KENAF BAST FIBER FILTER CARTRIDGE FOR REMOVAL OF HEAVY METALS AND DYES IN AQUEOUS SOLUTION

RIDWAN BIN SHAMSUDIN

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ABSTRACT

This research aimed to investigate the adsorption of heavy metals and dyes using adsorbent and filter cartridge from kenaf bast fiber (KBF). This research was conducted in several stages starting with adsorption and characterization studies followed by production and evaluation of filter cartridge prototype. Adsorption was studied through removal of heavy metals (Cd, Cu, Ni, Pb and Zn) and dyes (Congo red, Methyl orange, Methylene blue and Rhodamine B.) in single- and multi-systems. The effects of experimental variables (solution pH, initial concentrations and adsorbent dosage) on adsorption of KBF were also assessed. The adsorption equilibrium was analyzed using Langmuir and Freundlich isotherm models. The KBF adsorbent was characterized using Field Emission Scanning Electron Microscope (FESEM), Energy Dispersive X-Ray (EDX) spectrometer and Fourier Transform Infrared Spectrometer (FTIR) before and after adsorption process. The performance of filter cartridge prototype to treat synthetic and real wastewater effluent was evaluated in laboratory. The results showed that Pb(II) and Methylene blue were the most adsorbed contaminants for all experimental conditions in single-system. However, the removal of all heavy metals and dyes was significantly reduced in multi-system due to competition effect for active sites on the adsorbent. The values of equilibrium separation factor (R_L) and the Freundlich constants (n) indicated that the uptake of all contaminants by KBF was favorable. FESEM analysis revealed significant changes on adsorbent's surface following interaction with contaminants. The uptake of heavy metals by KBF was confirmed by EDX analysis. FTIR analysis proved that hydroxyl, carboxyl and amine are the main functional groups involved in heavy metals and dyes uptake. To conclude, the filter cartridge prototype was an excellent adsorbent to remove multi-contaminants in synthetic and real wastewater effluent. The implication of this study is KBF filter cartridge has great potential to replace conventional adsorbents for future environment friendly wastewater treatment.

KARTRIJ PENAPIS GENTIAN BASTA KENAF UNTUK PENYINGKIRAN LOGAM BERAT DAN PENCELUP DALAM LARUTAN AKUEUS

ABSTRAK

Penyelidikan ini bertujuan mengkaji penjerapan logam berat dan pencelup menggunakan penjerap dan kartrij penapis daripada gentian basta kenaf (GBK). Penyelidikan ini dijalankan dalam tiga peringkat bermula dengan kajian penjerapan dan pencirian diikuti dengan penghasilan dan penilaian prototaip kartrij penapis. Penjerapan dikaji melalui penyingkiran logam berat (Cd, Cu, Ni, Pb, Zn) dan pencelup (Kongo merah, Metil oren, Metilena biru dan Rhodamin B.) dalam sistem tunggal dan pelbagai. Kesan pembolehubah eksperimen (pH larutan, kepekatan awal dan dos penjerap) terhadap penjerapan GBK juga telah dinilai. Keseimbangan penjerapan dianalisis dengan model isoterma Langmuir dan Freundlich. Penjerap GBK dicirikan menggunakan Pengimbas Mikroskop Elektron Emisi Medan (FESEM), Spektrometer Penyebaran Tenaga Sinar-X (EDX) dan Spektrometer Inframerah Transformasi Fourier (FTIR) sebelum dan selepas proses penjerapan. Prestasi prototaip kartrij penapis untuk merawat air sisa sintetik dan sebenar juga dinilai dalam makmal. Hasil penyelidikan menunjukkan bahawa, Pb(II) dan Metilena biru adalah bahan cemar paling terjerap untuk semua keadaan eksperimen sistem tunggal. Walau bagaimanapun, penyingkiran semua logam berat dan pencelup berkurang dengan signifikan dalam sistem pelbagai disebabkan oleh kesan persaingan untuk tapak aktif pada penjerap. Nilai faktor pemisahan keseimbangan (R_L) dan pemalar Freundlich (n) menunjukkan bahawa pengambilan semua bahan cemar adalah cenderung kepada GBK. Analisis FESEM menunjukkan perubahan signifikan pada permukaan penjerap akibat interaksi dengan bahan cemar. Pengambilan logam berat oleh GBK disahkan melalui analisis EDX. Analisis FTIR membuktikan bahawa hidroksil, karboksil dan amina adalah kumpulan berfungsi utama yang terlibat dalam pengambilan logam berat dan pencelup. Kesimpulannya, prototaip kartrij penapis adalah penjerap yang sangat berkesan untuk menyingkirkan pelbagai bahan cemar dalam air sisa sintetik dan sebenar. Implikasi kajian ini adalah kartrij penapis GBK berpotensi tinggi bagi menggantikan penjerap konvensional untuk rawatan air sisa mesra alam pada masa hadapan.

