The Preparation and Characterization of Banana Peels, Eggshells, and Seashells for The Treatment of Wastewater

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***Abstract*—** In South Africa, lack of access to clean and safe water is one of the main causes of poverty because it makes agriculture, livestock raising cattle, forestry, fisheries, hydropower, and other innovative activities unstainable. This requires sustainable solution to address the present water crisis via the coagulation pretreatment process. Herein, using natural coagulants comes in handy to replace chemical coagulants, due to their potential of non-toxicity, biodegradability, readily available, and eco-friendly. Therefore, this study investigated the preparation and characterization of natural coagulants using bio-waste materials. This included banana peel (BP), eggshells (ES), and seashells (SS) and their calcinated counterparts. Brunauer-Emmett-Teller (BET), Fourier Transform Infrared (FTIR), and energy dispersive X-ray (EDX) were used to investigate the properties of the natural coagulants. The calcined coagulants are suited for water treatment and based on characterization, calcined banana peels were superior to the others. The optimum conditions for the calcination temperature of BP were 400℃ for a retention time of 2 hours and a temperature of 800℃ at a retention time of 3 hours for SS and ES. The findings demonstrate that the calcined banana peel had a larger surface area and pore size of 4.3889 m^2/g and 3.167 Å, respectively. Additionally, it had a potassium content of 34.1 wt.%, and the FTIR results suggest that the functional group OH may have been present. These factors make this bio-coagulant superior to other bio-coagulants, and hence, it would be beneficial for wastewater treatment.

***Keywords*—** Bio-coagulants, wastewater, eggshell, seashell, banana peel.

I. INTRODUCTION

The discharge of untreated and/or partially treated industrial wastewater into water-receiving bodies has presented major economic and environmental concerns for both developed and developing countries [1]. Industrial effluent is characterized by having a high content of organic and inorganic pollutants, some of them are bio-accumulative posing severe health problems to both aquatic life and humans. Hence, national and international environmental entities have imposed stringent discharging limits of wastewater to the water bodies and environment [2]. Therefore, the rigorous discharging limits have prompted the search for innovative and green technologies for wastewater treatment. Herein, exploring the use of bio-coagulants from natural resources such as agricultural waste [3, 4] comes in handy.

Conventionally, wastewater treatment technologies such as biological processes [5], physical processes [6], chemical processes [7], and advanced oxidation processes [5, 8] are reportedly used in the water sector. However, the applicability of these technologies depends on the source and nature of the wastewater [9]. Generally, pre-treatment of wastewater involves the use of chemical coagulation with aluminium and iron-based salts. During the coagulation process, a chemical reaction neutralizes the charged colloidal particles and reduces the repulsion forces between the particles to form flocs, which agglomerates to form larger flocs [10]. Despite the treatability efficiency associated with chemical coagulants, their drawbacks make their usage not friendly. This includes the production of large amounts of unwanted sludge [11], relatively high operation costs, reduction in treated water pH and adverse effects on human health [12], due to their toxicity effects [13]. The aforementioned drawbacks have made the use of natural coagulants, such as plant-based substances and bio-waste materials such as Moringa oleiferous seeds [14, 15], papaya seeds [16], banana peels [17], eggshells [4], and chitosan [18] gain research interest. Some of these natural coagulants have been reported to have high removal performance of turbidity and colour in wastewater treatment [19]. Natural coagulants derived from agricultural wastes such as banana peels, are defined to have essential compounds such as cellulose, lignin, pectin, pigments, hemicellulose, and other chemical substances containing large amounts of hydroxyl, carboxyl, and other functional groups [20, 21]. Another natural coagulant is eggshells are characterized as rigid material, containing proteins, amino acids, calcium carbonate, organic matter, magnesium carbonate, calcium phosphates and carbohydrates [22]. The composition of eggshells makes them viable to be used as alternative wastewater treatment materials. Seashells are one of the most

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prevalent sea trash products in the globe [23]. It is a complex substance mainly composed of calcium carbonate, which can take one of the two primary crystalline forms, calcite or aragonite [24, 25]. Calcium carbonate is a promising and effective adsorbent in wastewater treatment [26]. The inner smooth layer of seashells is composed of calcium carbonate crystals [26]. Active functional groups in natural coagulants can enhance contaminants removal via hydrogen bonding and other complexes , as well as chelating [27].

