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Application of Kenaf Bast Fiber to Adsorb Cu(II), Pb(II) and Zn(II) in Aqueous Solution: Single- and Multi-metal Systems

Ridwan Shamsudin, Hanisom Abdullah, and Azlan Kamari

Abstract**—Improper discharge of heavy metals such as cadmium, copper, nickel, lead and zinc to the environment could impose severe health and toxicological problems. Within Malaysian context, Cu(II), Pb(II) and Zn(II) are the most common heavy metals present in various industrial wastewater effluents. The removal of Cu(II), Pb(II) and Zn(II) from water bodies is of interest due to their high toxicity. Copper and lead are classified as carcinogenic agents. Accumulation of zinc in human and animal increases the risk of blood, nervous and reproductive disorders. In this study, the ability of Kenaf Bast fiber (KBF) adsorbent to sequester Cu(II), Pb(II) and Zn(II) from synthetic solution with respect to solution pH, initial metal concentration and adsorbent dosage was investigated. Both single-metal and multi-metal system studies were carried out in batch experiments. The adsorption equilibrium was analyzed by Langmuir and Freundlich isotherm models. The biomass adsorbent was characterized using Scanning Electron Microscope (SEM), Energy Dispersive X-ray spectrometer (EDX) and Fourier Transform Infrared Spectrometer (FTIR). The optimum conditions of metals adsorption was found at pH 4.0 (Pb(II)) and pH 5.0 for both Cu(II), and Zn(II). The maximum adsorption capacity estimated using Langmuir isotherm model was in the order of Pb(II) (50.0 mg/g) > Cu(II) (33.56 mg/g) > Zn(II) (13.68). The analysis of SEM, EDX and FTIR proved metal ions uptake by the adsorbent. The result highlights the significance of KBF as effective natural adsorbent for Cu(II), Pb(II) and Zn(II) removal from water bodies.**

Index Terms**—Heavy metals, kenaf bast fiber, single- and multi-metal system, wastewater.**

I. INTRODUCTION

Rapid industrialization and global urbanization have released significant amount of heavy metals into the environment [1], [2]. Industrial activities such as electroplating, alloys and acid batteries manufacturing and, electrical components and paints manufacturing are the main sources of heavy metals [3], [4].

Heavy metals are non-biodegradable and potentially toxic elements. They cannot be degraded or destroyed naturally therefore persist in our environment [5], [6]. Heavy metals are dangerous especially when they contaminate the aquatic ecosystem [7] thus increasing risks of diseases such as insomnia, nausea, anemia, Wilson's disease, liver damage, skin irritations to human [4], [8].

There are several techniques available to sequester heavy metals in wastewater such as adsorption, membrane filtration, chemical precipitation, ion exchange, flocculation, extraction and coagulation [9], [10]. In choosing the appropriate method, several factors must be taken into consideration such as effectiveness, operational cost and production of toxic by-products [11]. All available techniques were designed in order to meet the standard discharged for wastewater. According to Malaysian Environmental Quality (Industrial Effluent) Regulations 2009, the permissible discharge downstream for Cu, Pb and Zn must be lower than 1.0, 0.5 and 2.0 mg/L, respectively [12].

In recent decades, adsorption is the most employed and has been regarded as an effective technique to remove heavy metals in wastewater [2]. Activated carbon has been widely used as an adsorbent for water treatment [13]. This scenario can be related to its high surface area and excellent adsorption capacity [14], [15]. However, the application of activated carbon in wastewater treatment has several drawbacks. For example, the market price for bamboo based activated carbon (800-1300 m^2/g) is USD 1000-1500/ tonnes. The expensive price would contribute to high operational cost to run wastewater treatment facilities. Therefore, activated carbon is not economic especially for developing and undeveloped countries [16]. Secondly, alienation of exhausted activated carbon from wastewater and regeneration are also expensive and complicated [17].

Alternatively, utilization of lignocellulosic materials such as kenaf fiber, cotton wool [18], coconut coir fiber [19], *Luffa cylindrical* fiber [20], sugarcane bagasse [21]-[23] and jute fiber [24] to remove heavy metals from aqueous solution create opportunities for production of inexpensive technologies to treat wastewater effluent. In fact, these methods have received great attention from environmental scientists due to their availability, environmental friendly and non-hazardous waste production during wastewater treatment [25]-[27]. Most importantly, those biomasses are either available as waste or can be purchase at lower price than activated carbon. For example, the price for biomass commodity such as coconut coir fiber, kenaf and jute are in the range of USD 310-450/tonnes.

In Malaysia, kenaf cultivation is being extensively promoted as national focus under the 9th Malaysia Plan to replace tobacco [28]. Currently, there are about 2000 ha of kenaf plantation in Malaysia. According to Malaysian National Kenaf and Tobacco Board, NKTB (2014), 8 tonnes of kenaf fiber can be yielded from 1 ha of land. Therefore, the estimated production of kenaf fiber at 2014 is 16,000 tonnes

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[29]. This scenario encourages studies on the performance of kenaf-based bio-composite as natural adsorbent for wastewater treatment.

