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Preparation and Characterisation of Corncob-Based Biosorbents in Côte d'Ivoire

Miezan Gnoan Ghislaine De Bouanzi[1], Patrick Grah Atheba[1], Serge Kouassi Gbamélé[2*], Martin Alla Aka[1], Albert Trokourey[1]

[1]Laboratory of Constitution and Reaction of Matter (LCRM), Félix Houphouët-Boigny University, Abidjan, Côte d'Ivoire
[2]Laboratory of Environmental Sciences (LSE), Nangui Abrogoua University, Abidjan, Côte d'Ivoire
Email: *sergegbamele@gmail.com

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Abstract

This study focuses on the preparation of corncob-based biosorbents. The chemical impregnation method was used to vary the chemical agent namely phosphoric acid H_3PO_4 (BA) and sodium hydroxide NaOH (BB). The physicochemical analysis of the two biosorbents indicated that under the same preparation conditions, the bio-sorbents have after activation yields lower than 50% (24.37% for BB and 49.09% for BA). In addition, the biosorbents have iodine index values between 444.17 mg/g and 418.79 mg/g and specific surfaces related to the adsorption of methylene blue ranging from 18.54 m^2/g to 19.70 m^2/g. The study of surface functional groups by using the Boehm test and pH zero point charge (pH_{PZC}) confirmed the acidic nature of BA and BB biosorbents with respective values pH_{PZC} = 4.01 and pH_{PZC} = 4.90. The Langmuir method and BET analysis determined the specific surface areas by liquid phase adsorption of methylene blue as well as the porosity. The BET surface areas of BA and BB obtained are 72.01 m^2/g and 63.10 m^2/g respectively. The influence of the chemical activating agent on the formation of pores was confirmed by electron microscopy (SEM) analysis. From this study, it is found that the best activating agent for corn cobs was found to be phosphoric acid because the BA biosorbent was revealed to be the most favourable due to its surface area and good pore volume which are high compared to sodium hydroxide NaOH. Moreover, their application as adsorbent for effluent treatment could be explored.

Keywords

Biosorbent, Corncobs, Chemical Activation, Phosphoric Acid, Sodium Hydroxide

1. Introduction

A healthy environment ensures human well-being and balance, and so it is our duty to preserve it. Today, however, we can see that in developing countries the emergence of several industrial societies and human activities are generating pollution that poses an increasingly alarming threat to humans and ecosystems. To remedy this problem, the scientific community is working to develop effective depollution processes aimed at reducing the toxic power of pollutants. Among the many processes that have been developed, adsorption on activated carbon, as reported by Choualeb *et al.* [1], is recognised as one of the best water and wastewater treatment techniques for eliminating organic and inorganic pollutants. However, the use of activated carbons has a number of drawbacks, generally linked to their relatively high cost [2] and the high energy required for pyrolysis or physical activation. The search for low-cost adsorbents that perform as well as commercially activated carbons is one of the main themes that has attracted the attention of some researchers. Among the materials studied are magnetic adsorbents, which are oxidised in air during synthesis, so surface manipulation has been used to improve the adsorption capacity of these materials [3]. In addition, once adsorption has taken place, the adsorbent can be separated from the medium by a simple magnetic process. In our study, we chose maize cobs because of their abundance, given the maize plantations covering almost 350,000 ha, mainly in the north of the country (Côte d'Ivoire), with the Savanes region alone accounting for 60% of production, with an average yield of 1.9 T/ha [4]. Although this material serves as a precursor to magnetic biosorbent, it could also be a source of income for farmers, and its widespread use will reduce the amount of agricultural waste on the surface of our environment. The present work focused on the preparation and comparison of the characteristics of biosorbents resulting from chemical activation with two different agents, namely phosphoric acid (H_3PO_4) and sodium hydroxide (NaOH). The aim of this work is to convert maize cobs into a magnetic adsorbent to help treat domestic and industrial wastewater.

2. Materials and Methods

2.1. Materials

The precursor is an adsorbent obtained by impregnating and magnetising maize cobs from a trader at Siporex in the Yopougon district of Abidjan (Côte d'Ivoire). Once in the laboratory, we broke off the ends and removed the pith from the cobs, which were then washed several times with distilled water to remove surface impurities, then dried in an oven at 80˚C for 72 hours. Finally, the stalks were crushed, ground in a mill and sieved through a 250 m PIERRON EDUCATION sieve [3]. The chemicals used in this study were methylene blue (from Merck Eurolab), phosphoric acid (85%), sodium hydroxide (98%), sodium thiosulphate (99% purity), iodine, hydrochloric acid (99% purity) and ferrous sulphate ($FeSO_4$), which were of analytical quality and used as received. All solu-

tions and reagents were prepared with demineralised water.

2.2. Impregnation

Chemical activation was carried out according to the method described by Allou *et al.* [3] using a chemical agent such as NaOH, and for the purposes of our study the chemical agent H_3PO_4 was used in the same proportions as sodium hydroxide. This method consists of pouring 5 g of crushed and sieved corn cobs (biosorbent) into two Erlenmeyer flasks, then pouring 100 mL of NaOH solution (2.5 mol/L) into one of the flasks and 10 mL of 10% dilute phosphoric acid stock solution into the other, then shaking the two solutions vigorously (magnetic stirrer) for 24 hours at room temperature. The mixtures obtained were filtered and washed several times with distilled water until the pH of the washing solutions became neutral (7.0 ± 0.5). The activated biosorbents were oven-dried at 80˚C for 24 hours, then sieved to obtain a uniform particle size [3].

