ORIGINAL ARTICLE

Physical Structures and Adsorption Efficiencies of Sugarcane Bagasse, Coconut Pulp and Sawdust as Natural Adsorbents in Removal of Heavy Metals From Car Wash Activity

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ABSTRACT

Introduction: Car wash premises consume large amounts of water that can later end up in the public irrigation system. This production of wastewater, which contains heavy metals, are both detrimental to the marine environment and unsustainable. **Methods:** In this study, sugarcane bagasse (SB), coconut pulp (CP) and sawdust (SD) were investigated to determine their potential usage as low-cost, heavy metals adsorbents. The morphology of these adsorbents was characterized using Spectrometry Electron Microscope (SEM), while presence of heavy metals constituents on selected adsorbents was analysed using Atomic Absorption Spectrometry (AAS). Adsorbents Adsorption efficiencies were calculated to determine the best adsorbent. **Results**: CP with a more porous structure promotes a larger surface area, compared to SB and SD. Adsorption was optimized at pH 4 in room temperature for 4 hours, with adsorbents particle between 0.5 mm and 2.5 mm in size. SD was the best adsorbent for Iron (Fe) and Copper (Cu) removal with 95.6% and 86.5% removal efficiencies. Meanwhile, CP was the best adsorbent for Zinc (Zn) and Manganese (Mn), with percentage removal of 78.9% and 24.8% respectively. **Conclusion:** The findings of this study can be used by relevant agencies for a better policy regarding on wastewater management and support the concept of turning waste to useful products.
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INTRODUCTION

The increase of car ownership is directly proportional with the existence of car wash services. Besides its economic impact, car wash services are also causing an environmental effect, as it consumes large volumes of treated water supplied by water utility companies , a practice that is unsustainable especially in light of the limited treated water resource. In fact, the average water usage for car wash services is 400 L per car when hand-washed using a water hose and 150 L per car when using a conventional installation (1). Car wash stations are of particular environmental and sustainability concern, as it not only consumes large volumes of water, but it also produces equal volume of wastewater, which is contaminated with petroleum products and toxic chemicals that will eventually be released into the aquatic environment (2-3). The presence of petroleum in the wastewater is from residues of gasoline, engine oil, diesel, greases, and lubricants that can be found on the surface and engine of the vehicle (4-5). Additionally, car wash wastewater also contains various other contaminants, in particular detergents, phosphates, chemicals, metals, and different hydrocarbons. In elevated concentration, these contaminants are harmful not only to the aquatic environment, but also affects the portability of groundwater (6), making an already dwindling resource more contaminated. In fact, this linear flow practice meant that an average car wash produced approximately 150 L to 400 L of wastewater per car, clearly an unsustainable practice that contributed to global water issues, especially when taken into account the over 1 billion cars that are currently on the road in the world (7).

The car wash industry is thriving, thanks to the increasing number of privately owned vehicles, and the situation in Malaysia is parallel to this global phenomena. In 2019, 604,287 vehicles have been registered in Malaysia, including passenger cars and commercial vehicles (8). Due to its convenience, car wash premises are utilised frequently, especially in the urban areas. This means as the number of vehicles on the road increases, so do the services for car wash, and subsequently the volume of wastewater produced.

In Malaysia, even though the majority of the carwash premises offer a manual hand wash service, the water consumed is still relatively high. On average, between 150-600 L of water is needed to wash every car, which depends on the size of vehicles and what sort of installation used by the carwash service (9). This may contribute to the increased demand of treated water for commercial use, a worrying trend in an era of climate change and resource scarcity. In fact, the high volume of contaminated wastewater produced from washing vehicles activity is of concern not only to the aquatic lives and environment (10), but it also adds to the burden of extracting water resources that is becoming more and more limited.

Subsequently, heavy metals that are released to the aquatic environment can bioaccumulate along the aquatic food chain (11), with prolonged and continuous consumption of contaminated aquatic organisms posing a significant health risk to the community (12). In fact, even in small amounts, heavy metals can either in the body or in a metabolically available form that affects essential biochemical processes (13).

