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Comparative Study of Single and Multi-layered Fixed Bed Columns for the Removal of Multi-metal Element using Rice Husk Adsorbents

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Abstract: The effect of mechanical and multi-step chemical treatments on the adsorptivity of rice husk for the removal of multi-metal element from simulated wastewater was evaluated in this study. Furthermore, the adsorption performance of single- and multi-layered fixed bed columns were also studied using Blended Rice Husk as adsorbent. The metals being studied are: Be, Ca, Cd, Cr, Cu, Fe, Li, Mg, Mn, Mo, Ni, Pb, Sb, Sr, Tl, V and Zn. There are two types of rice husk adsorbents prepared from hybrid modification of mechanical and multi-step chemical treatments, namely Acetone-Benzene Treated Rice Husk (ABRH) and Acetone-Benzene-Methanol Treated Rice Husk (ABMRH). Surface morphology and BET analyses of ABRH and ABMRH revealed that the application of acetone, benzene and methanol solvents able to open up internal surface area of top and bottom part of the pores, predicting a new structure of pore shape termed as Hypothetical T-shirt Pore Model. This pore shape exhibited larger pore diameters, higher porous and surface areas, as well as higher adsorption capacity, owing to its middle narrow section which reducing desorption rate. The theory of Hypothetical T-shirt Pore Model coincided with results obtained by adsorption studies based on numerical technique of area under the graph. With respect to Raw Rice Husk in single-layered bed, the highest percentage reduction of area under the graph was demonstrated by ABMRH in multi-layered bed by 94.49%. The present work also found that, the adsorption was favored for multi-layered with 82.45% reduction of area under the graph by using numerical technique, as compared to single-layered fixed bed columns.

Key words: Rice husk, wastewater treatment, adsorption, multi-component, multi-metal

INTRODUCTION

Industrialization activities for nation development caused depletion and degradation of natural resources and biodiversity. In addition, these activities indirectly overload water body with thousands of water pollutant and subsequently polluting the environment. One of the major water pollutants is heavy metal. Heavy metals have some common characteristics which are: susceptibility to biological degradation, inability to degrade into harmless end products, toxicity to many life forms and tendency to accumulate in living tissues.

It is therefore necessary to remove heavy metals from wastewater in order to comply with environmental regulations and for the sake of human health and safety. Thus, various treatment techniques have been employed such as filtration, flocculation, chemical precipitation, ion exchange, membrane separation and adsorption (Tarley and Arruda, 2004). Among such treatment methods, adsorption is determined to be the most desirable treatment to remove water pollutants from wastewater due to its simple design and produce sludge free environment. The most common adsorbent used for adsorption process is activated carbon. Its extended surface area and micro-porous structure has made activated carbon the most efficient adsorbent.

However, it has been identified that activated carbon suffers from major drawbacks which are not practical in small and medium industries, as well as being expensive materials. Further, 10-15% loss occurs during regeneration of activated carbon adsorbent (Hashem, 2007). Thus, based on such situation, it is necessary to seek for other natural and inexpensive materials which have strong capability to adsorb metals in wastewater streams. Compared to conventional adsorbents, the natural adsorbents pose a lot of advantage: they are inexpensive, effective, readily and locally available, technical feasible and widely applicable in engineering. Accordingly, one of the waste materials in the world as reported in the literature with the most potential is rice husk, due to its high availability (Chuah *et al*., 2005).

In recent years, there has been an increasing amount of literature investigate the potential of rice husk as adsorbent to remove heavy metals from wastewater, such

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as done by Daifullah *et al*. (2003), Chockalingam and Subramaniam (2005), Aluyor *et al*. (2009), as well as Wongjunda and Saueprasearsit (2010). However, most of the works on the adsorption of metals elements by rice husk adsorbent has focused on the uptake of single element. Since there is a potential of discharging combined wastewater effluents from various industries into various compartment of water body, it is necessary to study the simultaneous adsorption of multi-metal element. Besides that, industrial wastewater may also be discharged into a sewerage system serving commercial and residential areas which subsequently form combined wastewater known as municipal wastewater. Therefore, the combined wastewater is characterized by high toxicity level of various types of metal elements and need to be removed for the sake of environmental preservation as well as human health and safety. Apart from industrial effluents, all the identified metals elements studied in the present work might also been found in polluted groundwater. Additionally, this area of study was once suggested by previously reported review paper of Bhatnagar and Sillanpaa (2010). They pointed out that, the potential of low cost adsorbents (i.e. rice husk) under multi-component element need to be investigated to make a significant impact on its potential for real industrial applications. In particular, there is also no doubt that progress has been made in studying adsorption under fixed bed column by using rice husk include Kumar and Bandyopadhyay (2006), Hosseinnia *et al*. (2007) and Ong *et al*. (2009). One question that needs to be asked, however, is whether a single-layered fixed bed column able to give total adsorption of multi-metal element from simulated wastewater. On top of that, since there have been no studies which compare the adsorption performance between single- and multi-layered fixed bed columns, this research will focus on comparative study between these columns by using modified rice husk adsorbents. This study also focused using hybrid modification of mechanical and multi-step chemical treatments for modified rice husk to treat 17 types of metal elements from simulated wastewater by using different types of solvents, non-polar, polar apotic and polar protic solvents. The main idea is to increase upper cross section area of pore, wall of the pore and bottom area of the pore to reach high performance by using all particles of modified rice husk and reduce vacant space between particles.

