A Potential Waste to be Selected as Media for Metal and Nutrient Removal

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A Potential Waste to be Selected as Media for Metal and Nutrient Removal

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Abstract: This study describes the potential of application of cassava peel, banana peel, coconut shell, and coconut coir to be selected as metal removal while limestone and steel slag for nutrient removal. The media were characterized by X-Ray Fluorescence (XRF), Fourier Transform Infrared (FTIR), Field Emission Scanning Electron Microscopy-Energy Dispersive X-Ray (FESEM-EDX), and X-Ray Powder Diffraction (XRD). The results of XRF analysis medias show the present of calcium oxide, CaO which confirm the high efficiency in adsorbing metal ions and nutrient which is in agreement with the result of XRD. The characteristics of medias by FTIR analysis also confirmed the involvement of alcohol, carboxylic, alkanes, amines and ethers which play important role to reduce ions while FESEM-EDX indicates the porous structures of study medias. The characterization analysis highlight that cassava peel and steel slag were selected as a potential media in this study.

Keywords: Heavy metal, nutrient, cassava peel, steel slag.

1. Introduction

The discharged of large amount of wastewater with heavy metals and nutrients in water body leads to environmental problem. Nutrient compounds are becoming increasingly significant in water and wastewater management because the nutrients discharge of nitrogen and phosphorus into river and lakes can cause adverse influences on our environment and life. An excessive increase in the quantities of these nutrients in the aquatic surroundings disturbs the ecological balance, resulting in severe damage to environment including of eutrophication. For heavy metals once they enter the food chain, high concentration of heavy metals may accumulate in the human body through biomagnification process. Excess nutrients lead to alga bloom at the water body and finally deplete oxygen transfer and light penetration from atmosphere, owing to drying of aquatic life [1][2].

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Due to the problems and situation arise of heavy metals and nutrients in water body, interest toward potential of natural and industrial wastes has gain attention among the researchers in order to sequester these pollutants. Current literature indicates different types of pollutants were treated with different types of media.
Natural waste most often used to treat heavy metal while industrial waste were focused on removal of nutrients and only few studies on removal of heavy metals [3][4][5].

Natural wastes such as agriculture wastes are cheap, unlimited, easily disposed by incineration, and even reusable after being rejuvenated shell [6]. Agricultural wastes such as cassava peel, banana peel, coconut coir, coconut shell have metal-binding capacities and are able to remove unwanted heavy metals from contaminated water at low cost [7][8][9][10].

Previous research also shows that steel slag and limestone show a high affinity for nutrient binding. Steel slag and limestone which mostly co-product of industrial waste was an interesting potential market for its use as filter substrate to treat wastewater [11][12][13].

Among the media mention previously, conditions for potential wastes will be selected based on largely available, cheap, rich in functional groups which potentially able to bind heavy metals, the presence of rich basic cations (Calcium and Magnesium) to facilitate nutrient removal, and its unique properties such as large surface area, highly porous and adsorptive [14][15][16].

In order to meet these criteria, this paper were focused on characterization of media through XRF, FTIR, FESEM-EDX, XRD and TG analysis. In this study, agricultural wastes namely cassava peel, banana peel, coconut coir, and coconut shell were compared to be selected as heavy metals removal while industrial wastes such as limestone and steel slag for nutrient removal. Once selected, the most potential agricultural waste were converted to activated carbon to improved their life cycle. Limited research has been reported on using combination media to treat heavy metals and nutrient. Therefore, this research will explore the potential used of media through characteristic studies.

2. Materials and Methods

2.1 Preparation of media
Cassava peel, banana peel, coconut coir and coconut shell were collected at Kilang Kerepek Ahmad Shah, Parit Raja Darat, Johor. Raw fruit peels were soaked together with distilled water for further clean up for a minimum of 24 hours and dried in an oven overnight at 60 °C [17].

Meanwhile, Electric Arc Furnace Slag (EAFS) were collected at Antara Steel Mills, Pasir Gudang, Johor, while limestone (LS) were collected from Perwaja Steel Sdn. Bhd., located in Telok Kelong Industrial Area, Kemaman, Terengganu. EAFS and LS were washed with tap water two times and then followed by distilled water once. This process was done in order to remove any dirt or particulate that adheres to the media before being used for batch study. The washed media were oven dried at 105 °C for 24 hours and sieved to obtain 10 – 20 mm of particle size [18].