In the previous studies, chemically-treated kenaf fiber was used to sequester selected heavy metals from synthetic wastewater. Sajab *et al*. (2010) investigated an alkali treated kenaf core fibers to remove Cu(II) [8]. In addition, Chowdhury *et al*. (2012), Macías García *et al*. (2012) and Othman *et al*. (2008) studied kenaf-activated carbon to eliminate several heavy metals namely Cu(II), Pb(II), Hg(II), Mg(II) and Fe(II) respectively [30]-[32]. Graft polymer developed from kenaf fiber was also used to adsorbed Cr(III) and Zn(II) [33]. Most of these studies were conducted in single-metal system therefore the effect of metal ion in multi-metal system was not well determined. The lack of fundamental understanding about performance of kenaf fiber in multi-metal system in previous studies defined the research gaps in this area. If the adsorbent would be implies to treat real wastewater effluents that is formed by mixture of metal ions, multi-metal system studies is more significant to assess the effect of metal ions competition. Besides, most of these studies employed chemicals to produce the adsorbents; which in turn contributes to additional processing cost especially for material and waste treatment. In view of the concept of sustainable wastewater treatment and waste minimization, investigation about performance of natural untreated kenaf fiber to adsorb heavy metals is therefore significant.

This study focused on the investigation of natural Kenaf Bast Fiber (KBF) for the removal of Cu(II), Pb(II) and Zn(II) from aqueous solution in single and multi-metal systems. This article reports the influence of several experimental parameters such as solution pH, initial metal concentration and adsorbent dosage on adsorption capacity of KBF. The adsorption equilibrium data were fitted to Langmuir and Freundlich isotherm models. The characteristics of kenaf bast fiber that can be related to the adsorption mechanism(s) were discussed by FTIR, SEM and EDX analyses.

II. PROCEDURE

A. Preparation of Adsorbent

In this study, the outer part of kenaf stalks namely kenaf bast fiber was used in the adsorption studies. KBF was kindly supplied by Malaysian National Kenaf and Tobacco Board. KBF was ground using a laboratory mill and washed several times using distilled water followed by deionized water. The material was then dried in an oven at 60 ^{O}C for 7 days before used. The KBF was sieved using an American Society for Testing and Materials (ASTM) standard to obtain uniform size particles of 1.0 mm.

B. Preparation of Stock Solutions

Metal salts of $Cu(NO_3)_2.2.5H_2O$ (HmbG Reagent Chemicals), $Pb(NO_3)_2$ (Bendosen Laboratory Chemicals) and $Zn(NO_3)_2$ (GENE Chemicals) were added to the deionized water to prepare metal ions (1000 mg/L) solution. These stocks solutions were then diluted into desired concentrations before use. All reagents used were analytical reagent grade and deionized water was used throughout this study.

C. Batch Adsorption Studies

The adsorption studies for Cu(II), Pb(II) and Zn(II) were carried out by immersing 0.5 g of KBF particle into 50 mL metal ion solution in 250 mL Erlenmeyer flask. The metal solutions were agitated using a Protech 720 Orbital Shaker for 60 minutes at 100 rpm. In this study, the effect of solution pH was studied between pH 2.0-6.0. pH 6.0 was chosen as the highest pH due to the fact that precipitation of Cu(II), Pb(II) and Zn(II) occurred simultaneously at pH value greater than 6.0 (Mahmoud 2013; Taşar *et al*. 2014). It is known that the formation of insoluble hydroxide precipitates will give inaccurate interpretation of adsorption results. To obtain the desired pH, 0.05 mol/L of HCl and 0.05 mol/L of NaOH were added to metal ion solution. The pH was measured using a Thermo Scientific Orion 2-Star pH meter. The effect of initial metal concentration was investigated at concentration range of 10.0-200.0 mg/L. Meanwhile, the effect of adsorbent dosage was studied using four dosage variables that were 0.125, 0.250, 0.500 and 0.750 g.

The adsorption capacity of KBF towards Cu(II), Pb(II) and Zn(II) at equilibrium were calculated using equation (1):

$$q_e = \left(\frac{C_o - C_e}{W} \right) V \tag{1}$$

where q_e is the amount of metal ion adsorbed by KBF (mg/g), C_o is the initial concentration of metal ion (mg/L), C_e is the equilibrium concentration of metal ion (mg/L), W is the weight of the KBF (g), and V is the volume of metal ions solution (L). Meanwhile, the percentage of removal (%) was computed using equation (2):

$$\left(\frac{C_o - C_e}{C_o} \right) \times 100 \tag{2}$$

For multi-metal system study, 0.5 g of KBF was added into 50 mL of 100 mg/L multi-metal solution containing Cu(II), Pb(II) and Zn(II). The adsorption studies for multi-metal system were performed at optimum conditions obtained in the single metal system.