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrometer
ASTM	American Society for Testing and Materials
BDAC	Bamboo Derived Activated Carbon
BET	Brunauer-Emmett-Teller
BJH	Barrett, Joyner and Halenda
CR	Congo Red
DOE	Department of Environment
EDX	Energy Dispersive X-Ray
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared
IARC	International Agency for Research on Cancer
IUPAC	International Union of Pure and Applied Chemistry
IWK	Indah Water Konsortium
KBF	Kenaf Bast Fiber
KCF	Kenaf Core Fiber
MARDI	Malaysian Agricultural Research and Development Institute
MB	Methylene Blue
MO	Methyl Orange
NKTB	National Kenaf and Tobacco Board
RB	Rhodamine B
SW	Scheduled Wastes
USEPA	United States Environment Protection Agency

UV-Vis	Ultraviolet-Visible Spectrophotometer
WHO	World Health Organisation

CHAPTER 1

INTRODUCTION

1.1 Research Background and Motive

Earth consists of 71% of water and therefore preservation of water is crucial to maintain clean water access for all living things (United States Geological Survey, 2015). Water resources might be polluted due to improper management of wastewater. As mentioned by Anastopoulos & Kyzas, (2014), wastewater that comes from various activities are a major reason contributes to deterioration of water quality globally.

Wastewater is defined as a complex mixture of domestic, industrial and agricultural wastes. A collection of wastewater in wastewater tanks in often termed as “sewage” (Mateo-sagasta, Raschid-sally, & Thebo, 2015). Sewage contains variety of organic as well as inorganic substances (Abdel Raouf, Al Homaidan, & Ibraheem, 2012; Ali, Asim, & Khan, 2012).

Generally, wastewater consists more than 99% of water, but the remaining 1% contains ions, suspended solids and harmful microorganism that must be removed before the wastewater is released into the river/sea. Different industries may release different substances based on their raw processing materials. Wastewater can be characterized based on their physical, chemical and biological properties as described below (Indah Water Konsortium, 2015a).

I. *Physical properties*

Physical properties refer on wastewater odor, color, temperature and amount of solids.

II. *Chemical properties*

Chemical properties can be divided into three constituents namely organic, inorganic and gases. Organic materials referring to the amount of carbohydrates, grease, fats, oil, proteins and surfactants while an example of inorganic substances are chlorides, phosphorus and so on. Lastly, gases referring to the amount of chlorides and phosphates in the wastewater.

III. *Biological properties*

Biological properties refer to the amount microorganisms such as bacteria, protozoa, fungi and algae that may exist in wastewater.

In this era, the world productions of wastewater keep increasing due to several factors. Rapid industrialization, global urbanization, high rate of population growth and agricultural activities are the main reason of increasing amount of effluent being disposed to the environment (Ali et al., 2012; Hegazi, 2013; Kamari, Yusoff, Abdullah, & Putra, 2014; Tzu, Tsuritani, & Sato, 2013). Therefore, wastewater must be treated properly before being discharge to the environment.

