion. J. Supercritical Fluids, 54: 308-319.

Mohan, D. and K.P. Singh, 2002. Single and multi-component adsorption of cadmium and zinc using activated carbon derivated from bagasse-an agricultural waste. Water Res., 36: 2304-2318.

Nurul'Ain, J., 2007. The production and characterization of activated carbon using local agricultural waste through chemical activation process. Masters, Thesis, Universiti Sains Malaysia.