After the metal adsorption experiment for both systems, the metal solutions were filtered through Filtre Fioroni, (125mm) filter paper. Metal free blanks were used as controls. All the experiments conducted were done in triplicates and average values (with respective standard error of average) are reported in the results section. The residual metal ion concentration was measured using a Perkin-Elmer AAnalyst 400 Atomic Absorption Spectrometer (AAS). The concentration of metal ions in filtrate was measured using AAS and the dried adsorbents were further characterized.

D. Characterization Studies

Several analytical techniques such as Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDX) and Fourier Transform Infrared Spectroscopy (FTIR) were used to investigate the physical and chemical characteristics of KBF before and after the reaction with metal ions. Brunauer-Emmett-Teller (BET) and Barrett, Joyner and Halenda (BJH) techniques were used to determine the surface area and average pore diameter of KBF. Both analyses were done using Quantachrome Autosorb 1 Surface Analyser.

The surface morphology of KBF was observed using a Hitachi 8U 8020 UHR Field Emission Scanning Electron Microscope (FESEM). The analysis was carried out at an accelerating voltage of 15 KV to ensure a suitable image resolution. The FESEM was equipped with a Horiba Energy Dispersive X-ray Spectrometer to perform elemental composition analysis on the surface of KBF.

A Thermo Scientific Nicolet Nexus FTIR spectrometer was used to determine the surface functional group and the possible adsorption mechanism(s) of KBF towards metal ions. The analysis was performed with 32 cumulative scans at a wavenumber range between 4000-400 cm^{-1}.

III. RESULT AND DISCUSSION

A. Batch Adsorption Studies

1) Effect of solution pH

The pH of solution is one of the significant factors that affect metal binding process and the availability of functional groups on the surface of adsorbent [34]. The effect of solution pH on adsorption of metal ion by KBF is shown in Fig. 1. The value of standard error for this data set was less than 1.8%. From Fig. 1, there was a remarkable increase in adsorption capacity of KBF for Cu(II), Pb(II) and Zn(II) from pH 2.0 to 3.0. At very acidic medium (pH 2.0), the concentration of H_3O^+ ions were high and therefore causes strong competition between H_3O^+ and metal ions for an active site at the surface of the KBF. The low amount of metal ion uptake at low pH also could be due to protonation of functional groups of the adsorbent surface [6], [35]. This scenario induced the repulsive forces between protonated functional groups and metal ions, reducing the adsorption capacity of KBF for metal ions.

From Fig. 1, a marginal increase was obtained when the pH of solution was adjusted from pH 3.0 to 6.0. For example, the amount of Pb(II) absorbed onto KBF was calculated as 9.488, 9.728, 9.501 and 9.269 mg/g at pH values of 3.0, 4.0, 5.0 and 6.0, respectively. This is because less H_3O^+ ions were available at pH values higher than 3.0. Therefore, the competition between H_3O^+ and metal ions was reduced, increasing the electrostatic attraction between metal ions and active site at the adsorbent [36], [37]. Therefore, the adsorption process becomes more favorable. A similar trend in adsorption capacity was observed in previous studies using *Ricinuscommunis* leaves to remove Cu(II) [38] and activated carbon, kaolin, bentonite, blast furnace slag and fly ash to remove Pb(II) and Zn(II) [3].

In this study, the optimum pH for adsorption of Cu(II) and Zn(II) onto KBF was 5.0 and 4.0 for Pb(II). The results were similar with those found by Igberase *et al*. (2014) (Cu(II): chitosan beads) [39], Asadi *et al*. (2008) (Zn(II): modified rice hull and sawdust) [40] and Chen *et al*. (2011) (Cu(II) and Zn(II): hardwood and corn straw bio chars) [41]. Meanwhile, optimum pH for Pb(II) in this study was similar to that of reported by Shukla & Shukla (2013) on alkali treated coir fibers [19]. The trend of metals adsorption in this study were in agreement with Gautam *et al*. (2014) that mentioned high percentage of metal ion removal normally occurs at pH near to neutral [42].

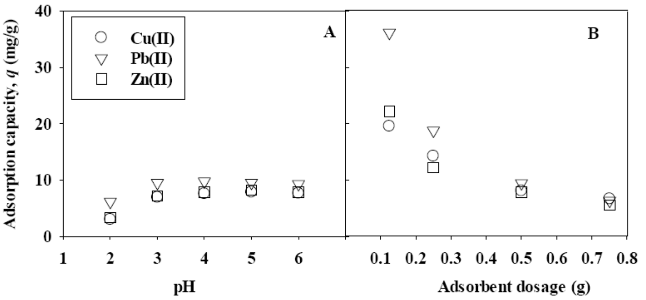


Fig. 1. Effect of solution pH (A) and adsorbent dosage (B) on adsorption of metal ion by KBF.