Basically, wastewater treatment system can be divided into four phases that start with preliminary treatment followed by primary treatment, secondary treatment and tertiary treatment where each stage has different functions as described in Figure 1.1 (Indah Water Konsortium, 2015b).

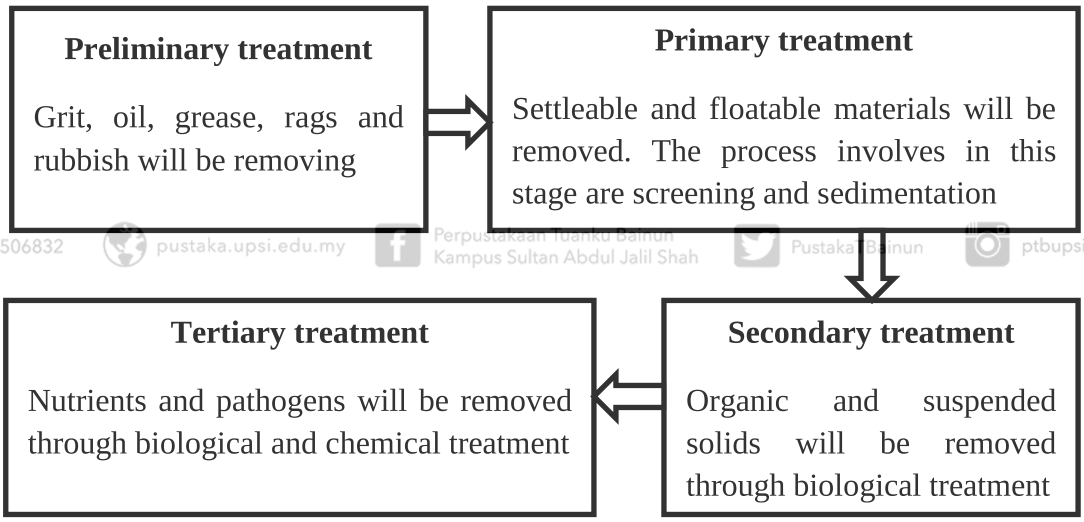

Figure 1.1. Stages in wastewater treatment

However, many wastewater treatment plants in Malaysia did not provide tertiary treatment system and were more focused on improving the available treatment systems (Azman, Shaari, & How, 2013).

In wastewater treatment plant, the treatment processes can be divided into physical unit operation, chemical unit operation and biological unit processes. The process involves in physical unit operation are screening, mixing, flocculation, sedimentation, filtration and flotation in order to treat sewage physically. Meanwhile, chemical unit operations comprised of adsorption, precipitation, and disinfection processes. Lastly, in biological unit processes, contaminants are removed through biological activity (Indah Water Konsortium, 2015b). Table 1.1 shows the differences between these three operations of wastewater treatment.

Table 1.1

The description on physical, chemical and biological unit operations in wastewater treatments

Aspects	Definition	Types	Material used
Physical	Application of physical forces to treat wastewater	Screening, mixing, flocculation, sedimentation, filtration, flotation, etc.	Sand filters
Chemical	Consumption of chemicals to remove pollutants	Chlorination, adsorption, ion exchange, etc.	Use of chemicals such as chlorine, lime, etc.
Biological	Use of microorganisms and other biological means to treat the wastewater	Aerobic and anaerobic, digestion, adsorption, etc.	Use of microbes, agricultural wastes, natural materials, etc.

Note. Adapted from *Dhir*, 2014; *Indah Water Konsortium*, 2015c.

In adsorption-filtration stages in wastewater treatment system, the filters used in current adsorption-filtration process are not environment friendly. The application of activated carbon filters and plastic-based filter made from polypropylene in wastewater treatment plant have several drawbacks to the environment. Therefore, this study intends to improve existing adsorption-filtration stages, so that a better management of wastewater treatment could be achieved.