MATERIALS AND METHODS

Preparation of simulated wastewater: One gram of Iron (II) Sulphate powder was weighed by Mettler Toledo Electronic Analytical Balance. Then, it was dissolved in 250 mL distilled water by stirring in a Thermo Scientific Cimarec Display Hot Plate Magnetic Stirrer at 600 rpm for 5 min. Distilled water was obtained from Aquatron Cabinet Water Still. The similar steps were also applied for ionic metal powders of Cadmium Chloride, Copper (II) Nitrate Trihydrate, Lead Nitrate, Chromium (VI) Oxide, Magnesium Chloride, Manganese (IV) Oxide, Zinc Sulphate and Aluminium Chloride. Subsequently, simulated wastewater sample was prepared by mixing all metals solutions and diluted with distilled water until the volume of the sample reached 10 L.

Preparation of rice husk adsorbents: Raw Rice Husk was obtained from Padi Beras Nasional Berhad (BERNAS) Rice Milling in Sekinchan, Selangor, Malaysia. The Raw Rice Husk was then washed with distilled water and filtered by using GAST Diaphragm Vacuum Pump, prior to drying in MEMMERT Universal Oven at the temperature range of 105-110°C. The sample was stored in plastic bottles without further treatment and used for the reference experiment.

Some fraction of Raw Rice Husk was blended for size reduction by using WARING COMMERCIAL Laboratory Blender. Then, it was sieved to 150-250 μm size by using Retsch Mechanical Sieve Shaker. The blended and sieved rice husk was washed with distilled water by stirring at 600 rpm for 15 min. After that, it was filtered prior to drying. At this point, grinded rice husk was termed as Blended Rice Husk. The sample was also stored in plastic bottles and used for the first set of experiment.

Accordingly, there are two types of adsorbent samples prepared from multi-step chemical treatment. The first sample was prepared by soaking the Blended Rice Husk in 99% purity of acetone for 24 h. Then, the sample was filtered before drying at 110°C. After the sample has been completely dried, then it was washed with distilled water prior to drying as previous steps. This was followed by soaking the acetone treated rice husk sample in 99% purity of benzene for 24 h. The aforementioned procedural steps were then carried out, as to increase efficiency of adsorption by increasing top diameter of pores and also, increase pores diameter from the bottom to predictably produce T-shirt shape of pores structure of rice husk adsorbent. The second sample was obtained by soaking ABRH in 99% purity of methanol for 24 h with the same preparation method as the first sample.

Screening analysis of simulated wastewater: Random concentration of multi-metal element in the simulated wastewater sample was analyzed and quantified by using

Thermo Scientific Inductively Couple Plasma (ICP) Spectrometer. For this purpose, 8 mL of simulated wastewater sample was taken out from the 10 L chemical container.

Characterization of rice husk adsorbents: Total carbon, hydrogen, nitrogen, sulphur and oxygen contained in all types of rice husk adsorbents were determined by using FlashEA Elemental Analyzer (CHNS-O). Field Emission Scanning Electron Microscope (FESEM) was also used to study the surface morphology of the rice husk adsorbents. Specifically, FESEM studies were carried out by using a ZEISS SUPRA 40VP FESEM at an electron acceleration voltage of 1 kV and magnification of 1000 times. The rice husk adsorbents were also characterized by using Brunauer, Emmett, Teller (BET) method. In particular, BET single point surface area of rice husk adsorbents were obtained from Micromeritics ChemiSorb Surface Area Analyzer, while the analysis of BET multi point method of rice husk adsorbents was performed by Quantachrome Instruments.

Experimental procedures of adsorption studies: A series of adsorption studies were carried out which initiated by using Raw Rice Husk in single-layered fixed bed column. This experiment was considered as reference experiment in order to evaluate the effects of rice husk treatments in terms of adsorption capacity. The reference experiment was conducted using a burette of 1.6 cm diameter. Six grams of Raw Rice Husk were wrapped by Whatman No. 1 filter paper. Then, the wrapped Raw Rice Husk was loaded from the top of the burette. The burette was regularly shaken while being loaded with wrapped Raw Rice Husk to minimize void volume as well as air gaps and allow settling by gravity. The burette was charged with simulated wastewater in the down flow mode manually. The treated wastewater samples were then collected at certain time intervals until the volume for each sample is 8 mL.