Bioaccumulation of heavy metals in living organisms can lead to severe health problems. For humans, heavy metal can enter the body by ingestion, inhalation, and absorption. Accidental or deliberate ingestion via contaminated food is the most common route for heavy metal to enter the human body (11,13) while exposure through inhalation can only happen when breathing in heavy metal in dust or vapour. Some heavy metals may cause acute and chronic toxicity while others will pass and excrete in the urine. Lead, cadmium and chromium are some of the examples of heavy metals that can cause several health problems such as cancer and kidney failure. In an aquatic environment, unnecessary manganese levels can endanger the ecosystem as it induces iron deficiency in algae that causes the inhibition of chlorophyll synthesis. Furthermore, excessive consumption of copper can also lead to serious health issues, among them "severe muscle irritation and corrosion, widespread capillary damage, hepatic and renal damage, and central nervous system irritation followed by depression" (14).

In most developed countries, the wastewater is transported to municipal treatment plants, most of which utilizes conventional treatment processes that may not be able to remove persistent organic pollutants efficiently (15). However, recent reports showed that various European countries have introduced new legislations that requires wastewater recycling in carwash services. This practice not only reduces the volume of water consumed as well as pollutants released to the municipal treatment systems, but also promotes the sustainability of water resource use. In fact, earlier on, certain countries such as Netherlands and Scandinavian, have already imposed a maximum water consumption limit of between 60 L and 70 L per car (16). While this was introduced in order to control the water usage, an automatic carwash, however, still consumes an average of 400 L of water per car (17). On the contrary, Malaysia currently has no specific policy for water recycling or water usage limit for commercial car washing premise, except for waste water which is placed under the Environmental Quality Act 1974 and Industrial Effluent Regulation 2009.

Previous studies have shown that there have been various efforts to treat car wash wastewater. This includes membrane processes, membrane bioreactor, crystallization, flocculation, flotation, micro- and ultrafiltration, adsorption, solvent extraction, electro/chemical coagulation, electrochemical and physicochemical processes, photo-catalytic degradation and chemical oxidation (1, 4-5,16,18-22, 23). Not only that, these techniques have been tested for both individual applications as well as in various combinations.

For the specific removal of heavy metals on the other hand, a variety of technologies are available, which includes chemical precipitation, ultrafiltration, ion-exchange, reverse osmosis, electrowinning, phytoremediation, and carbon adsorption. All of which with varying degrees of success. However, these methods all require very high operational and maintenance costs, an issue that can become a bigger problem when taken into account that these methods also generate toxic sludge, and require complicated procedures for heavy metal removal. Therefore, adsorption processes are comparatively preferable for water treatment because it's convenient, allows easy operation and is very simple to design (24).

Adsorbents materials from natural resources such as algae, fungi, bacteria and waste plant materials are called biosorbents. Biosorption is an alternate and eco-friendly method which uses natural products in heavy metals removal from wastewater (25). When producing adsorbent materials, the use of alternative and renewable raw materials are preferred as an organic component for the development of hybrid materials, particularly since it means low cost, easily available and abundant materials, which are both biocompatible and biodegradable in nature (26). Apart from that, these materials promote sustainability of agricultural processes. This is because the adsorbents, which are developed from low-cost bio-based raw materials from diverse origins, utilizes agriculture residue, which may help overcome the issue of agricultural waste (27). The precursor on the most common types of agricultural residues includes cocoa (28), coconut shells (29), cherry stones (30), potato peels (31), Isabel grape bagasse (32), coffee residues and almond shells (33), among many others.

Sugarcane bagasse, coconut pulp and sawdust are known to be effective biosorbents of removing pollutants from wastewater. The usage of raw, modified and even activated carbon from these materials are well-known, even for heavy metals removal. Sugarcane bagasse has the potential to remove manganese (34), copper (35), and arsenic (36, 37). Not only that, studies done by (18) and (38) concluded that sawdust can adsorb silicon, aluminium, iron, lead and copper. Although there is a lack of studies on coconut pulp as biosorbent for heavy metals removal, previous studies have shown that some part of coconuts (shells) are able to remove gold (39) and chromium (40).

The behaviour and performance ability of biosorption is determined by the physical and chemical characteristics of the biosorbent itself. This includes its physical structure. Materials with porous structure promote higher surface area to adsorb pollutants. This is because the surface area of such particles is inversely proportional to its pore size. The smaller the size of pore, the larger the surface area. Therefore, it is important to determine the characteristic of biosorbent and adsorbent during the selection of the potential biosorbance materials.

