Metal removal with activated carbon from banana peels

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1 Introduction

Water pollution is becoming one of the most devastating ecological problems due to intense industrial production and inaccurate domestic use. Enormously high containment of oil waste, microorganisms and heavy metal cations in the water, which exceeds maximal permissible level established by OOH, bring negative effects on both aquatic and terrestrial ecosystems. Hence, there is an urgent demand ti mitigate this problem. Recent solutions include using treatment methods such as sedimentation, coagulation, chemical precipitation [1, 2]. However, higher price and request in devices pose it in a undesirable position.

So, in recent decades, there has been increasing interest in activated carbon produced from agricultural waste as an effective adsorbent. Activated carbons are attractive materials for industrial applications due to their good chemical properties, low cost, high adsorption capacity, non-toxicity, and physical properties, as well as their high surface area and well-developed porosity, which can be doped and adapted with different active surface functionalities. These properties make them very good candidates for not only for metal removal but for several application such as adsorption of liquid [3] and gas pollutants, biomedical applications [4], as well as energy storage like supercapacitor devices. Chemical composition of lignocellulosic agriultural species make them appropriorate for usage. By utilizing local waste and achieving the high surface area that allows to restrain hazardous compounds, scientists are making powerful contributions to addressing the ecological issue.

In this study banana peels have been chosen as the potential source of activated carbon. Because the purpose of this study was to prove the competitive performance of adsorbents obtained from agricultural waste, specific synthesis parameters have been selected in order to reach the most productive outcome. Indeed, this plant-based waste's thermal decomposition temperature varies between 500-700∘C. Rise until 600∘C develops amorphous porous structure that allows to enhance the quality of ultimate product. Additionally, acidic property of activating agent H_3PO_4 within its eco-friendliness compared to other alternatives, develops acidic carbonyl functional groups that attract anions. In contrast, utilisation of KOH, the strong base, provides with effective cationic retention reached with the help of electrostatic attraction between oppositely charged ions and radicals, such as chromonium ion.

2 Literature Review

2.1 Activated Carbon from Agricultural Waste

Special attention must be given to the relationship among the selected precursor characteristics, the final microstructure, and properties of carbon to produce highly activated carbon. The selection of the precursor essentially determines the range of adsorptive and physical properties that can be attained in the activated carbon products. Important considerations to be made in selecting a source material include cost, availability, consistency of quality, and particularly for coals, peat, and lignite, the mineral matter and sulfur contents [5]. It is very effective to use agricultural products. Producing activated carbon from lignocellulosic biomass has many advantages: the precursors are diverse, abundant, and renewable; the synthesis is a relatively simple process due to the high reactivity of the biomass; and it contributes to decreasing costs of waste disposal and the negative impact on the environment [6].

The presence of high amounts of C, O, and H are related to the nature of the three major structural polymers present in most lignocellulosic precursors: cellulose, hemicellulose, and lignin, which make them a good fit as a source of activated carbon. Hemicellulose, located in secondary cell walls, is main component in natural fibers. Hemicelluloses are relatively sensitive to operation conditions; therefore, parameters such as temperature and retention time must be controlled so that ash is not formed. Tar prevention includes adjusting temperatures, activation times, and the use of appropriate activating agents [6].

Among the three fractions of lignocellulosic materials, lignin has been identified as the main component in lignocellulosic biomass responsible for the adsorption process [7]. Due to the rich carbon content of lignin, lignocellulosic biomass is a good option to be used as a precursor to produce activated carbon.

Banana peel is defined as a promising source of activated carbon . Banana peel shows competitive performance to commercially activated carbon due to its cost effectiveness and eco-friendliness. Banana cultivation and industrialization generates a considerable amount of waste that is rich in cellulose and starch, which makes this waste potential as a raw material to make activated carbon [8]. Adsorbent produced from banana peel, compared to commercial activated carbon, had slightly tenuous characteristics: surface area equal to 841 $\pm$ 20 m $_2$/g, while traditional adsorbent demonstrated 953 $\pm$ 25 m$_2$/g; the smaller pore volume equal to 0.47 $\pm$ 0.02 cm $_3$/g which is equivalent to 90,38% of commercial activated carbon pore volume [9]. Noticeably, BPAC's adsorption capacities of 3.20 $\pm$ 0.15 mg/g for Pb and 2.45 $\pm$ 0.12 mg/g for Cd, with percentage removal values of 68.9 $\pm$ 1.5 % and 61.3 $\pm$ 1.2 %, respectively. [10]

As the banana peel consists of many layers, we supposed that the outer layer contains large amount of lignin and hemicellulose, whereas the inner fibres contain an undesirable amount of ash. Therefore, in this research we further determine this theory.