2) Effect of initial metal concentration

Fig. 2 presents KBF capacity for metal ions uptake by varying initial metal concentrations (with standard error of average <0.6%). The amount of metal ion adsorbed by KBF increased when the initial metal concentration was increased from 10 mg/L to 200 mg/L. This scenario can be explained by the fact that there was a high probability of collision between adsorbent surface and metal ions at high concentrations. Therefore, the rate of diffusion of metal ions towards the adsorbent surface was expected to increase [2].

Meanwhile, the percentage of metal ion removal was found to decrease when the initial metal concentration was increased as shown in Fig. 2. This was due to low ratio at active sites available on the adsorbent surface to metal ions at high concentration [37]. However, there was no significance reduction for Pb(II) where the percentage of removal maintained above 92%. A similar trend was obtained by Lasheen *et al*. (2012) for Pb(II) removal using modified orange peel [43].

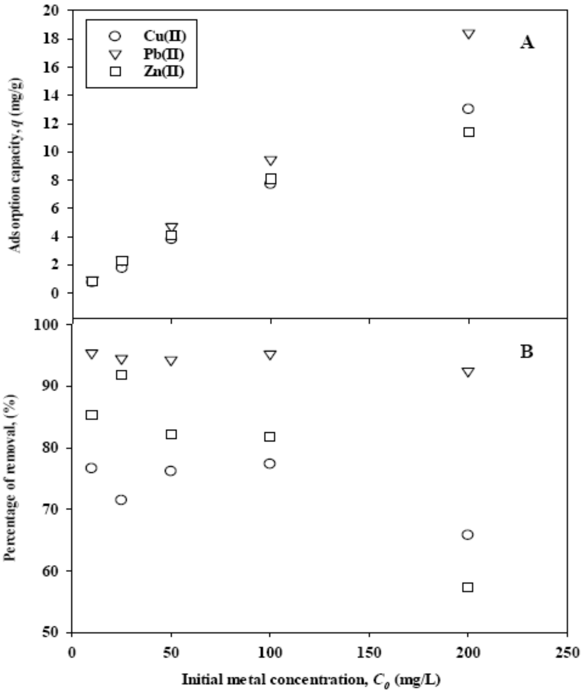


Fig. 2. Effect of initial metal concentration on adsorption capacity (A) and percentage of removal (B) of metal ion by KBF.

3) *Effect of adsorbent dosage*

Adsorbent dosage is other critical parameters that should be considered in designing an effective adsorption system [10]. This is because; the amount of adsorbent dosage is directly proportional towards the availability of the active binding sites [6] and the operational cost.

Fig. 1 showed an increasing of adsorbent dosage gave an inverse effect towards the adsorption capacity. For this data set, the value of standard error of average was less than 0.6%). The adsorption capacity for Cu(II), Pb(II) and Zn(II) decreased drastically as the adsorbent dosage increased from 0.125 to 0.750 g. A similar observation was reported by Yargıç *et al*. (2015) for Cu(II) removal using tomato waste [37]. This trend can be explained by the fact that all the active sites on the surface of the adsorbent are unsaturated due to high dosage of adsorbent [44].

However, an increase in KBF dosage was found to increase the metal ions removal. For example, the removal percentage for Cu(II), Pb(II) and Zn(II) increased from 49.22 to 99.26, 90.82 to 94.65 and 55.67 to 82.42 %, respectively when the amount of KBF adjusted from 0.125 to 0.750 g. This phenomenon can be explained by the fact that more active sites are available for metal ion binding at high dosage [20], [45]. An extra amount of adsorbent available also provides high surface area which is favorable for adsorption process [46], [47].

B. *Adsorption Isotherms*

Adsorption isotherms are essential in adsorption study as they give the mathematical description of the adsorption behavior at equilibrium [48]. Adsorption isotherms provide information on how adsorbent and adsorbate interact to each other [49]. The equilibrium adsorption isotherms for metal ions were expressed by means of the Langmuir and Freundlich isotherm models.

Langmuir isotherm model assumes contaminants (metal ions) form a monolayer on the adsorbents [34]. This model describes maximum adsorption occurs at fixed homogenous site that formed saturated monolayer at the exterior surface of the adsorbent [39], [50]. Langmuir isotherm also assumes that all the adsorption sites of the adsorbent are exact and energetically equivalent [7], [51]. The linear form of the Langmuir isotherm can be expressed as equation (3) [52]:

$$\frac{C_e}{q_e} = \frac{C_e}{Q} + \frac{1}{Qb} \tag{3}$$

where C_e is the equilibrium concentration of metal ion, (mg/L), q_e is the amount of metal ion adsorbed per unit weight of adsorbent at equilibrium concentration (mg/g), Q is the maximum adsorption at monolayer (mg/g), and b is the Langmuir constant related to the affinity of binding sites (mL/mg) as well as a measurement of the energy of adsorption. The values of Q and b can be calculated from linear plot of C_e/q_e against C_e.