In Malaysia, Sugarcane bagasse is easy to find as it is the by-product after the stalk is crushed to obtain the juice. It can be found at the sugarcane juice stalls at night market around the country. Whereas coconut pulp is produced when processing the coconut milk. Since there are a lot of Malaysian cuisines that use coconut milk such as curry, rendang, coconut rice, and even desserts, to obtain coconut pulp is not a difficult job. The same situation goes for sawdust. The existence of wood furniture industry makes sawdust can be easily retrieved. These wastes are abundant in volume and are always thrown away as they no longer have other use or purpose.

Therefore, this study was conducted to explore the potential of suitable natural waste materials that are abundance, renewable, biocompatible, and biodegradable in order to improve the water quality derives from carwash premise before being released into water drainage systems. In this case, materials tested in this study was selected as it meet the criteria as mention above. In addition, this study was in line with the Goal 6 of the Sustainable Development Goals 2030 which to ensure availability and sustainable management of water and sanitation for all.

MATERIALS AND METHODS

Sample Collection

The samples collected are sugarcane bagasse (SB), coconut pulp (CP), sawdust (SD), and carwash wastewater. These materials were obtained from local nearby shops and stalls in Puncak Alam, Selangor (3.2284° N, 101.4282° E).

Collection of sugarcane bagasse, coconut pulp and sawdust

A 500 mg each of raw materials were collected from nearby study area. Sugarcane bagasse and coconut pulp was obtained from a local sugarcane juice stall and a coconut milk shop while the sawdust was gathered from local furniture factory. These materials were collected using plastic bags and brought back to the laboratory.

Collection of carwash wastewater

1 L of carwash wastewater was obtained from a carwash premises in the study area. The wastewater samples were collected in polyethylene bottles with labels and carried in a cool box to the lab. The samples were stored in the chiller until further procedure is done. In order to prevent the samples from undergone precipitation, adsorption to container wall and to minimize the microbial degradation of the metals, nitric acid (HNO3) was added into the samples until the pH achieved <2. Even though any type of acid can be used, the oxidizing nature of HNO3 is preferred. In fact, adding HNO3 promotes conversion of metal ions into their nitrate salts, which are highly soluble (41). As a quality control measure, all wastewater collected was from car washing categories activities only and the frequency of the car wash was once weekly.

Sample Preparation

The biosorbent samples were dried in the oven at 90 °C for 24 hours until the dry weight of the samples became constant. Subsequently, dried samples were grinded into powder and sieved using three different sizes of sieve; 500µm, 1mm and 2mm (42). The carwash wastewater was filtered to remove solid materials.

Adsorption Process

The adsorption process was utilized to identify the ability of the adsorbents to adsorb heavy metals from the car wash wastewater. The concentration of heavy metals before and after adsorption processes were noted for calculation purposes. In this study, a total of 18 samples (9 samples of waste water and 9 control samples containing distilled water) underwent an adsorption experiment process. For wastewater samples, each potential adsorbents sample (SB,SD and CP) underwent an adsorption process with three different sizes; 500µm, 1mm and 2mm. Another 9 samples with the same three adsorbents size category acted as control underwent an adsorption process with distilled water. This process was adopted from (18).

Acid Digestion

Prior to analysis with AAS, the samples were digested with HNO3. The digestion would give significant effect on the recovery of various analyte contents in highly complex matrices (43). Acid digestion also prevents interference during atomization by destroying the matrix. The preliminary treatment of samples follows the 22th version of APHA 3030-F Nitric Acid-Hydrochloric Acid Digestion.

Analysis Technique
Two analyses techniques were performed in this study, which were absorption and scanning using atomic absorption spectrometry (AAS) and scanning electron microscope (SEM). SEM was used to analyse the physical structure of the adsorbents while AAS was used to analyse the heavy metal content in the wastewater. All instruments used in this study were calibrated to ensure the reliability of the result obtained. Several concentration solutions were used to determine the calibration curve of AAS. Whereas for SEM, the magnification correction calculation and the measurement correction calculation were used to calculate the correction factor of the images.

Atomic Absorption Spectrometry (AAS)
Water samples were analysed using Atomic Absorption Spectrometry (AAS) Perkin Elmer PinAAcle 900T. The samples included were carwash wastewater before adsorption and after process together with distilled water before and after adsorption process. The signal released by the samples was compared with the standards to find out the heavy metal concentration in the samples.