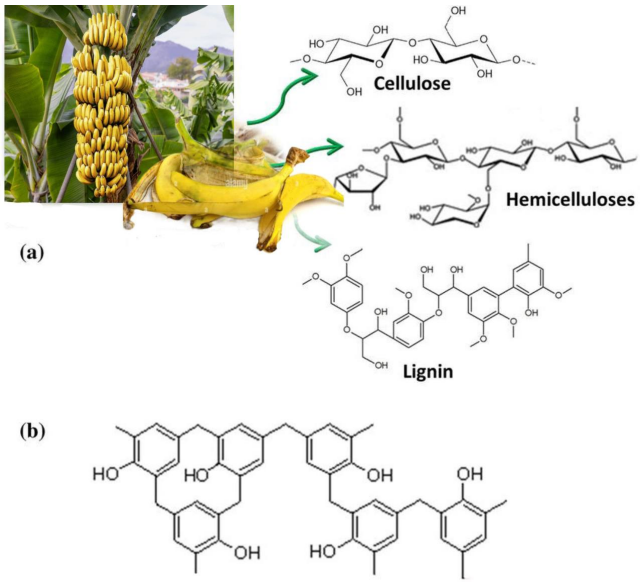


Figure 1: Banana peel's structures

2.2 Activated Carbon Production

Carbonization/Pyrolysis

Carbonization is a process, sometimes used prior to activation, where the raw lignocellulosic undergoes a thermal treatment (pyrolysis) to enrich the carbon content in the precursor. Here, moisture and low molecular weight volatiles are first released, followed by light aromatics, and finally, hydrogen gas [11]. The resultant product obtained is a fixed carbonaceous skeleton. In this process, initial porosity is formed even though it is still comparatively low. The pores formed during carbonization are filled with tarry pyrolysis residues and require activation in order to develop the specific characteristics of the carbon.

Careful selection of carbonization parameters is important because this process leaves a significant effect on the final product. In this process, the carbonization temperature has the most significant effect, followed by the heating rate, the presence of an inert atmosphere and its rate, and finally, the residence time. Normally, carbonization temperatures higher than 600 °C result in a reduced yield of char while increasing the liquid and gas phases.

Physical Activation

Physical activation is a dual-stage process that features the carbonization stage in the presence of an inert gas (N_2 or Ar) followed by the activation stage with the aid of an oxidizing gas (O_2, CO_2, H_2O steam) in the temperature range of 800–1200 °C [12]. The most important benefits of physical activation are its clean, green production without any secondary waste disposal compared to chemical activation. These are related to its high activation temperature,

considerably long processing time, relatively low carbon yield, and poor specific surface area [13]. Low yields of physically activated carbon are attributed to carbon loss during both the pyrolysis and activation stages. Depending on the raw material and operating conditions, only 43%–63% of carbon in biomass is converted to char during pyrolysis [13].

Steam pyrolysis is one of the examples of physical activation. Steam pyrolysis at 600 °C generates porosity in the mesopore range. This single-step steam pyrolysis appears to be promising in producing activated carbon, although with low-adsorbing capacity under the tried condition [14].

Chemical Activation

Chemical activation agents are dehydrating agents that influence pyrolytic decomposition and, by inhibiting the formation of bitumen, increase the activated carbon content and, with subsequent changes in the thermal degradation of precursors, result in the development of the porous structure of carbon materials. [15]. Major advantages of chemical activation are the higher yield, lower temperature of activation (less energy costs), less activation time and, generally, higher development of porosity [16]. However, corrosion is the drawback of chemical activation.

Chemical Activation vs Physical Act

Because of differences in the activation process, the chemically and physically activated products are considered to have different surface states, which are expected to greatly influence their adsorption properties. Chemically activated products showed more hydrophilic behavior than the physically activated product. This is attributed to the higher concentration of surface functional groups in this sample [17].

3 Influence of Different Conditions on the Synthesis

Elaborating and finding the optimal conditions for the activated carbon production process plays a crucial role in enhancing its adsorption characteristics. This research paper section objectively compares specific effects to suggest the most attractive conditions to show positive outcomes.

3.1 Temperature

In general, with an increase in activation temperature, the yield of the ultimate product decreases [18]. This inverse proportional relationship can be explained by the decomposition of lignocellulosic and hemicellulosic compounds at high temperatures, which leads to the release of volatile CO_2 and H_2O [19].However, temperature plays a significant role in forming surface area and porous structure. Increasing the activation temperature results in increased surface area of the AC up to a certain point, after which the surface area decreases as the temperature increases. Generally, the occurrence of the main two weight-loss steps has been reported in literature on the pyrolysis of different lignocellulosic materials [20,

21]. So, thermal analysis must be conducted for a better understanding about activation process and identifying optimal temperature. For banana peel, the first stage occurs at a temperature below 100 °C. This event is due to the evaporation of water molecules adsorbed on the surface and within the pores. The second stage occurs at a temperature ranging from 200 to 450 °C and corresponds to the liberation of volatile components like hemicellulose, cellulose, and lignin [22].