2.2 X-Ray Fluorescence (XRF)
XRF is particularly used in the analysis of chemical compounds of specimen. XRF analysis were conducted in Analytical Environmental Laboratory, Faculty of Civil and Environmental Engineering, UTHM [19]. Agricultural wastes and industrial waste were prepared as pressed powder pellet XRF, meanwhile coconut coir was performed by loose technique.

2.3 Fourier Transform Infrared (FTIR)
FTIR were used to determine functional groups of medias. FTIR analysis were conducted in Statics and Dynamics Laboratory, Faculty of Mechanical and Manufacturing Engineering, UTHM [20].

2.4 Field Emission Scanning Electron Microscopy (FE-SEM) coupled with Energy Dispersive X-ray spectroscopy (EDX spectra)
FE-SEM coupled with EDX analysis were used to identify the size, particle shape, and surface microstructures. Analysis were performed at Microelectronics and Nanotechnology-Shamsuddin Research Centre (MINT-SRC), UTHM. The FE-SEM images are recorded using JEOL JSM-7600F Field Emission Scanning Electron Microscope (USA).
2.5 X-ray diffraction (XRD)

XRD were used to characterize the precipitates (covering the surface of media). The samples were analyzed by Cu K radiation with a scanning rate of 0.05° per second 40 K/20A, at 10°≥2≤90° at Material Science Laboratory, Faculty of Mechanical and Manufacturing Engineering, UTHM.

3. Result And Discussion

3.1 XRF

The results from Table 1 and 2 show XRF analysis of agricultural wastes. Based on the results, calcium oxide, (CaO) of cassava peel demonstrates as the highest chemical compound compared to other agricultural wastes. Meanwhile, Table 3 also shows the presence of CaO which is highest in limestone compared to EAFS. However, the presence of iron oxide, silicon oxide, aluminium oxide and magnesium oxide is also important factors to be considered in nutrient removal as it also proved to provide adsorption sites for anions like As, Cr, and P [21].

XRF analysis of industrial wastes show that most of the important chemical compounds were highest in EAFS compared to limestone. Therefore, result of XRF analysis for both media indicates that cassava peel and EAFS has high potential in heavy metals nutrients removal, respectively.

3.2 XRD

The XRD pattern of agricultural wastes (see Figure 1) obtained reveal that, the major diffraction peaks are around 27° to 33° and Table 4 demonstrates most of agricultural wastes contain calcium compounds in their media. Meanwhile, Figure 2 show XRD pattern of industrial wastes of limestone and EAFS. From Figure 2, most of major diffraction peaks of limestone and EAFS are around 28° to 31° and 21° to 57°, respectively. Table 5 indicates most of calcium compounds were also found in EAFS and limestone. Similar trends were also observed from previous studies [22]. This result of XRD is in agreement with the result of XRD obtained. Therefore, the present work suggests the possibility of using cassava peel and EAFS since most of the significant compound were found at major diffraction peaks.

3.3 FTIR

FTIR groups of agricultural wastes of cassava peel, banana peel, coconut shell, and coconut coir is shown in Table 6. The adsorption band at 3330.4 cm⁻¹, 3305.3 cm⁻¹, 3343.9 cm⁻¹, and 3336.2 cm⁻¹ of cassava peel banana peel, coconut shell, and coconut coir is attributable to the alcohol group, respectively. Similar functional group were also observed from previous studies of this medias [7][8][10].

| Table 1. XRF analysis of agricultural wastes. | Table 2. XRF analysis of coconut coir (loose technique). |
|--------------------------------------------|--------------------------------------------------|
| **Formula** | **Media** | **Cassava peel (%)** | **Banana peel (%)** | **Coconut shell (%)** | **Concentration** |
| C | 10 | 10 | 10 | **Al** | 0.011 |
| CaO | 4.6 | 2.45 | 0.16 | **Ca** | 0.155 |
| K2O | 3.43 | 13.70 | 1.03 | **CH2** | 98.6 |
| SiO2 | 1.73 | 0.94 | - | **Cl** | 0.207 |
| P2O5 | 0.36 | 0.62 | - | **Cr** | 0.0151 |
| Al2O3 | 1.11 | - | - | **Cu** | 0.0012 |
| Fe2O3 | 0.90 | - | 0.76 | **Fe** | 0.07006 |
| SO3 | 0.55 | 1.05 | - | **K** | 0.5478 |
| Cl | 0.50 | 4.60 | 0.28 | **Mg** | 0.0355 |
| MgO | - | 0.19 | - | **Mn** | 0.0018 |
| Br | - | 0.15 | - | **Ni** | 0.0044 |
| MoO3 | - | - | 0.20 | **P** | 0.0779 |
| | | | | **S** | 0.00463 |
| | | | | **Si** | 0.186 |
| | | | | **Zn** | 0.0011 |
Table 3. XRF analysis of industrial waste.