The carwash wastewater collected from all three carwash premises was analysed to identify heavy metals elements. Six types of element were tested based on findings from previous literature review. Out of six, only three heavy metals element with the highest content in the waste water sample were selected for the absorption procedure .

Scanning Electron Microscope (SEM)
The elemental analysis and morphology of the adsorbents were examined by using scanning electron microscope (SEM); model Teneo VS SEM located at National Institute of Health (NIH). The sugarcane bagasse, coconut pulp and sawdust were examined before the adsorption process to observe the surface. The samples were gold coated to improve their conductivity to obtain good images (36). Sample preparation was adopted from (44). At first, samples were sprinkled evenly on a SEM sample stub with double sided sticky tape before a hand blower was used to blow loose particles away to prevent stacking. Finally, the samples are sputtered with gold (Au) and examine using SEM.
follows the 22th version of APHA 3030-F Nitric Acid-Hydrochloric Acid Digestion.

Data Calculation and Analysis
After obtaining heavy metal concentration before and after adsorption process, the data collected were analysed for their adsorption efficiency and adsorption capacity.

Calculation of Adsorption Efficiency
Adsorption efficiency is expressed as a percentage of adsorbed metal compared to initial metal concentration. Equation 1 is used to calculate the adsorption efficiency (39).

$$E=\frac{(C_i-C_f) \times 10}{C_i} \quad (1)$$

Where
E = metal removal efficiency (%)
C_i = initial concentrations of metal (mg/L)
C_f = final concentrations of metal (mg/L)

RESULTS

Scanning Electron Microscope (SEM) Analysis of SB, SD and CP samples
The surface appearance of sugarcane bagasse (SB) was flaky, while sawdust (SD) had rough surface and coconut pulp (CP) had beehive-like structure. The number of dark pores in the field of view decreased with the increase of magnification, but each pore was more prominent. All the sample analysed using SEM had the same particle size which was at 2.0 mm. The SEM results of other particle sizes of SD SB and CP were not included as it can be expected to have the same surface characteristic except it is in different size. The analysis results of SB samples are shown in Fig. 1, while SEM of SD samples are displayed in Fig. 2, whereas the SEM results for CP samples are shown in Fig. 3.

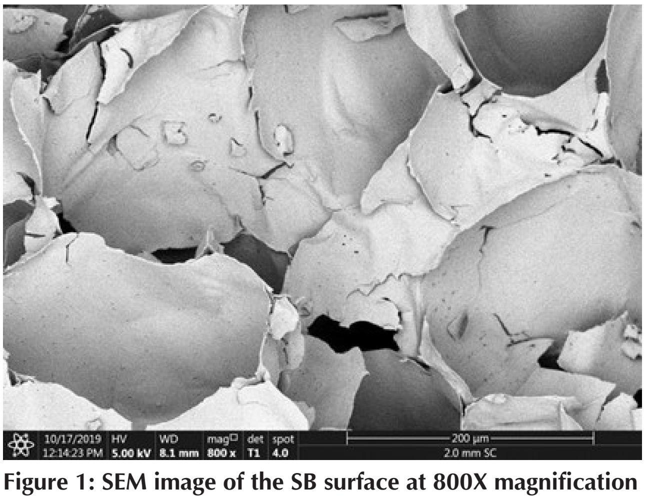

Figure 1: SEM image of the SB surface at 800X magnification

At lower magnification, which represents a wider field of view, allows a variety of pore sizes to be observed, although only larger pores would be identified. At higher magnification, the field of view narrows and only a portion of the micro pore could be observed. The distribution of various characteristics of pore size in different magnifications shows the importance of magnification in image analysis (45). International Union of Pure and Applied Chemistry (IUPAC) has approved a