Then, the first set of experiment was carried out by using Blended Rice Husk. The objective of the first set of experiment was to perform the comparative study of adsorption performance between two different experimental rigs, namely single- and multi-layered fixed bed columns in order to adsorb multi-metal element from simulated wastewater. The previous steps were also applied for Blended Rice Husk in single-layered fixed bed column study. Then, the multi-layered fixed bed column study was conducted by following the similar experimental procedures, except the burette was packed with Blended Rice Husk in three layers of bed, each having 2 g of adsorbent. The distances between layers inside the burette were fixed to 2 mL. The experimental rig with high capacity to adsorb multi-metal element from simulated wastewater was then determined via evaluating the adsorption performance of the columns by means of numerical technique of area under the graph.

The second set of experiment involved the study of adsorption capacity of ABRH and ABMRH in the best fixed bed column, which is determined from the first experiment. The abovementioned experimental procedures were also applied for this experiment. The experimental rigs were assumed as semi-batch because it involved continuous inlet and outlet wastewater flows and batch adsorbent displacement. The adsorption system inside the column is in atmospheric pressure. Inlet simulated wastewater flow rate, mass of adsorbent and volume of treated wastewater at certain time interval were also fixed throughout the studies.

Numerical technique of area under the graph: The adsorption performance of all experiments was evaluated by numerical technique of area under the graph using Simpson's 1/3 Rule (Chapra and Canale, 2006).

RESULTS AND DISCUSSION

Screening analysis of simulated wastewater: The initial concentration of metals elements in simulated wastewater sample before adsorption which was analyzed by ICP Spectrometer are Berium (Be); 0.000779 ppm, Calcium (Ca); 2.7731 ppm, Cadmium (Cd); 66.1193 ppm, Chromium (Cr); 40.4602 ppm, Copper (Cu); 52.4220 ppm, Iron (Fe); 16.92 ppm, Lithium (Li); 1.0629 ppm, Magnesium (Mg); 28.34717 ppm, Manganese (Mn); 9.6 ppm, Molybdenum (Mo); 8.9181 ppm, Nickel (Ni); 0.0896 ppm, Lead (Pb) 0.5433 ppm, Antimony (Sb); 2.1270 ppm, Strontium (Sr); 0.006267 ppm, Thallium (Tl); 1.6876 ppm, Vanadium (V); 1.7012 ppm and Zinc (Zn); 27.2892 ppm. These results were then used as reference concentrations of multi-metal element for all adsorption studies. Furthermore, the screening analysis of simulated wastewater also indicated that, the sample was characterized by high toxicity of metals elements.

Elemental analysis: Blended Rice Husk was found to contain 37.72% carbon, 4.72% hydrogen, 56.44% oxygen and 2.26% nitrogen. On the other hand, elemental analysis of ABRH revealed that it consists of 35.04% carbon, 3.23% hydrogen, 59.43% oxygen and 2.32% nitrogen. Besides that, elemental analysis also indicated the presence of 34.38% carbon, 5.76% hydrogen, 58.91% oxygen and 0.96% nitrogen in ABMRH. It has been identified that, no sulphur was found in all types of rice husk adsorbents. It also has been noted that, there were no significant differences regarding to elemental analysis of all types of rice husk adsorbents. The analysis indicates that, mechanical and multi-step chemical treatments did not affect the composition of natural rice husk.

Surface morphology analysis: Micrographs show considerable changes in morphology of rice husk adsorbent after mechanical treatment. In particular, the surface of Blended Rice Husk was much rougher and highly heterogeneous than that of Raw Rice Husk, demonstrating the effect of size reduction. The heterogeneous surface of Blended Rice Husk provided more exposed surface area of rice husk adsorbent towards highly potential adsorption of multi-metal element. On the other hand, this study also observed that, the morphological characteristic of rice husk was altered by multi-step chemical treatment. Treatment with acetone, benzene and methanol solvents induced the cracking of the origin and natural surface as well as increased the surface roughness. The surface of ABRH and ABMRH showed there were high development of pores due to removal of hemicelluloses, lignin and silica. Thus, these findings suggested that, multi-step chemical treatment able to open up internal surface area of the top part of cylindrical pore structure. Micrographs of all types of rice husk adsorbents are shown in Fig. 1 until 4.

BET Analysis: Specific surface area of Blended Rice Husk, ABRH and ABMRH as calculated by BET method were found to be 5.06, 18.07 and 14.46 m^2 g^{-1}, respectively. These values were significantly greater than previously reported values for Raw Rice Husk, which are 0.68, 0.69 m^2 g^{-1} (Mohan and Sreelakshmi, 2007); 0.70 m^2 g^{-1} (Asadi *et al*., 2008); 0.83 m^2 g^{-1} (Aydin *et al*., 2008), 0.01 m^2 g^{-1} (Daffalla *et al*., 2010); as well as 0.92 m^2 g^{-1} (Luo *et al*., 2011). In particular, reported surface areas of ABRH and ABMRH in the present study are also significantly higher compared to previous reported value as listed in Table 1. Thus, by comparison with previous studies, the differences of the present study may be attributed to the effect of size reduction by