| Formula | EAFS (%) | Limestone (%) |
|---------|----------|---------------|
| Fe₂O₃   | 29.20    | 0.48          |
| CaO     | 21.80    | 70.10         |
| SiO₂    | 16.90    | 1.43          |
| Al₂O₃   | 7.10     | 0.46          |
| MnO     | 5.59     | -             |
| MgO     | 3.70     | 0.29          |
| Cr₂O₃   | 1.46     | -             |
| C       | 1.00     | -             |
| TiO₂    | 0.72     | -             |
| BaO     | 0.25     | -             |
| P₂O₅    | 0.34     | -             |
| Na₂O    | 0.21     | -             |
| K₂O₅    | -        | 0.15          |
| Zn      | 0<LLD    | -             |
| S       | 0<LLD    | -             |
| Mn      | -        | 0<LLD         |

Figure 1. XRD pattern of agricultural wastes.

Figure 2. XRD pattern of industrial wastes.
| Media          | Peak | Compound                                      | Media          | Peak | Compound                                      |
|---------------|------|----------------------------------------------|----------------|------|----------------------------------------------|
| a) Cassava peel | 26   | Carbon                                       | b) Banana peel | 21   | Adipic acid                                  |
|               | 17   | L-Lactide-poly(ethylene glycol)              |                | 18   | Magnesium adipate tetrahydrate               |
|               | 15   | Iron Chloride Hydrate                        |                | 32   | Calcium Silicon                              |
|               | 17   | 4-Chlorophenyl sulfone                       |                |      |                                              |
|               | 27   | Diclone                                      |                |      |                                              |
|               | 17/23| Starch (maize)                               |                |      |                                              |
|               | 27   | Silicon Oxide                                |                |      |                                              |
|               | 17   | Diosgenin                                    |                |      |                                              |
| c) Coconut shell | 23   | Decamethylene glycol                         | d) Coconut coir | 27   | Carbon                                       |
|               | 22/34| Sulfur Oxide Graphite                        |                | 27   | Potassium Magnesium Silicate                 |
|               | 30   | Mucochloric acid                             |                | 27   | Silicon Oxide                                |
|               | 19/23| n-Docosane                                   |                | 27   | Magnesium Chromium Oxide                     |
|               | 30   | Ascorbic acid                                |                | 26   | Potassium Chromium Oxide                     |
|               | 27   | Carbon                                       |                | 27   | Calcium Hydrogen Phosphate                   |
|               | 32   | Calcium Hydride                              |                | 27   | Magnesium Phosphate                          |
|               | 33   | Calcium Carbide                              |                | 27   | Potassium ethyl malonate                     |
|               | 27   | Potassium Iron Sulfate                       |                |      |                                              |
|               | 16   | p-Hydroxybenzaldehyde                        |                |      |                                              |
|               | 28   | Potassium Calcium Sulfate                    |                |      |                                              |
|               | 21   | Adipic acid                                  |                |      |                                              |
|               | 29   | Calcium Chlorate                             |                |      |                                              |
|               | 36   | Potassium Hydrogen Tartrate                  |                |      |                                              |
|               | 28   | Calcium Sulfite Hydrate                      |                |      |                                              |

The characteristic band region at $2919.7 \text{ cm}^{-1}$ were found similar for agricultural wastes which suggests the presence of alkanes groups. Alcohol and alkane groups are the potential sites for biosorption and the uptake of metal depends on various factors such as abundance of sites, their accessibility, chemical state and affinity between the adsorption site and metal. This finding is comparable with the previous study whereas FTIR analysis confirmed the involvement of these groups [7][8][10]. The involvement of these groups in the media might involved in adsorption of metal ions.
Table 5. Identified patterns list of industrial wastes.