3.2 Chemical Activation Reagent KOH

KOH can suppress the generation of tar, lower the temperature of the activating reaction, accelerate the removal of non-carbon constituents, and enhance the reaction rate of pyrolysis [23]. It induces a positive charge and has the most beneficial effect on creating a large surface area and microporous structure [24]. Also, KOH produces functional groups, such as pyrones or keto-derivatives, and also induces a positive charge.

3.2.1 Mechanism

The development of pores is associated with a gasification reaction, which occurs according to the following chemical reactions:

$$2KOH \rightarrow K_2O + H_2O \tag{1}$$

$$K_2O + CO_2 \rightarrow K_2CO_3 \tag{2}$$

$$4KOH + C \rightarrow K_2CO_3 + K_2O + 2H_2 \tag{3}$$

$$K_2O + C \rightarrow 2K + CO \tag{4}$$

$$K_2CO_3 + C \rightarrow 2K + 3CO \tag{5}$$

The vapor of metallic potassium formed from the reduction reaction of K_2CO_3 or K_2O by carbon atoms above 762°C is responsible for the continued increase in total pore volume [25]. The metallic potassium can penetrate the internal structure of the carbon lattice, expanding the space of the aromatic layer, distorting the carbon layer, and creating new pores. Additionally, metallic potassium may change the electron cloud distribution of carbon atoms around the aromatic layer, producing more active reaction sites. The role of metallic potassium vapor is unique and key for the development of pores [25].

3.2.2 Amount

Moreover, the pore diameter and volume are affected by the carbon preparation method and the ratio of KOH used. An excess amount of KOH decreases the surface area. Impregnation ratio of 1:1 has shown to be the most effective.

3.3 Chemical Activation Reagent $ZnCl_2$

The $ZnCl_2$ activating agent is used in the production of hierarchical mesoporous materials and acts as a dehydrator, increasing the carbon yield. In fact, the

mesoporous structure enhances adsorbate diffusion to active sites, increasing adsorption capacity.

3.3.1 Mechanism

If the degradation of lignin and cellulose are catalysed by protons, zinc chloride—which at high concentrations gives Brønsted acidity to the solution and dissolves the cellulose—must act degydrator during impregnation. It also supports aromatic reactions at high temperature. The changes observed: swelling of the particle, lower mechanical resistance and presence of tars on the surface [26]. Since zinc chloride does not react with carbon, the obtained activated carbon has a higher yield than that produced with potassium hydroxide.

3.3.2 Amount

Increasing the mass ratio of zinc chloride causes easier release of volatile substances, increasing nitrogen absorption on the activated carbon. However, increasing the amount of zinc chloride may cause more cracks in the structure of activated carbon, resulting in a decline in productivity and an increase in mesoporosity. Therefore, 1:1 impregnation ratio is found to be effective.

3.4 Chemical Activation Reagent H_3PO_4

Activated carbon produced with H_3PO_4 is tunnel-shaped and generally has a honeycomb structure. The use of H3PO4 is highly efficient in the production of activated carbons with high specific surface area and a good development of porosity [15, 27, 28]. Phosphorus groups are among the most important substances for the adsorption of heavy metals from acidic solutions. Therefore, H_3PO_4-activated carbon is the promising method for metal removal.

3.4.1 Mechanism

It has been shown that activated carbon prepared with phosphoric acid has fewer C=O groups than the raw material, instead it contains large amount of aromatic compounds with C=C bonds [29]. The reduction of carbonyl groups may be due to the effect of H_3PO_4 hydrolysis, which deteriorates these groups. [30].

3.4.2 Amount

Carbon impregnated with low impregnation ratio is almost identical to that of the char, but increasing concentrations of the acid show a surface more clearly attacked. At high concentrations the original cellular morphology of the precursor is lost because a large part of the cellulosic structure has been degraded and extracted from the interior to the exterior of the particle [26]. Optimal concentration is considered to be 1:1 [26, 31].

4 Optimizing production of activated carbon from banana peel

If chemical activation is essentially considered as a reaction between the solid precursor and the chemical it is clear that concentration, temperature and activation time determine the extent of reaction. However, such reaction cannot proceed to completion because it would mean the destruction of the precursor. Consequently, it is important to select a range of experimental conditions in which reaction does not finish. [32].

Several scientific approaches have suggested that one-stage production is much more efficient in terms of expanding surface area compared to two-stage production [33, 34]. Since the former type of the production involves only one heat treatment measurement, the process not only decreases cost of the final adsorbent, but also the environmental impact by significantly minimizing carbon footprint.