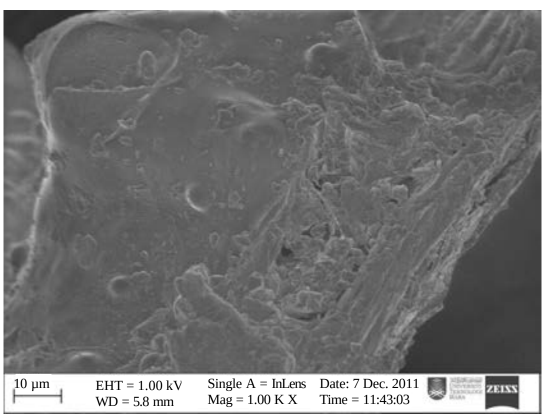

Fig. 1: Micrograph of the raw rice husk

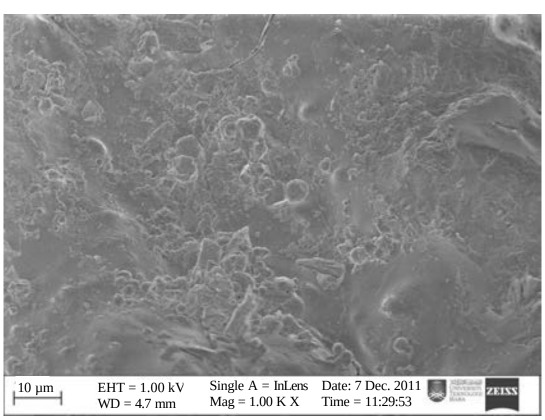

Fig. 2: Micrograph of the blended rice husk

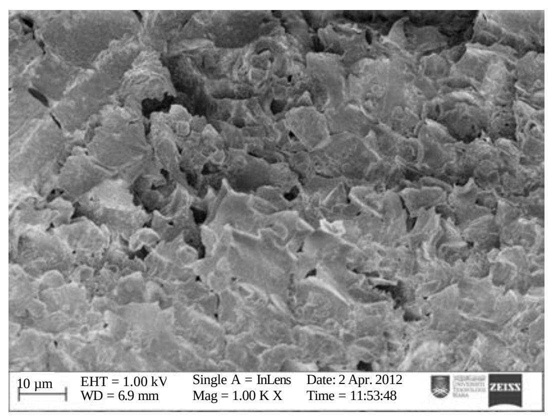

Fig. 3: Micrograph of the ABRH

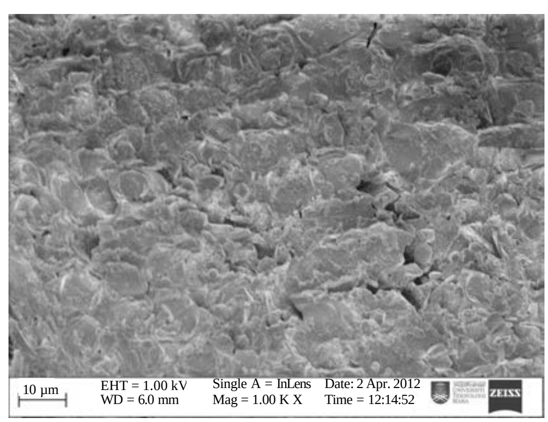

Fig. 4: Micrograph of the ABMRH

Table 1: Comparison of BET surface area for chemically modified rice Husk

Types of chemical treatments	Chemicals	BET surface area (m^2 g^{-1})	References
Multi-step	Acetone-benzene (ABRH)	18.07	Present study
	Acetone-benzene-methanol (ABMRH)	14.46	
Single step	Hydrochloric acid	4.10	Asadi *et al.* (2008)
	Sodium hydroxide	4.30	
Multi-step	Sodium hydroxide-hydrogen peroxide	1.92	Aluyor *et al.* (2009)
Single step	Sulphuric acid	0.02	Daffalla *et al.* (2010)
	Sodium hydroxide	0.01	
	Formaldehyde	0.02	

mechanical treatment as well as multi-step chemical treatment with strong solvents of acetone, benzene and methanol. These treatments may significantly affect the surface area as a result from reduction of impurities contents as well as hemicelluloses, lignin and cellulose crystallinity. Hence, this study suggested that, the surface area of rice husk adsorbent can be increased by shifting conventional single- to multi-step chemical treatments which predicted to enhance rice husk adsorptivity as a result from optimum treatment by chemical agents.