| Media | Peak | Compound | Diffraction |
|-------|------|----------|-------------|
| a) LS | 29 | Calcium Carbonate | 104 |
| | 28 | Calcium Aluminum Silicate | 004 |
| | 31 | Calcium Aluminum Silicate | 211 |
| | 28 | Potassium Aluminum Oxalate Hydrate | 231 |
| | 11 | Silicon Oxide | 100 |
| | 27 | Silicon Oxide | 101 |
| | 27 | Calcium Oxide | |
| | 28 | Silicon | 111 |
| | 28 | Calcium Aluminum Silicate | 004 |
| b) EAFS | 21/30 | Potassium Carbide | 111/113 |
| | 34/50/57 | Calcium Iron Silicate | 211/222/260 |
| | 24 | Nickel benzenesulfonate hexahydrate | 660 |
| | 28 | Iron di(hydroxybenzenesulfonate) octahydrate | -216 |
| | 31 | Calcium Aluminum Silicate | 211 |
| | 28 | Calcium | 111 |
| | 28 | Calcium Aluminum Silicate | 004 |
| | 34/50 | Calcium Iron Silicate | 211/222 |

3.4 SEM

The SEM is one of the useful techniques applied in the examination of the surface morphology of biosorbents. The surface morphology of the agricultural and industrial wastes was studied with the use of FESEM (Figures 3 to 8). The pictures indicate that the media has a rough, irregular and porous surface thus providing large area for metal–surface interaction and biosorption. Meanwhile, a microporous structure was observed for EAFS and limestone.

Tables 7 and 8 shows EDX results of agricultural and industrial wastes and most of the element were also found in XRF and XRD results. Si was found to be highest in cassava peel among others agricultural wastes while Fe were found to be highest in EAFS compare to limestone. These elements were considered as important factor in heavy metals and nutrient removal [15].

Table 6. FTIR groups of agricultural waste.

| Sample | Wave number (cm⁻¹) | Classification | Bond | Mode |
|--------|-------------------|----------------|------|------|
| Cassava peel | 3330.4 | alcohols | OH | stretching |
| | | amines | NH | stretching |
| | 2919.7 | alkanes | CH | symmetric stretching |
| Banana peel | 3305.3 | alcohols | OH | stretching |
| | | amines | NH | stretching |
| | 2919.7 | alkanes | CH | symmetric stretching |
| Coconut shell | 3343.9 | alcohols | OH | stretching |
| | | amides | NH | antisymmetric stretching |
| | 2919.7 | alkanes | CH | symmetric stretching |
| Coconut coir | 3336.2 | alcohols | OH | stretching |
| | | amines | NH | stretching |
| | 2919.7 | alkanes | CH | symmetric stretching |
Figure 3. Cassava peel.  
Figure 4. Banana peel.  
Figure 5. Coconut shell.  
Figure 6. Coconut coir.  
Figure 7. Limestone.  
Figure 8. EAFS.

| Table 7. EDX results of agricultural waste | Table 8. EDX results of industrial wastes |
|-------------------------------------------|------------------------------------------|
| **Element** | **Weight (%)** | | **Element** | **Weight (%)** | **Limestone** | **EAFS** |
| | Cassava peel | Banana peel | Coconut shell | Coconut coir | | |
| C | 52.37 | 52.84 | 59.52 | 58.99 | C | 13.58 | 12.18 |
| O | 42.26 | 47.01 | 40.00 | 39.67 | O | 53.75 | 44.78 |
| Al | 1.85 | - | - | - | Al | 3.12 | 1.35 |
| Si | 2.98 | 0.15 | 0.05 | 0.21 | Si | 2.68 | 1.81 |
| Ca | 0.10 | - | 0.10 | 0.36 | Ca | 25.52 | 17.66 |
| Fe | 0.44 | - | 0.19 | 0.19 | Fe | 0.89 | 18.20 |
| Cl | - | - | 0.02 | 0.12 | Na | - | 0.94 |
| K | - | - | 0.12 | 0.32 | | |
| Mg | - | - | - | 0.14 | | |
| **Totals** | 100.00 | 100.00 | 100.00 | 100.00 | **Totals** | 100.00 | 100.00 |

4. Conclusion
Characterization study XRF, XRD, FTIR, and FESEM-EDX indicates that cassava peel and EAFS as potential wastes to be selected for heavy metals and nutrient removal. The presence of Si, Ca, Mg, Fe, rich in functional groups and surface porosity of media were significant factors which attribute to facilitate heavy metals and nutrient removal. In future work, to increase the performances of cassava peels several modifications will be apply in term of the preparation. Cassava peel and EAFS can effectively be used to remove heavy metals and nutrient in polluted water.

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