Figure 2: SEM image of the SD surface at 400x magnification

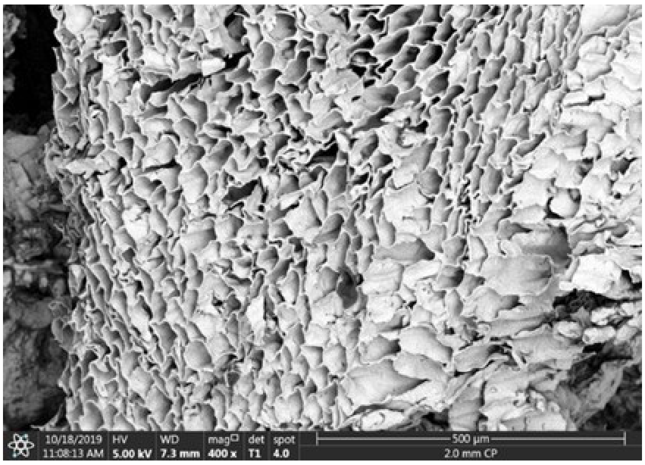

Figure 3: SEM image of the CP surface at 400X magnification

standard to define pore size based on the size width. Micropores refer to pores with an internal width of less than 2 nm, those with an internal width between 2 nm and 50 nm are known as mesopores, and those larger than 50 nm are called macropores (46).

Determination of Adsorption Efficiency; E (%) of SB, SD and CP

Adsorption efficiency was calculated using Equation (1) to estimate the percentage of adsorbed metal compared to initial metal concentration. In addition, adsorption efficiency was calculated for each heavy metal adsorbed using SB, SD and CP with different particle sizes.

Fig. 4 shows the adsorption efficiency of Fe using SB, SD and CP with different particle sizes. The adsorption efficiency of Fe decreased with the increase of particle size when using sawdust. SD with the particle size of 0.5 mm indicated the highest adsorption efficiency with as much as 95.61%. The adsorption efficiency for 1.0 mm particle size was 91.43%, and 88.61% for 2.0 mm. Next, the trend of the adsorption efficiency for SB and CP was similar as it dropped and later rose as the particle size increased. The adsorption efficiency of Fe using SB was 76.05%, 70.51%, and 70.49% for particle

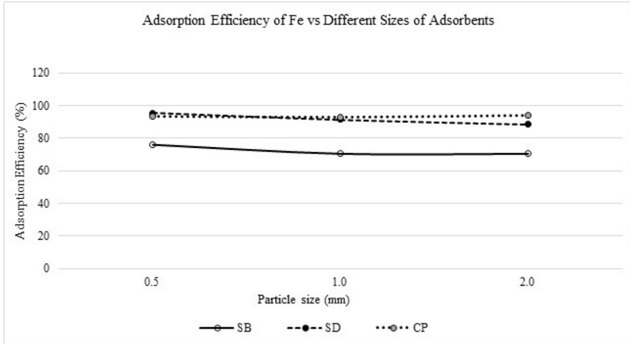

Figure 4: Adsorption Efficiency for Fe using SB, SD and CP with Different Particle Sizes

sizes of 0.5 mm, 1.0 mm, and 2.0 mm, respectively. For CP, the adsorption efficiency was 93.62%, 93.12%, and 94.20% as the size of particle was increased.

Fig. 5 shows the adsorption efficiency of Zn using SB, SD and CP with different particle sizes. CP had the highest adsorption efficiency of Zn metal, followed by SD and SB. Sugarcane bagasse (SB) and coconut pulp (CP) showed a similar trend where the adsorption efficiency decreased then increased as the particle size was increased. The SB had adsorption efficiency of 26.64%, 23.99%, and 28.18% for 0.5 mm, 1.0 mm, and 2.0 mm sizes of particle. Meanwhile, the adsorption efficiency of CP was 78.85% for 0.5 mm, 73.49% for 1.0 mm, and 78.49% for 2.0 mm. The SD had an increase in adsorption efficiency before it decreased with the increase of particle size. As the particle increased from 0.5 mm to 1.0 mm, the adsorption efficiency of Zn also increased 28.1% to 43.15% using SD as adsorbent. Then, the adsorption efficiency reduced slightly to 38.51% when the size of particle was 2.0 mm.