Freundlich isotherm model is an empirical equation based on the adsorption at multilayer heterogeneous surface [49]. The adsorption process can occur at any sites of the adsorbent due to randomly distribution of active sites and their energies [51], [53]. The linear form of the Freundlich isotherm model is given as equation (4) [54]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

where n is the Freundlich constant that representing adsorption intensity and K_F (mg/g) related to the adsorption capacity. The linear plot of log q_e against log C_e will give values of K_F and n.

The calculated results based on Langmuir and Freundlich isotherm models were listed in Table I. Based on correlation coefficient (R^2) values, the adsorption of Cu(II) and Pb(II) onto KBF fitted well to Freundlich isotherm model while Zn(II) was best fitted to Langmuir isotherm model. The maximum adsorption capacities, (Q) for Cu(II), Pb(II) and Zn(II) as calculated from Langmuir isotherm model were 33.56, 50.00 and 13.68 mg/g, respectively. The order of metal ion uptake by KBF was Pb(II) > Cu(II) > Zn(II). High uptake of Pb(II) as compared to Cu(II) and Zn(II) could be due to its strong ion electronegativity, large ionic radius and high atomic weight [23], [33]. The ion electronegativity values for Cu(II), Pb(II) and Zn(II) were 1.93, 2.33 and 1.63, respectively. Besides, the ionic radius of Pb(II) (0.132 nm) was found to be larger than ionic radius for Cu(II) (0.072 nm) and Zn(II) (0.083 nm).

TABLE I: LANGMUIR AND FREUNDLICH ISOTHERM CONSTANTS AND CORRELATION COEFFICIENTS

Metal ion	Langmuir				Freundlich		
	$Q_{\max}$ (mg/g)	b (L/mg)	R^2		K_F (mg/g)	$1/n$	R^2
Cu(II)	33.56	0.01	0.6542		0.37	0.89	0.9684
Pb(II)	50.00	0.04	0.8775		1.89	0.87	0.9926
Zn(II)	13.68	0.06	0.9792		1.07	0.59	0.8859

Another important parameter that should be considered in adsorption study is separation factor, (R_L). This dimensionless constant is derived from the Langmuir isotherm model and can be used to evaluate the suitability and the effectiveness of an adsorbent for decontamination of effluent [13], [53]. The separation factor, (R_L) can be expressed as equation (5) [55]:

$$R_L = \frac{1}{1 + bC_{\text{o}}} \tag{5}$$

where C_{o} is the initial concentration of metal ion (mg/L) and b is the Langmuir constant (L/mg). Based on R_L values, the isotherm shape of an adsorption process can be categorized into four systems [55]:

$R_L = 0$, Irreversible
$0 < R_L < 1$, Favorable
$R_L = 1$, Linear
$R_L > 1$, unfavorable

The R_L values calculated at different concentration of Cu(II), Pb(II) and Zn(II) were lie between 0 and 1. Therefore, it suggests that the adsorption of metal ions studied onto KBF was favorable. The applicability of KBF for metal ion removal was further evaluated in terms of Freundlich isotherm constant (n) values. The n values obtained were in the range of 1 to 10 suggesting that the removal of metal ion by KBS was favorable. The maximum adsorption capacity (Q) values of KBF for Cu(II), Pb(II) and Zn(II) estimated from Langmuir isotherm model are given in Table II. From Table II, it is interesting to note that kenaf bast fiber had greater adsorption capacity for Cu(II), Pb(II) and Zn(II) in comparison to chemically modified natural cotton wool and oxidized jute fibers. In overall, the adsorption capacity of KBS was comparable with other adsorbents studied in recent years.

TABLE II: COMPARISON OF ADSORPTION CAPACITIES OF CU(II), PB(II) AND ZN(II) ONTO VARIOUS ADSORBENTS (SELECTED PAPERS)

Adsorbents	Q_{max} (mg/g)			Reference
	Cu(II)	Pb(II)	Zn(II)	
Kenaf bast fiber	33.56	50.00	13.68	This study
Activated *Abelmoschus esculentus* fiber	19.21	67.24	16.85	[56]
Alkali treated coir fibers	9.41	29.41	-	[19]
Untreated coir fibers	2.77	10.41	-	
African beech sawdust (Raw)	4.36	1.06	1.35	[5]
Chemically treated African beech sawdust	5.25	1.69	1.96	
Chemically modified natural cotton wool fiber	6.12	21.62	4.53	[18]
Coconut dregs residue	2.76	9.74	-	[2]
Fly ash	0.18	-	0.18	[57]
Natural zeolite	1.12	-	1.32	
Peanut husk charcoal	0.35	-	0.37	
Gisenyi volcanic rock	14.31	13.85	4.85	[58]
Iranian natural zeolite	4.70	5.90	-	[59]
Modified fly ash	-	0.17	0.11	[60]
Oxidized jute fiber	7.73	-	8.02	[24]
Untreated olive mill solid residues	0.59	0.58	-	[61]

C. *Characterization Study*

1) *SEM analysis*

The effects of metal ion adsorption on surface morphology of KBF were studied using SEM. The SEM images of KBF at 10,000x magnification before and after the interaction with Cu(II), Pb(II) and Zn(II) are shown in Fig. 3. From Fig. 3, KBF had a groove, uneven and tousled surface texture. As described by Ahmad *et al*. (2009), such characteristics give an advantage for metal ion adsorption [7].