Therefore, the current study focused on surface modification via calcination and characterization of banana peels, eggshells, and seashells to investigate their potential application as bio-coagulants in wastewater treatment processes. Characterization was conducted using energy dispersive X-ray (EDX), Brunauer-Emmett-Teller (BET), and Fourier-transform infrared (FTIR).

II. METHODS AND METHODS

A. Calcination

Calcination is a process used to produce an adsorbent that is more porous, and rougher and leaves voids behind that eventually become pores. This is a result of volatiles inside the particles' microstructure escaping due to high temperature. Calcination Also, it was discovered that, although chemical modification reduces the adsorbent's overall surface area, it increases the adsorption capacity due to changes in functional groups [28].

B. Sample Preparation

2.2.1. Banana peels

Fresh waste banana peels were collected from a local Fruits and Vegetables Market in Durban, South Africa. Banana peels were thoroughly washed using deionized water (ELGA PURELAB Option-Q water deionizer, UK) to remove the dirt and associated impurities. The washed peels were placed on trays and oven-dried at a temperature of 105ºC for 24 hrs. to remove any moisture content. Thereafter, dried banana peels were cut into small pieces and ground to powder using a blender and using laboratory sieve trays, was sieved to uniform particles of 300 – 425 µm. The ground powder was calcinated at 400ºC for 2 hours. The calcinated banana peel was stored in an airtight container before being characterized.

2.2.2. Seashells

Seashells were collected from a local public beach as beach sand leachate in Durban, South Africa. The seashells were thoroughly washed using tap water to remove dirt material, followed by rinsing using deionized water. The seashells were then oven-dried at 105ºC for 24 hours. The dried seashells were first crushed into small pieces and ground using a blender to a fine powder and sieved to uniform size particles ranging from 300 – 425 µm using laboratory sieve trays. Ground seashells were calcinated at 800ºC for 3 hours, thereafter, the calcinated seashells were stored in an airtight container.

2.2.3. Eggshells

Eggshells were collected from a local bakery as waste in Durban, South Africa. The eggshells were thoroughly washed using tap water to remove all adhering dirt followed by rinsing using deionized water. The eggshells were oven-dried at 105ºC for 24 hours. The dried eggshells were first crushed, ground using a blender to fine powder, and sieved to uniform particle sizes ranging from 300 – 425 µm, then calcinated at 800ºC for 3 hrs. and stored in an airtight container.

III. RESULTS AND DISCUSSION

This section presents the results obtained from the characterized raw and calcinated bio-coagulants. The elemental compositions of the coagulants were defined using the energy-dispersing X-ray (EDX) analysis. The EDX characterization results are depicted in **Table 1** for all model bio-coagulants.

TABLE 1: EDX RESULTS OF BANANA PEEL, EGGSHELL, SEASHELL, CALCINED BANANA PEEL, CALCINED EGGSHELL AND CALCINED SEASHELL.