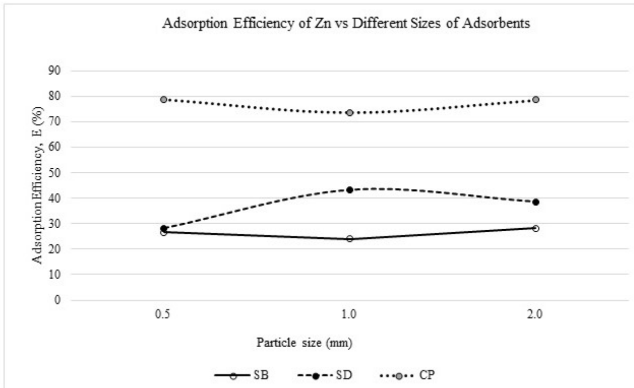

Figure 5: Adsorption Efficiency for Zn using SB, SD and CP with Different Particles Size

Fig. 6 indicates the adsorption efficiency of adsorbents (SB, SD and CP) on different sizes towards Cu. The Fig. shows that sawdust had the highest adsorption efficiency of Cu. The adsorption efficiency increased from 42.76%, to 53.1% and 57.93% as the particle size was increased from 0.5 mm to 1.0 mm and 2.0 mm for SB. However, SD and CP showed an increase of adsorption efficiency when the particle size increased from 0.5 to 1.0 mm

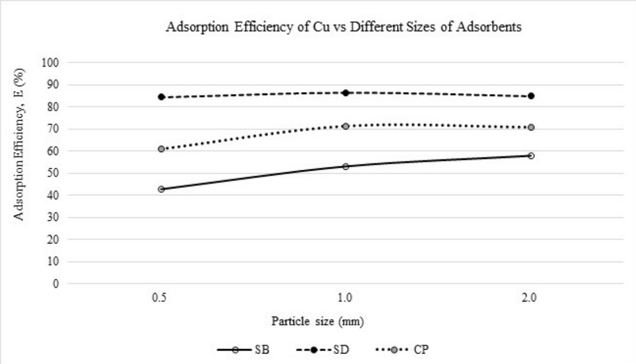

Figure 6: Adsorption efficiency for Cu using SB, SD and CP with Different Particles Sizes

while adsorption efficiency decreased when the particle size was increased to 2.0 mm. The adsorption efficiency of Cu using SD increased from 84.4% to 86.47% as the particle increased from 0.5 mm to 1.0 mm, before slightly decreased to 84.91% when the particle size reached 2.0 mm. For CP, the increase of adsorption efficiency could be seen from 61.21% to 71.29% with the increase of particle size 0.5 mm to 1.0 mm, later decreased slightly to 70.78% at 2.0 mm.

Fig.7 shows adsorption efficiency of Mn using SB, SD and CP with different particles sizes. Adsorption efficiency for Mn was found to had negative percentage towards SB and SD which indicates that both materials were not suitable to adsorb Mn from carwash wastewater. SB with 2.0 mm particle size desorbed the most with the percentage of -54.25%, followed by -46.12% at 1.0 mm size and -21.87% at particle size 0.5 mm. Besides, SD with particle size of 0.5 mm and 2.0 mm desorbed similar adsorption efficiency which was -15.97% and -15.90% respectively. In contrast, 1.0 mm of SD desorbed the least with adsorption efficiency of -4.1%, while CP on contrary from the other two was the best adsorbent for Mn. The adsorption efficiency of CP decreased with the increase of particle size. The 0.5 mm particle size showed 24.78%, 1.0 mm indicated 22.24%, and 2.0 mm with 14.18% of adsorption efficiency.

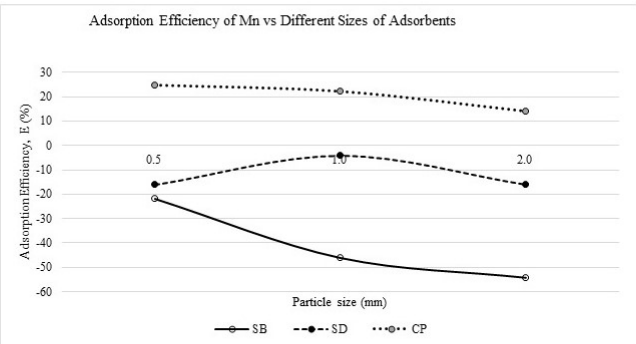

Figure 7: Adsorption Efficiency for Mn using SB, SD and CP with Different Particles Sizes

DISCUSSION

Adsorption capacity, efficiency and pore size

The main factor that affecting the adsorption capacity and efficiency is the pore size of the adsorbents. Pore size and particle size are two independent variables. Larger particle size may have smaller surface area, but it has more pores compared to the smaller particle size. Thus, larger particle size is more efficient adsorbent. A study by (34) found that adsorption capacity of Mn(II) ions is at best with particle size of 30 mesh (1.0161 mg/g) compared to 10 mesh (0.8947 mg/g) and 20 mesh (0.4332 mg/g).