The surface morphology of KBF changed significantly following interaction with metal ions (Fig. 3). Cu(II) and Zn(II) had a similar effect on KBF surface, whereby the KBF surface changed from groove to irregular and rough texture (Fig. 3). Meanwhile, the contact of Pb(II) with KBF formed lump-like deposits (Fig. 3). It can be speculated that the lump-like deposits represent Pb precipitates. The observations were later confirmed with result of EDX analysis.

2) *EDX analysis*

The EDX elemental spectra of KBF before and after the adsorption process are shown in Fig. 4. KBF consists of several elements such as carbon (C), oxygen (O) and potassium (K) as shown in Fig. 4. The features of C, O and K were observed at energy values of 0.277, 0.523 and 3.313 keV, respectively. The feature of platinum appeared at the energy value of 2.048 keV. The occurrence of platinum is largely due to surface coating during sample preparation.

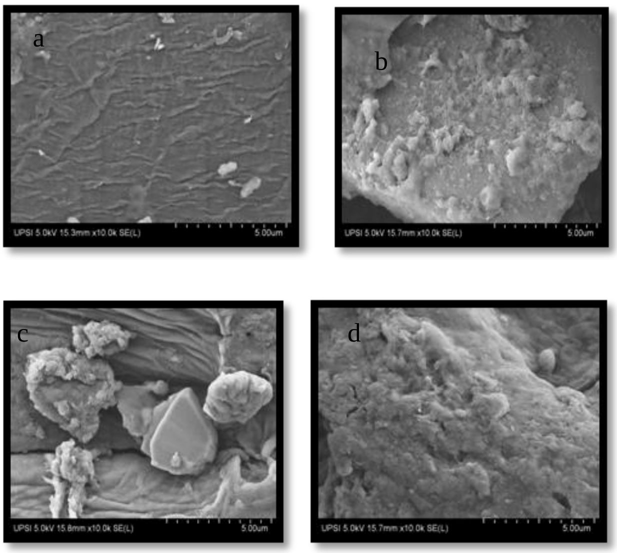
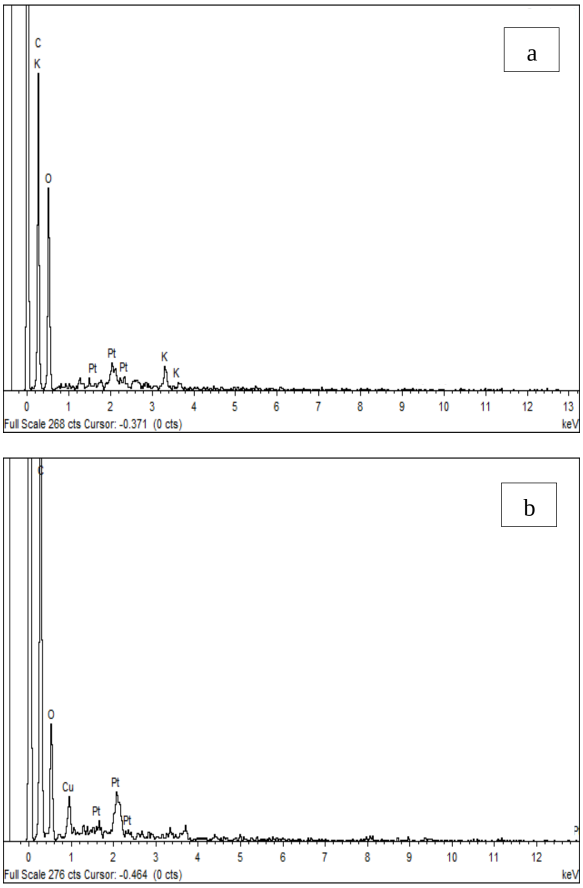


Fig. 3. SEM images of KBF at 10000× magnification before adsorption of metal ion (a), and after adsorption of Cu(II) (b), Pb(II) (c), and Zn(II) (d).

Following adsorption process, the features of Cu, Pb and Zn were observed on the KBF surface (Fig. 5). The feature of Cu observed at energy value of 0.930 keV (Fig. 5). EDX analysis was performed on lump-like deposits which resulted in Pb feature at energy value of 2.342 keV (Fig. 5). In the case of Zn, its feature was observed at 1.012 keV (Fig. 5). Overall, results from EDX analysis suggest that KBF was able to bind with metal ion [Cu(II), Pb(II) and Zn(II)].