Moreover, pore diameter and pore volume of ABRH as determined by BET method are 22.5 nm and 0.28 cm^3 g^{-1}, respectively. The reported pore diameter of the present study is notably larger compared to previous study done by Siriluk and Yuttapong (2005). They found that, the pore diameter of Silica Based Rice Husk Ash was 3.6 nm with the same pore volume of 0.28 cm^3 g^{-1}. Moreover, Ismagilov *et al.* (2009) also reported that, the pore diameter of Activated Carbon Rice Husk was 3.2 nm with the same pore volume of 0.28 cm^3 g^{-1}. Therefore, by comparison, the pore length of the present study is less than that studied by Siriluk and Yuttapong (2005) as well as Ismagilov *et al.* (2009) due to larger pore diameter. Similar trend was also observed for ABMRH. BET analysis revealed that, the pore diameter and pore volume of ABMRH are 23.8 nm and 0.18 cm^3 g^{-1}, respectively. In particular, the reported pore diameter of ABMRH is slightly larger than ABRH owing to additional treatment by methanol solvent, which opened up more internal surface areas of the pores. The reported pore diameter of ABMRH is also significantly larger compared to the one studied by Mahvi *et al.* (2004). They claimed that the pore diameter of RHA was 14.5 nm with the same pore volume of 0.18 cm^3 g^{-1}. Consequently, as comparison, the pore length of ABMRH is also less than the one that was investigated by Mahvi *et al.* (2004), due to larger pore diameter. Thus, the reduction in pore lengths of ABRH and ABMRH with the same respective pore volumes precisely indicated that, multi-step chemical treatment was predicted to open up internal surface area of the bottom part of cylindrical pore structure and consequently lead to deviation of conventional geometries of cylindrical pore, which having middle narrow section of pore.

Hypothetical t-shirt pore model theory: Surface morphology and BET analyses of the present study revealed that, hybrid modification of mechanical and multi-step chemical treatments enhanced surface area development and pore structure evolution, which might have altered the conventional cylindrical pore structure. The following assumptions are made in predicting and hypothesizing the new structure of pores, the original pore shape of natural rice husk is considered as conventional cylindrical shape, molecules of solvents loaded directly to the bottom part of cylindrical pore network due to gravitational effect and no direct contact of solvents molecules towards horizontal directions of pore network.

Acetone, benzene and methanol which were used in multi-step chemical treatment are characterized by polar aprotic, non-polar and polar protic solvents, respectively. These characteristics made each type of solvents functioned as the cleaning agent for the removal of organic and metallic impurities in rice husk structure by attraction forces.

According to Asadi *et al.* (2008), common organic impurities that usually present in rice husk surface are lignin, hemicelluloses, starch, pectic materials and gums. Figure 5 depicts a sketch for the formation mechanisms of Hypothetical T-shirt Pore Model. Figure 5a illustrates original pore of natural rice husk with pore diameter, D_1 and pore length, L_1. This pore geometry can be approximated as conventional cylindrical pore for better illustration as shown in Fig. 5b. The amount of organic and metallic impurities present in rice husk surface was predicted to be diminished as natural rice husk soaked in each type of solvents for treatments. Furthermore, the removals of impurities by these solvents also able to open up internal surface area of the top part of conventional cylindrical pore. The solvents were then activating the micro structure network at the bottom part of pore due to gravitational effect and increases available adsorption sites at the bottom part of cylindrical pore structure, as portrayed in Fig. 5d. As a result, pore diameter of D_2 as well as surface area increased and this possibly favour chemical interactions between the more exposed rice husk surface and multi-metal element. Thus, this new structure of pore shape enhances rice husk adsorptivity. The

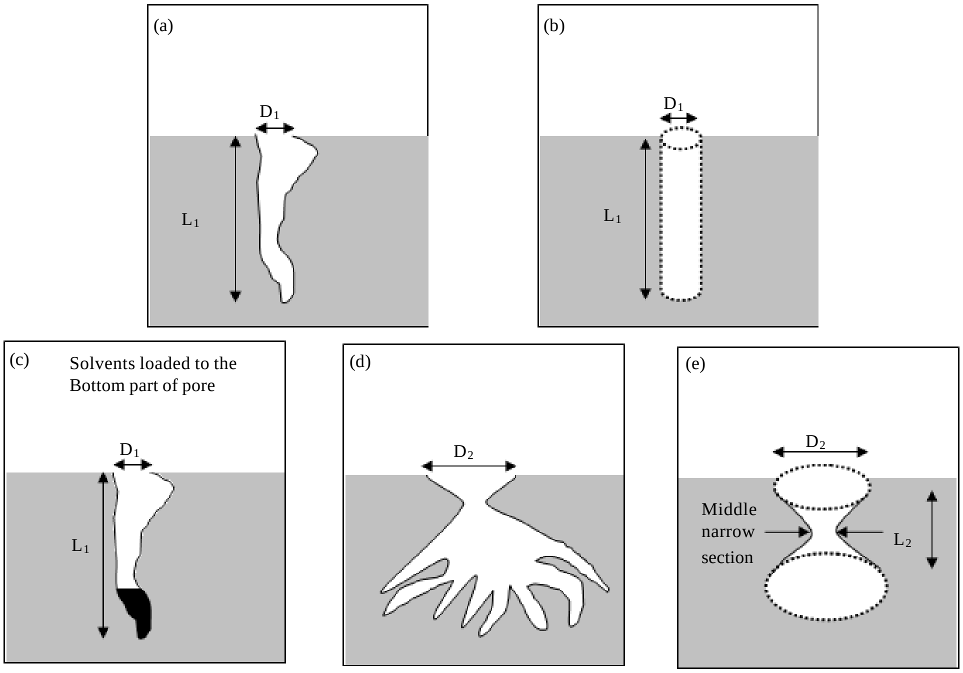

Fig. 5(a-e): Sketch for the formation mechanisms of hypothetical t-shirt pore model