Neglecting by the importance of the pre-treatment measurement can diminish porosity of the activated carbon, leading to tenacious surface area. With the aim to to remove any soluble constituents and compounds that are not bound to the carbon matrix it is highly recommended to leave the carbon precursor in acidic and alkaline aqueous solution (at room temperature) until upcoming carbonization [35]. Therefore, we used liguid impregnation method, and left the mixture for 12 h for stirring/soaking.

Indeed, plant-based waste which were initially granulated into smaller particles showed a higher surface area ($1089.2\,m^2g^{-1}$) compared to whole shells ($789.2\,m^2g^{-1}$) [36]. Pelleted and powdered waste did not demonstrate significant differences; hence, with the aim to reach minimal material loss and energy efficiency, grinding has been chosen as the standard procedure.

Additionally, selecting the optimized gas flow for the carbonization step is equally critical as the previously mentioned size related parameter. It has been clearly stated that providing similar experiments under nitrogen gas or in the absence of any gas flow marginally increased the surface area of the ultimate adsorbent derived from peach waste [37]. Therefore, we decided to use the absence of any gas by the cost and energy efficiency privileges.

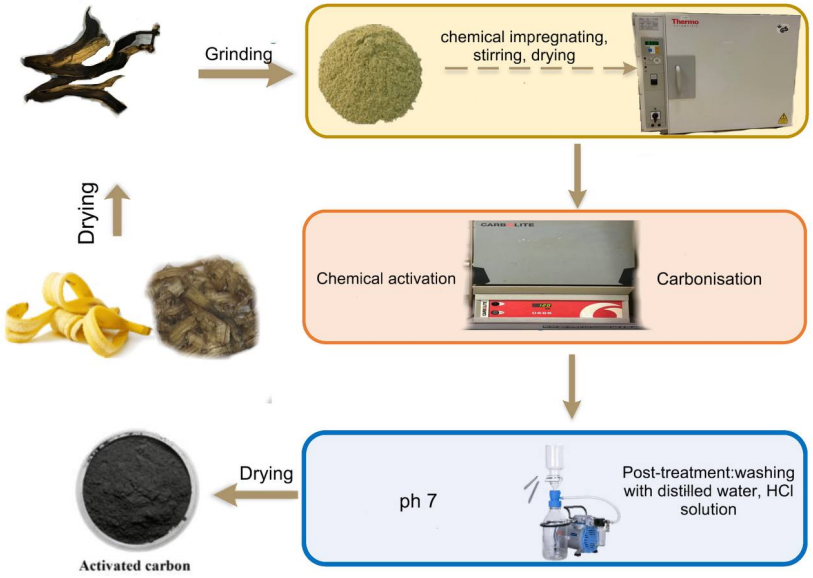


Figure 2: Visualisation of the methodology

5 Metal affiliation

High absorption ability of metals towards chemically activated carbon can be related to several mechanisms. Activation with certain chemical reagents produce appropriate functional groups which induce chemical binding/affiliation. They are: electrostatic interaction, chelating, and precipitation effect [38].

Precipitation effectoccurs with activated carbon that contains soluble carbonate and/or phosphate, which can co-precipitate with many heavy metals such as Pb_2^+ Cd^+ and Pb [39].

Electrostatic: Carboxylic groups are known to produce negative charge which attracts positively charged metal cations by Coulumbic forces [40].

Chelating effect: Phenolic groups are accumulated to form stable complexes [41].

6 Methodology

1)Banana peel(Sample-1)/ Banana fiber(Sample-2)/ Banana peel+fiber(Sample-3) were removed from impurities by mechanical cleaning and washed, afterwards dried in an oven for 80∘C(for water vaporisation);

2)After, they were grounded and sieved until powder;

3)A 2.0 g powder of samples and 2.5 ml of 75% H_3PO_4 solution/ 2 g KOH were mixed in 20 ml of distilled water. Left for stirring for 12 hours;

4)The mixture was kept at 85 ∘C for 12 hours. (In this way, the hydration

of the precursor is facilitated, and the swelling of the interior channels of the botanic structure allows for a better access of the reactant to the interior of the particle. Further partial or complete evaporation of the solution will force the incorporation of the reactant to the interior of the particles;

5)After sample were put in a furnace for chemical carbonization proces at 500∘C for 2 hours;

6)It was washed with HCL solution to get rid of ash. Then, it was rinsed with hot distilled water (85∘C) several times and rinsed again with dilute NaOH solution to neutralize the acidity and subsequently dried in open air.



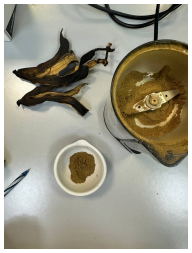
(a) Drying raw material

$\longrightarrow$



(b) Mechanical grinding

$\longrightarrow$



(c) Mechanical powdering

Figure 3: Raw material preperation



Figure 4: Muffle Furnace



Figure 5: Activated carbon samples

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