Elementals (%wt.)	Banana peel	Eggshell	Seashell	Calcined Banana peel	Calcined eggshell	Calcined seashell
Carbon	63.3	38.1	57.4	35.7	23.9	23.9
Oxygen	33.9	35.7	30.3	18.7	38.7	33.9
Potassium	1.6	-	-	34.1	0.2	0.4
Calcium	0.8	25.2	11.1	1.3	36.2	40.9
Chlorine	0.7	-	0.1	6.9	0.1	0.2
Magnesium	0.3	0.3	0.3	0.5	0.3	-
Silicon	0.2	-	0.4	1.3	0.1	0.1
Sodium	0.1	0.1	0.2	0.5	-	0.4
Sulphur	0.1	0.6	0.1	0.4	0.2	0.1
Phosphorus	-	0.1	-	0.5	-	-
Aluminum	-	-	0.1	-	-	-
Total (%)	100	100	100	100	100	100

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Table 1 presents characterization results for raw banana peels, spectrum 11 depicted the composition carbon (C) > oxygen (O) > potassium (K) > calcium (Ca). The observed elemental composition can be attributed to the presence of proteins and polysaccharides in banana peels (Kamsonlian *et al*., 2011). A significant change in elemental composition was observed for the calcinated banana peels. Such a change in the elemental composition of the calcinated banana peels is attributed to the high affinity of potassium to negatively charged areas through a weak electrostatic attraction induced through calcination [29]. The high composition of element C could be attributed to the doping of carbon gas during the analysis.

It is noted that eggshells have a relatively porous structure that allows gas exchange because they are composed of high content of inorganic materials compared to organic material [30]. In the characterization results for raw eggshells, it is apparent that surface modification of raw eggshells by calcination resulted in a significant increase in terms of elemental composition. The increase in the mass composition of Ca in calcined eggshells can be attributed to the presence of calcium carbonate which enhances the adsorption process of targeted contaminants in aqueous environments [31], however, this is not explicitly accounted for in the present study. Moreover, the efficacy of the solid-liquid adsorption process increases with increasing C and decreasing O content in the adsorbent (Ajala *et al*. 2018). A higher surface area for the adsorption of target pollutants is made possible by the ability of the shell to develop pores onto the surface of the carbon when there is C present. The results presented in eggshells and calcined eggshells suggest that comparison studies need to be conducted aimed at investigating the effect of C content and calcium carbonate in the form of Ca on the adsorption process efficacy.

The composition of raw seashells and calcinated seashells are presented, and it can be observed that raw seashells have a high mass composition of elemental carbon. However, following calcination the elemental mass compositions changed as seen, where calcium mass composition increased from and lowered the composition of carbon[32].

TABLE II: FT-IR PEAKS FOR RAW AND CALCINED BIO-COAGULANTS FUNCTIONAL GROUPS.

Absorption (cm^{-1})	**Functional group**	**Compound class**
3300-2500	O-H stretching	carboxylic acid
3000-2840	C-H stretching	Alkane
1420-1330	O-H bending	Alcohol
1070-1030	S=O stretching	Sulfoxide
1085-1050	C-O stretching	primary alcohol
900-700	C-H bending	1,2,4-trisubstituted

The FT-IR spectra of raw and calcinated bio-coagulants were obtained to ascertain the nature of the functional groups present on the surface of each model bio-coagulant and the characterization results obtained are presented in **Table 2**. Based on the results obtained, as presented in **Table 2**, bands appearing at 3300 cm^{-1}, 3000 cm^{-1}, 1420 cm^{-1}, 1085 cm-1, 1070 cm-1, and 900 cm-1 are attributed to O-H stretching (carboxylic acid), C-H stretching (alkane), O-H bending (alcohol), C-O stretching (primary alcohol), S=O stretching (sulfoxide), and C-H bending (1,2,4-trisubstituted), respectively [33]. The carboxylic acid and hydroxyl functional groups facilitated the adsorption of heavy metal ions in aqueous environments [3, 34]. The raw banana peels show strong, distinct bands which can be attributed to the alkyne group near the 3280.1 cm^{-1} peak. The banana peel's strong band can also be attributed to the stretching of the C-H group, whereas the stretching of the strong S=O group was at 1029 cm^{-1}. The bands at 3153 cm^{-1} and 1364 cm^{-1} of the calcined banana peels indicate the presence of the carboxylic acid group on the surface of the bio-coagulant. This can be attributed to the stretching vibrations on these O-H bands and the potential existence of the sulfonamide group, respectively. From. All the bio-coagulants reported for the current work exhibit bands between 1300 cm^{-1} and 1600 cm^{-1}, which suggests that all model bio-coagulants exhibit stretching on the O-H functional group and may belong to the class of alcohol compound. It should be noted that O-H functional groups act as adsorption sites for contaminant remediation in aqueous environments [35].