Table 2: Total area under the graphs for adsorption studies by different types of rice Husk adsorbents

Types of rice husk adsorbents	Total area	Types of fixed beds
Raw rice husk	37721.37	Single-layered bed
Blended rice husk	36775.30	
Blended rice husk	6452.57	Multi-layered bed
ABRH	3897.52	
ABMRH	2078.99	

indefinite pore shape at the bottom part of pore can be approximately illustrated as large circle shape as depicted in Fig. 5e, demonstrating higher number of adsorption sites. These changes in micro structure of rice husk were termed as Hypothetical T-shirt Pore Model, which was sketched in Fig. 5e.

Moreover, larger pore diameter made the length of the new pore structure, L_2 to be reduced with the formation of middle narrow section of pores. This exceptional feature of the new pore offered reduction in desorption rate. This will solve one of the problems encountered by cylindrical pore shape. The reduction in desorption rate simultaneously reduces resistance for metals adsorptions. Consequently, a complete route of multi-metal adsorption can be achieved.

Numerical technique of area under the graph: The pattern of area under the graphs for each type of metal element by different types of rice husk adsorbents were varied without consistent pattern due to competition factors in multi-component adsorption. The adsorption performance of adsorption studies were indicated by total area under the graph based on rice husk adsorbents used for the removal of multi-metal element, instead of individual area under the graph for each metal element. Accordingly, total area under the graphs for adsorption studies by different types of rice husk adsorbents are shown in Table 2. Besides that, specific percentage reductions of area under the graphs for adsorption of each metal element by different types of rice husk adsorbents are also listed in Table 3.

Comparison of adsorption in single- and multi-layered fixed bed columns: Total area under the graph for adsorption of multi-metal component by Blended Rice Husk in single- and multi-layered fixed bed columns are determined to be 36775.30 and 6452.57, respectively. Since the total area under the graph for multi-layered is significantly lowered by 82.45% than single-layered fixed bed column, then it can be concluded that, the adsorption performance of multi-layered was remarkably increased. In addition, with respect to reference experiment of Raw Rice Husk in single-layered fixed bed column, total area under the graph for Blended Rice Husk in multi-layered fixed bed column is notably lowered by 82.89%. The experimental error band is depended on quality performance of system analysis of measuring concentration of a sample.

Table 3: List of percentage reduction of area under the graphs for adsorption of each metal element by different types of rice husk adsorbents

	Percentage reduction of area under the graphs (%)			
Metals	Blended rice husk (single-layered bed)	Blended rice husk (multi-layered bed)	ABRH (multi-layered bed)	ABMRH (multi-layered bed)
Beryllium	n/a	n/a	14.45	43.78
Calcium	n/a	98.67	98.18	99.92
Cadmium	n/a	n/a	n/a	26.04
Chromium	n/a	n/a	n/a	21.65
Copper	14.76	n/a	n/a	14.76
Iron	n/a	n/a	n/a	3.91
Lithium	8.02	38.30	n/a	n/a
Magnesium	50.37	92.20	96.06	94.84
Manganese	n/a	n/a	38.72	59.73
Molybdenum	n/a	n/a	44.33	30.87
Nickel	80.02	73.96	74.08	77.18
Lead	77.80	96.86	80.16	98.97
Antimony	89.68	n/a	n/a	89.68
Strontium	n/a	n/a	n/a	97.82
Thallium	98.79	98.29	99.52	99.59
Vanadium	n/a	n/a	n/a	90.48
Zinc	19.82	n/a	n/a	19.64
Total	2.51	82.89	89.67	94.49

n/a refers to area of insignificant size under the graphs for specific metal element which means that adsorption process is not active

Table 4: Comparison of area under the graphs for adsorption of each metal element by blended rice husk adsorbents in single- and multi-layered fixed bed columns

	Area under the graphs		
	Types of fixed bed		
Metals	Single-layered	Multi-layered	Percentage reduction (%)
Beryllium	0.07	0.02	76.74
Calcium	25694.91	319.41	98.76
Cadmium	1345.27	1323.28	1.63
Chromium	2738.38	809.20	70.45
Copper	349.48	1048.44	n/a
Iron	1660.28	338.40	79.62
Lithium	31.69	21.26	32.92
Magnesium	3621.71	569.31	84.28
Manganese	364.18	192.00	47.28
Molybdenum	340.06	481.77	n/a
Nickel	13.08	17.05	n/a
Lead	78.28	11.08	85.85
Antimony	14.18	326.33	n/a
Strontium	1.94	3.77	n/a
Thallium	43.56	61.50	n/a
Vanadium	296.33	383.72	n/a
Zinc	181.93	546.05	n/a
Total	36775.30	6452.57	82.45

n/a refers to area of insignificant size under the graphs for specific metal element which means that adsorption process is not active