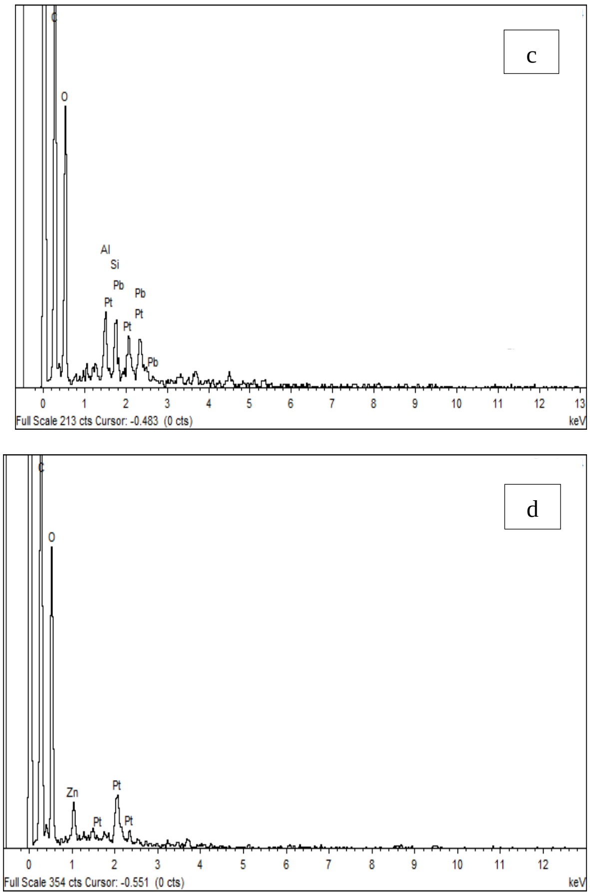


Fig. 4. EDX spectra of KBF before (a) and after adsorption of (b) Cu(II), (c) Pb(II) and (d) Zn(II).

3) *FTIR analysis*

The presence of certain functional groups and possible adsorption mechanism(s) were confirmed using FTIR analysis [13], [62]. The FTIR spectrum of KBF is shown in Fig. 5. From the figure, a broad absorption band observed at 3344 cm^{-1} represents hydroxyl functional group. The absorption band appeared at 2929 and 2887 cm^{-1} can be assigned as to alkyl stretching vibration. The presence of carboxylic acid group was confirmed by the appearance of absorption band at 1725 cm^{-1}. A discernible absorption band observed at 1645 cm^{-1} can be related to the amine groups.

There were changes on FTIR spectra of KBF after adsorption of metal ions (Fig. 5). For example, the adsorption band of OH stretching vibration shifted from 3344 cm^{-1} to 3357 cm^{-1}, 3361 cm^{-1} and 3364 cm^{-1} following interaction with Cu(II), Pb(II) and Zn(II), respectively. The absorption band of carboxylic acid experienced a similar scenario, of which it was shifted from 1725 cm^{-1} to 1730 cm^{-1}, 1729 cm^{-1} and 1731 cm^{-1}. Meanwhile, in the case of amine groups, there was a shift in wavenumber as well as a significant change in absorption intensity of absorption band. The band was shifted from 1645 cm^{-1} to 1607 cm^{-1}, 1648 cm^{-1} and 1612 cm^{-1} respectively.

From FTIR analysis, the shift in wavenumber and change in absorption intensity can be related to the adsorption mechanism(s) involving several functional groups such as hydroxyl, carboxylic and amine groups. Theoretically, kenaf is a type of cellulosic fiber where the main constituents of kenaf are cellulose and lignin [56], [63]. Hence, the O-H stretching vibration presence may be attributed to the cellulose and lignin components that may involved in metal binding through ion exchange and/or complexation mechanisms [56].

To examine contribution of ion exchange mechanism to metal ion binding, the solution pH was measured before and after adsorption process. There was no great difference in pH value of the ion solution before and after adsorption (ΔpH< 0.3). This suggests that ion exchange was not the main adsorption mechanism for metal ion by KBF. Therefore, it is likely to conclude that Cu(II), Pb(II) and Zn(II) removal was through complexation mechanism. Abdolali *et al*. (2014) and Singha and Guleria (2014) discussed the possible involvement complexion mechanisms in metal ion adsorption by lignocellulosic materials [11], [56].