1.2 Problem Statement

In the last decades, sewage disposal and wastewater treatment has attract global attention in order to protect the environment especially in developed and developing countries (Cao, Zhu, Lu, & Xu, 2005). However, treating wastewater can be very challenging because wastewater consists of mixture of organic and inorganic chemical, organic matters and many type of toxic substances (Bendida, Tidjani, Badri, Kendouci, & Nabou, 2013) which is dangerous to human being and the natural environment.

Therefore, when the domestic, municipal and industrial wastewater is not being treated effectively, it will contribute to environmental and health problems. The consequence highlights the significance of wastewater treatment, so that rivers and streams as drinking water resources can be protected (United States Environmental Protection Agency, 2004). This is because untreated wastewater that contain contaminate toxic substances such as heavy metals and dyes might enter our drinking resources (Henze & Comeau, 2008).

There are several techniques available to sequester heavy metals and dyes in wastewater such as adsorption, membrane filtration, chemical precipitation, ion exchange, flocculation, electrochemical treatment, extraction, electro dialysis and coagulation (Bilal et al., 2013; Erto, Giraldo, Lancia, & Moreno-Piraján, 2013; Rawat, Giri, & Rai, 2014; Taşar, Kaya, & Özer, 2014). In choosing the appropriate method, factors such as effectiveness, operational cost and production of toxic by-products must be taken into consideration (Abdolali et al., 2014). Within the context of this research, the adsorption-filtration description by activated carbon and polypropylene filters is further discussed in the following subsections.

1.2.1 Adsorption-filtration process by activated carbon

In recent decades, adsorption is the most employed and has been regarded as an effective techniques to remove contaminant such as heavy metals and dyes in wastewater (Albadarin et al., 2014; H. Guo, Lin, Chen, Li, & Weng, 2015; Gusmão, Gurgel, Melo, & Gil, 2013; Kamari et al., 2014; Rangabhashiyam, Anu, Giri Nandagopal, & Selvaraju, 2014). For adsorption, activated carbon has been extensively used as an adsorbent in wastewater treatment (Banerjee, Sharma, Chattopadhyaya, & Sharma, 2014; H. Chen, Zhao, & Dai, 2011; Coelho et al., 2014; Motahari, Mozdianfard, & Salavati-Niasari, 2015; Politi & Sidiras, 2012). This scenario can be related to activated carbon high surface area and excellent adsorption capacity (Al-Ghouti et al., 2010; Bharathi & Ramesh, 2013; Iakovleva & Sillanpää, 2013).

However, the application of activated carbon in wastewater treatment as adsorbent and filter has major drawbacks especially in large scale treatment system due to its high cost (Ponnusami, Vikram, & Srivastava, 2008; Rangabhashiyam, Anu, et al., 2014). For example, the market price for bamboo based activated carbon (800-1300 m^2/g) is USD 1000-1500 per metric tonnes. The expensive price would contribute to high operational cost to run wastewater treatment facilities.

Besides, the process to alienate contaminants from the exhausted activated carbon and the regeneration of used activated carbon are technically challenging and add up more to a treatment plant operational cost (Demir, Top, Balköse, & Ulkü, 2008; Weng et al., 2014). Therefore, activated carbon is not economic especially for developing and undeveloped countries that practice small-scale wastewater treatment facilities (Gong, Zhang, Liu, Sun, & Liu, 2007; Gusmão et al., 2013; Hossain & Alam, 2012).

1.2.2 Adsorption-filtration process by polypropylene

Another common filter applied in wastewater treatment plant is polypropylene-based filter. The polypropylene that broadly implemented in this stage is known as micro porous Melt-brown polypropylene filter (L. L. Wu et al., 2007). Polypropylene (C_3H_6) is a plastic polymer where it can be used both as a structural plastic and also as a fiber. However, there are certain major problems that rise due to the using of polypropylene as wastewater filter.