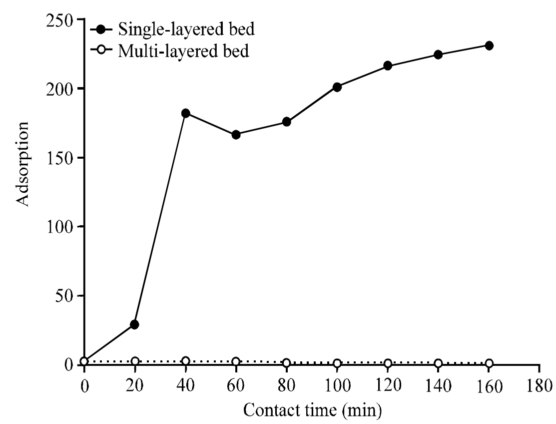

Fig. 6: Adsorption of calcium by blended rice husk in single- and multi-layered fixed bed columns

The advantage of using multi-layered over single-layered fixed bed column is that its design is able to overcome the limitation of single-layered fixed bed column particularly regarding to vacant spaces. In single-layered bed, the wastewater droplet tends to flow into less restrictive area, which is known as vacant space. Vacant space in the bed can be defined as space in the bed which contains no occupied adsorbents. The presence of vacant space in the bed causes the distribution of wastewater flow inside the bed to be non-uniform and the possibility of channeling effect to be occurred is higher. Besides that, the non-uniform distribution in the bed is also caused by high pressure. As a result, the contact time (residence time) between metal solutes and Blended Rice Husk will be less which then reduced the probability of the solute molecules reaching an available adsorption site. By dividing the layer into three layers, the adsorption performance increased because each of wastewater droplets will be redistributed as it enters the new layer of fixed bed. The multi-layered bed arrangement also leads to reducing pressure inside the bed. Thus, the probability of solute molecules to reach another part of adsorption sites will be gradually increased. This theory is in accordance with the adsorption data as tabulated in Table 4. The data indicates that, the adsorption of Calcium in multi-layered bed is the most favorable with percentage reduction of area under the graph of 98.76%, as compared to adsorption in single-layered bed (Fig. 6). On the other hand, the least favorable adsorption by Blended Rice

Table 5: Comparison of Area under the graphs for adsorption of each metal element by raw rice husk (single-layered) and ABRH adsorbents (multi-layered) fixed bed columns

	Area under the graphs		
	Types of fixed bed		
Metals	Single-layered	Multi–layered	Percentage reduction (%)
Beryllium	0.009238	0.007903	14.45
Calcium	24057.72	436.79	98.18
Cadmium	596.14	670.78	n/a
Chromium	344.28	410.47	n/a
Copper	409.97	531.82	n/a
Iron	117.39	171.65	n/a
Lithium	34.45	198.74	n/a
Magnesium	7297.60	287.58	96.06
Manganese	158.93	97.39	38.72
Molybdenum	183.04	101.89	44.33
Nickel	65.47	16.97	74.08
Lead	352.60	69.95	80.16
Antimony	137.38	335.74	n/a
Strontium	1.92	2.49	n/a
Thallium	3599.83	17.12	99.52
Vanadium	137.74	271.29	n/a
Zinc	226.90	276.85	n/a
Total	37721.37	3897.52	89.67

n/a refers to area of insignificant size under the graphs for specific metal element which means that adsorption process is not active

Table 6: Comparison of area under the graphs for adsorption of each metal element by raw rice husk (single-layered) and ABMRH adsorbents (multi-layered) fixed bed columns

	Area under the graphs		
	Types of fixed bed		
Metals	Single-layered	Multi–layered	Percentage reduction (%)
Beryllium	0.009238	0.005194	43.78
Calcium	24057.72	18.94	99.92
Cadmium	596.14	440.89	26.04
Chromium	344.28	269.73	21.65
Copper	409.97	349.48	14.76
Iron	117.39	112.80	3.91
Lithium	34.45	76.64	n/a
Magnesium	7297.60	376.80	94.84
Manganese	158.93	64.00	59.73
Molybdenum	183.04	126.54	30.87
Nickel	65.47	14.94	77.18
Lead	352.60	3.62	98.97
Antimony	137.38	14.18	89.68
Strontium	1.92	0.04	97.82
Thallium	3599.83	14.91	99.59
Vanadium	137.74	13.11	90.48
Zinc	226.90	182.34	19.64
Total	37721.37	2078.98	94.49

n/a refers to area of insignificant size under the graphs for specific metal element which means that adsorption process is not active

Husk in multi-layered bed is determined to be Cadmium with percentage reduction of area under the graph of 1.63%.