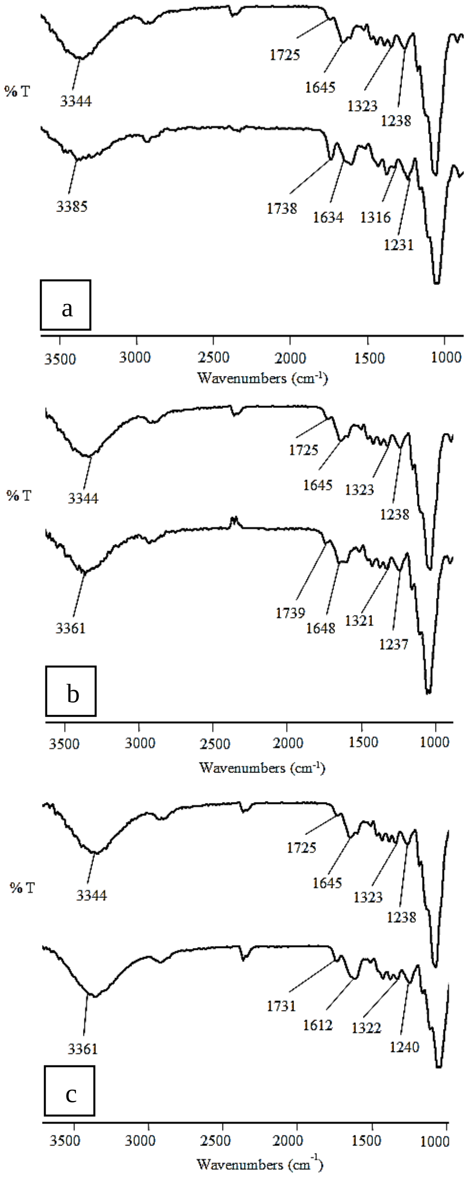


Fig. 5. FTIR spectra of KBF before adsorption (upper line) and (a) after interaction with Cu(II), (b) Pb(II) and (c) Zn(II).

D. *Competitive Adsorption Study*

Multi-metal study is also one of the critical aspects in wastewater treatment system. This is because most of the real wastewater contains more than one element. Besides, competitive studies among the elements also provide an important data to treat real wastewater in larger scale [64].

Hitherto, most of the environmental researchers focused on single-metal adsorption rather than multi-metal adsorption studies [65]. Hence, this study present an evaluation on KBF and Commercial Activated Carbon (CAC) for removal of Cu(II), Pb(II) and Zn(II) in multi-metal aqueous solution as shown in Table III.

The result shows that the metal ion adsorption capacity and the removal percentage by KBF in multi-metal system are lower compared to single-element system. This scenario can be related to the fact that an inhibitory effect among the metal ion in the multi-metal systems(Rawat *et al*., 2014). In this situation, two or more metal ions were competes for the same binding active sites significantly reduces the metal ion uptake [44], [66].

According to Table III, the performance of KBF was comparable to CAC at low initial metal concentration (10 ppm) while KBF had better metal ion capacity than CAC at high initial metal concentration (100 ppm) in multi-metal system. The data suggested that KBF has a great potential to replace activated carbon to remove heavy metals in wastewater.

Generally, Pb(II) shows the highest metal ion uptake in which there were 100% removal of Pb(II) in low initial metal concentration while Zn(II) is the most affected element in this tertiary systems for both adsorbents. Cho *et al*. (2005) also experienced same phenomenon in the removal of several metal ion using fly ash while Shaheen *et al*. (2013) that used various of adsorbents found that Pb(II) ions was the less affected metal ion in the multi-metal system [67], [68].

TABLE III: Removal of Cu(II), Pb(II) and Zn(II) onto KBF and CAC at pH 5.0 (Controlled pH) and at pH 5.24 (Uncontrolled pH) in Multi-metal System

Ads.	Init. met. mg/l	pH	Adsorption capacity (mg/g)			Percentage of removal (%)		
			Cu	Pb	Zn	Cu	Pb	Zn
KBF	10	pH = 5.0	0.72	0.99	0.82	73	100	82
CAC			0.88	0.99	0.72	86	100	72
KBF		pH = 5.24	0.72	0.98	0.85	72	100	86
CAC			0.86	0.99	0.74	87	100	75
KBF	100	pH = 5.0	6.97	9.39	4.41	69	94	44
CAC			3.38	4.61	2.34	33	46	23
KBF		pH = 5.24	6.96	9.47	5.47	69	95	54
CAC			3.55	5.09	2.32	35	51	23

IV. CONCLUSION

The Several conclusions can be drawn from the present study. Firstly, the data of single and multi-metal system adsorption investigation proved than KBF was an effective adsorbent for Cu(II), Pb(II) and Zn(II) in aqueous solution. Removal of the metals was strongly influenced by parameters such as solution pH, initial metal concentration and adsorbent dosage. The adsorption capacity of KBF is negatively correlated to the adsorbent dosage. The result would implies that future application of KBF to remove Cu(II), Pb(II) and Zn(II) from wastewater is more likely to be conducted at pH close to neutral. The KBF maximum adsorption capacity obtained from Langmuir isotherm model displayed that KBF is superior compared to other natural adsorbents such as coir fibers, coconut dregs residue. Characterization studies indicated that surface morphology and functional groups such as hydroxyl and carboxyl linked to lignocellulosic materials could be related to Cu(II), Pb(II) and Zn(II) uptake by KBF. The adsorption capacity of KBF in multi-metal system was reduced compared to single-metal system. This was believed to be caused by competition among metal ions for active sites in the adsorbent. The multi-metal system adsorption data also revealed that KBF had equipotential with CAC for metal ion removal. In view of adsorption efficiency and economic consideration, KBF could possibly be a good candidate to replace activated carbon in adsorption of heavy metals from water bodies.

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