Adsorption efficiency is closely related with adsorption capacity. If an adsorbent material has high adsorption capacity, more pollutant can be adsorbed to the material, therefore increase the adsorption efficiency of the material in removing pollutants from the wastewater. But, adsorption capacity is also correlated with water holding capacity which is associated with two main factors. The surface with greater water holding capacity has the higher adsorption capacity. The first factor associating to water holding capacity is porosity. It can be characterized using microscopy and BET (Brunauer-Emmett-Teller) isotherms. The other factor is the zeta potential and the cation exchange capacity. Samples with larger polar components can adsorb more hydrated ions on the surface; therefore, it has better water retention efficiencies. Thus, affecting the water holding capacity (47).

Possibility of ion exchanges as adsorption mechanism

Besides the two factors mentioned, ion exchange may be the main mechanism for adsorption. The removal of heavy metal ions depends on the active sites of the compound. Phenolic compounds found in adsorbents are the active sites, which are efficient in capturing heavy metal ions (48). Based on the structure of these phenolic compounds, a possible mechanism of ion exchange could be considered as a divalent heavy metal ion (M2+) attaching itself to two adjacent hydroxyl groups and two oxyl groups which could donate two pairs of electrons to metal ions, forming four coordination number compounds and releasing two hydrogen ions into the solution (47,49). The increase in carboxylic acid function concentration also can lead to higher adsorption capacity. SD has higher carboxylic acid function concentration than SB, therefore, showed greater Zn2+ adsorption capacity (49).

Mn experiences desorption as the concentration after adsorption process is greater than before the process. An adsorption process with distilled water was carried out to determine the possible concentration of Mn released from the adsorbents. The concentration of heavy metal Mn in SB, SD and CP was significantly lower compared to the carwash wastewater. There are some possibilities causing desorption to happen including the pH that is unsuitable for the adsorption process to occur accordingly. The pH can determine the surface charge of the adsorbent while the functional groups on the adsorbent surface may react differently at different pH (50). Moreover, the agitation time might be the reason heavy metal Mn being released back to the solution

This study was purposely designed to describe adsorption capacity and efficiency of selected biosorbents on heavy metals. The limitation of this study is that it only focused on the calculation of adsorption capacity and efficiency of SB, SD and CP to adsorb heavy metal Fe, Zn, Cu, Mn without considering isotherms, thermodynamic and kinetic studies. Suggestions and recommendations to improve this study are by running additional analysis such as FTIR and TGA analysis, isotherms of adsorption and desorption of nitrogen are recommended to obtain more information regarding surface area, total pore volume, and pore size distribution. Further assessment such as gas adsorption, mercury intrusion, and capillary flow porometry should be considered in identification the pore size. The structural characteristics and development of the pores can be analysed using digital image processing and box-counting dimension method for the purpose of calculating the porosity and the fractal dimension. Other than that, more analysis on chemical characteristics are recommended to show the relationship between selected heavy metal form with the biosorbent chemical compositions.

CONCLUSION

The biosorbents are by-product waste from natural raw materials, which make them the preferable choice as the organic component because of their low cost, abundance, renewable, biocompatible and biodegradable nature. This could overcome some problems regarding the released of carwash effluent to the environment. Vehicle washing has appeared to released high amount of wastewater together with heavy metals content derived from dust, dirt, and mud that comes with the rain or on the road that sticks on the surface of the car and also from the car paint. The release of high amounts of heavy metals into water bodies creates serious health and environmental problems and may lead to an upsurge in wastewater treatment costs. These pollutants will flow to the drainage system and straight to the sea, which can cause toxicity to the aquatic lives and partially accumulate at the base of aquatic food chains, ultimately reaching human beings as the contaminants move up the food chain.

Sugarcane bagasse, coconut pulp and sawdust were proven with several studies on their competencies to become great adsorbents. This study indicated the possibility of using SB, SD and CP as biosobent for selected heavy metals in the wastewater originating from carwashing activity.

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