Multi-step chemical treatment: It was found that, total area under the graph for ABRH and ABMRH are 3897.52 and 2078.98, respectively. These results revealed that, the adsorption capacity of ABRH and ABMRH are

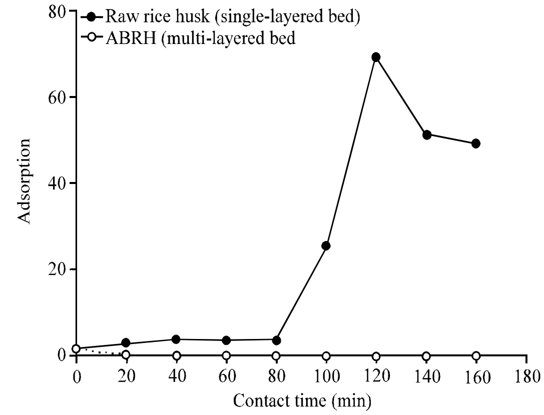

Fig. 7: Comparison of adsorption of thallium by raw rice Husk and ABRH

significantly higher than Raw Rice Husk in single-layered bed with percentage reduction of area under the graph of 89.67 and 94.49%, respectively. The adsorption of multi-metal element is more complimentary on ABRH and ABMRH over Raw Rice Husk due to the formation of Hypothetical T-shirt Pore Model, which is comprehensively discussed previously. The hypothesized theory of T-shirt pore is supported by the adsorption data of both ABRH and ABMRH. As presented in Table 5, the theory is applicable for adsorption of Beryllium, Calcium, Magnesium, Manganese, Molybdenum, Nickel, Lead and Thallium. These findings suggest that in particular, the adsorption of Thallium by ABRH in multi-layered bed is the most favorable with percentage reduction of area under the graph of 99.52%, as compared to adsorption by Raw Rice Husk in single-layered bed. On the other hand, the least favorable adsorption by ABRH in multi-layered bed is determined to be Beryllium with percentage reduction of area under the graph of 14.45%. Turning now to the adsorption of multi-metal element by ABMRH in multi-layered bed, it is apparent that, Calcium resulted in the highest value of percentage reduction of area under the graph which is determined to be 99.92%. In contrast, the least favorable adsorption by ABMRH in multi-layered bed is determined to be Iron with percentage reduction of area under the graph of 3.91%. As Table 6 shows, the hypothetical theory of T-shirt pore shape is applicable for all types of metals elements, except Lithium. Therefore, these analyses justified the formation of Hypothetical T-shirt Pore Model by demonstration of least total area under the graphs, as compared with all adsorption studies, owing to its exceptional feature of pore geometries (Fig. 7, 8).

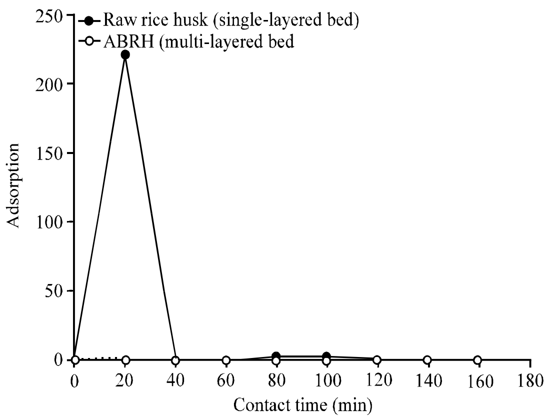

Fig. 8: Comparison of adsorption of calcium by raw rice Husk and ABMRH

CONCLUSION

After meticulously followed a structured and systematic methodology, the objective outlined at the beginning of this study had been fulfilled. The most significant finding of the present study is surface morphology and BET analyses which revealed that, the application of acetone, benzene and methanol solvents by multi-step chemical treatment induced the formation of new structure of pore shape known as Hypothetical T-shirt Pore Model. This hypothesized pore shape demonstrated higher porous area and surface area, larger pore diameters as well as higher adsorptivity, due to its middle narrow section which reduce the rate of desorption. It was found that, the theory of Hypothetical T-shirt Pore Model is in accordance with findings emerged from adsorption studies by numerical technique of area under the graph. However, one of the limitations of the present study is the formation mechanism and behavior of the new pore shape, which has been hypothetically discussed. Thus, further study is highly recommended for additional clarification and justification of accurate characterization and visualization of the proposed shape by using principal methods available such as ultrasonic and radiation scattering methods. Moreover, area of studies such as kinetic and mathematical modeling can also be employed for the future works to support the theory of the proposed pore shape. Nevertheless, the theory of Hypothetical T-shirt Pore Model can be proved and justified by demonstration of least total area under the graph, owing to aforementioned features of the proposed pore shape. This study also suggests that, multi-layered fixed bed column has high applicability for adsorption of multi-metal element by rice husk adsorbents. Finally, the findings of the present study also recommends that, rice husk represents the most promising natural material as low-cost adsorbent for the removal of any types of metals elements from wastewater.

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