TABLE III: BET RESULTS OF THE BIO-COAGULANTS

Bio-coagulant	**Surface Area (m^2/g)**	**Pore Volume (m^3/g)**	**Pore Size, (Å)**
Banana peels	2.7190	0.0054	0.569
Eggshells	0.8734	0.000127	5.515
Seashells	0.7921	0.0128	2.364
Calcined banana peels	4.3889	0.00569	3.167
Calcined eggshells	2.2272	0.00116	2.193
Calcined seashells	2.0920	0.00108	3.923

The BET analysis was conducted aimed at studying how calcined banana peels, eggshells, and seashells differ in terms of surface area, pore volume, and pore size. The BET results are presented in **Table 3** for the calcined bio-coagulants. Calcined banana peels have the highest surface area and pore volume of 4.3889 m^2/g and 0.00569 m^3/g, respectively, when compared to the calcined eggshells and seashells. Despite the least surface area and pore volume demonstrated by calcined seashells, a pore size of 3.923 Å was recorded which was bigger than that of calcined banana shells and eggshells. The large pore size of the calcined seashells suggests that in an aqueous environment, the pore-filling will be the dominant mechanism in contaminants remediation in a typical adsorption process, however, the pore-filling mechanism is not explicitly accounted for in the present study [36].

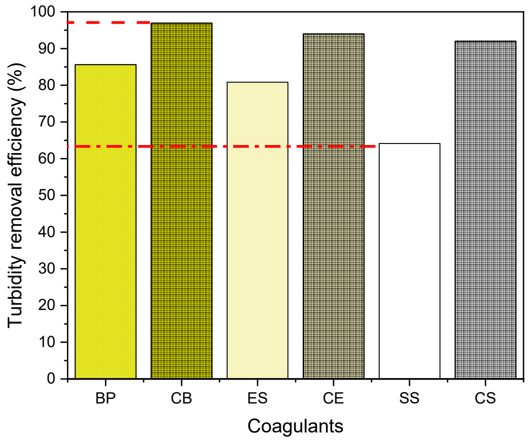

Fig. 1: Application of bio-coagulants in wastewater treatment

Figure 1 depicts the usage of several bio-coagulants in the coagulation process with the use of a jar tester to eliminate turbidity. The results obtained with a constant dosage of 3.5g/L, two distinct mixing rates (fast and slow) of 150 rpm and 30 rpm, 15 minutes for mixing, and 120 minutes for settling were as follows. The calcined banana peel had the highest percentage of removal (97.8%), whereas the seashell had the lowest percentage of removal (64.3%).

IV. CONCLUSION

This study explored the potential of eggshells, seashells, and banana peels as bio-coagulants for the treatment of wastewater. Bio-coagulants were characterized using analytical techniques such as EDX, FTIR, and BET. The results obtained affirmed that calcined banana peels were the best-performing bio-coagulant. The presence of calcium and oxygen in calcine eggshells and seashells and the presence of potassium in calcined banana peels indicates the presence of calcium oxide which is essential in the removal of contaminants in wastewater. The calcined banana peels had a higher surface area, pore volume and pore size compared to the calcined eggshell (1.2272 m^2/g, 0.000116 cm^3/g, 2.193 Å) and calcined seashell (0.7921 m^2/g, 0.000108 cm^3/g, 3.923 Å). The functional groups that were observed in the FTIR spectroscopy for all the bio-coagulants showed that these materials have the potential to act as a substitute in the treatment of wastewater.

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