Firstly, polypropylene has high melting point that prolong degradation time of exhausted polypropylene filters in landfill (Lenntech, 2015). It was reported that the degradation of polypropylene could take up to several decades in natural environment (Montagna, Forte, & Santana, 2013). Therefore, it might need high cost for its recycling or for disposal.

In general, the application of activated carbon and polypropylene filters are costly and the mismanagement of exhausted activated carbon and polypropylene filters could lead to secondary pollution. Therefore, investigation on alternatives filters developed from renewable resources such as lignocellulosic materials is significant.

Lignocellulosic materials refer to natural biomass substances, agro-industrial wastes and its by-products. One of the examples of lignocellulosic plants is kenaf fiber. At present, the integration of natural materials especially lignocellulosic materials in many sectors such as wastewater treatment attracts attentiveness of environmental researchers due to the limited source of petroleum globally as well as production of secondary contaminants that comes from available wastewater treatment plant (Singha & Guleria, 2014a).

1.2.3 Kenaf as an adsorbent and filter

In fact, interest on renewable lignocellulosic materials have received great attention from environmental scientists due to their low-cost, available at large quantities, environmental friendly and non-hazardous waste production during wastewater treatment (Barakat, 2011; Martins et al., 2013; Weng et al., 2014). One of the biomass that fulfills the characteristics is kenaf fiber.

Asadi, Shariatmadari, & Mirghaffari, (2008) reported that agricultural-based fiber and wood can be used as contaminants filter to treat polluted water. In addition, Saba et al., (2015) reported that kenaf is effective in term of cost and have environmentally friendly properties. A recent study conducted by Shamsudin, Abdullah, & Sinang, (2015) also suggested that kenaf can acts as oil or chemicals adsorbents.

One of interesting facts about natural fiber like kenaf is it is classified as renewable energy and do not have negative impacts on the environment due to its ability to self degrades (Basri., Arifin, Nasima, Hazandy, & Khalil, 2014; John, Bellmann, & Anandjiwala, 2010).Hence, kenaf provides a good alternative solution to replace activated carbon and polypropylene filter with comparable adsorption capacity and good biodegradability.

In Malaysia, the government encourages the cultivation of kenaf because kenaf fiber has high prospective market. Currently, there are about 2000 Ha of kenaf plantation in Malaysia. According to Malaysian National Kenaf and Tobacco Board, (2014), 1 ha of land can produce 8 tonnes of kenaf fiber. Therefore, the estimated production of kenaf fiber at year 2014 is 16 000 tonnes (Mingguan Malaysia, 2014). In addition, the Malaysian climate is also appropriate for kenaf planting (Basri. et al., 2014) and reassure kenaf planting in large scale. Malaysian kenaf fiber can be classified into two grades namely Temafa and MR grade. In this study, Kenaf Bast Fiber (KBF) (MR grade) was chosen due to its low-cost compare to Temafa grade.

1.3 Significance of Study

In overall, one of the factors that must be considered to build a good wastewater treatment plants is the design of the wastewater treatment plant. A system that is not only effective but minimize negative impacts to the environment should be selected. Therefore, this study focused on the potential of KBF to be applied as filter to replace activated carbon and polypropylene in wastewater treatment system. With the disadvantages of activated carbon and polypropylene filters as well as the potential of lignocellulosic materials, there are opportunities for production of green filter in adsorption-filtration stages to remove contaminants in wastewater.

In view of the concept of sustainable wastewater treatment and waste minimization, investigation about performance of natural untreated KBF to adsorb heavy metals and dyes is therefore significant. Based on literature, data on the adsorption and characterization studies of KBF in the removal of heavy metals and dyes is scarce. Besides, most of studies before employed chemicals to produce the adsorbents; which in turn contributes to additional processing cost especially for material and waste treatment.

In last 15 years, research on kenaf fiber mostly explained on Kenaf Core Fiber (KCF) and modified kenaf fiber. For example, acid treated kenaf fiber char