2.3. Magnetisation

Magnetisation consists of pouring a 0.5 g mass of corncobs impregnated with sodium hydroxide and acid into a flat-bottomed flask, where it is dispersed in 100 mL of a 10 mmol iron sulphate solution and then magnetically stirred. Next, 10 mL of a 10% sodium hydroxide solution was added dropwise to precipitate the hydrated iron oxides. The mixture was shaken on a magnetic stirrer and heated to 100˚C for 1 hour [5]. After cooling, the resulting magnetic biosorbent was washed several times with distilled water until its pH became neutral. The magnetised biosorbent is dried and stored in an airtight container [3].

2.4. Characterisation of Biosorbents

Yield

The activation yield (%) is defined as the ratio of the mass of biosorbent produced after activation to the mass of raw material used before activation. Biosorbent manufacturing yield values are estimated by applying formula (1):

$$\text{Activation yield } (\%) = \frac{\text{mass of activated biosorbent}}{\text{mass of biosorbent}} * 100 \quad (1)$$

Determination of iodine value

The iodine value is the most crucial parameter used to measure the biosorbent's performance in terms of activity. The higher the iodine value, the higher the degree of activity of the biosorbent. The Iodine Index (mg/g) is the quantity of iodine (I_2) adsorbed (mg) per gram of adsorbent in an aqueous solution of 0.02 N iodine. It characterises the zones accessible to any particle smaller than or equal to the size of the iodine molecule [6]. A mass m = 0.2 g of biosorbent is placed in a 100 mL beaker. Using a pipette, 20 mL of a 0.02 N solution of I_2 was added and stirred for 4 to 5 min. After filtering the mixture on filter paper, 10 mL of the filtrate was taken and measured with a 0.1 N sodium thiosulphate solution ($Na_2S_2O_3$) in the presence of a few drops of starch paste until

the solution was completely discoloured. From the reaction of I_2 with sodium thiosulphate, whose Equation (2) is described by:

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + NaI \quad (2)$$

The remaining concentration of I_2 (C_{I_2}) is determined and the iodine index (Q_{I_2}) is calculated from the following formula (3):

$$Q_{I_2} = \frac{\left(C_0 - \frac{C_n V_n}{2V_{I_2}}\right) \times M_{I_2} \times V_{abs}}{m} \quad (3)$$

where, V_n: Volume of sodium thiosulfate poured at the equivalence in mL;

C_n: Concentration of sodium thiosulfate;

C_0: Initial concentration of I_2;

V_{I_2} : Volume of I_2 dosed;

M_{I_2} : Molar mass of iodine (253.81 g/mol);

V_{abs}: Adsorption volume (20 mL);

m: Mass of the biosorbent (g).

Determination of the methylene blue index

The methylene blue index of a biosorbent is the capacity of this biosorbent to adsorb the methylene blue molecule. It is an indicator of the mesoporosity of an adsorbent. The study of its adsorption on a porous support therefore reflects the capacity of this material to adsorb medium molecular weight compounds [7]. To do this, a mass of 0.1 g of each biosorbent was brought into contact with 50 mL of methylene blue at an initial concentration of 5 mg/L. After stirring for 40 min (equilibration time), the suspension was filtered using a centrifuge and the residual concentration of methylene blue was measured at the maximum adsorption wavelength λ = 663 nm using a Helios OMEGA UV-visible spectrophotometer. The methylene blue index was calculated using the formula in relation 4:

$$I_{BM}\left(\text{mg/g}\right) = \frac{C_0 - C_r}{m_{ab}} * V \quad (4)$$

where, C_0: Initial concentration of methylene blue (mg/L);

C_r: Residual concentration of methylene blue (mg/L);

V: Volume of methylene blue solution (L);

m: Mass of biosorbent (g).

2.5. Chemical Characterisation

Surface functional groups

The measurements were carried out using the Boehm method [8]. This method was used to determine the composition of biosorbents in terms of acidic or basic surface groups. To neutralise the acidic groups, a 0.1 N solution of strong bases such as $NaHCO_3$, Na_2CO_3 and NaOH was prepared. A solution of HCl (0.1 N) was used to neutralise the basic groups. For each sample, 1 g of biosorbent was suspended in 50 mL of the prepared solutions and kept under con-

stant stirring for 72 hours. After filtration, a back titration was carried out with NaOH (0.1N) or HCl (0.1 N) depending on the nature of the solution, to determine the number of sites of the acidic or basic functions using formula (5) below:

$$N_0V_0 - N_fV_0 = n_{eqg}(R) \tag{5}$$

With, N_0V_0: Number of gram equivalents before the reaction;

N_fV_0: Number of gram equivalents after the reaction;

$n_{eqg}(R)$: Number of gram equivalents reacted.

Determining the pH of the zero charge point (pH_{PZC})

The pH_{PZC} or zero-point charge pH corresponds to the pH value for which the net charge on the surface of the biosorbent is zero. The method involves placing 50 mL of a 0.01 M NaCl solution in closed vials and adjusting the pH of each (values between 3 and 12) by adding a 0.1 M NaOH or HCl solution [9]. Next, 100 mg of adsorbent were added to the different solutions. The suspensions were kept under constant stirring at room temperature for 48 h and the final pH was measured. The pH_{PZC} is the point where the curve $pH_{final} = f(pH_{initial})$ intercepts the straight line $pH_{final} = pH_{initial}$ (the first bisector).

Characterisation of biosorbent surfaces

- **Surface morphology**

Scanning electron microscopy (SEM) was used to determine the morphology and structure of the prepared samples. Surface micrographs of the samples before adsorption were taken using a scanning electron microscope (SEM) model JSM-840 for surface microanalysis.

- **Specific surface of methylene blue**

The specific surface area of biosorbents was determined using both the Langmuir model based on methylene blue (BM) adsorption and the method developed by Brunauer-Emmet-Teller, commonly known as the BET method [10]. For the specific surface related to BM adsorption, it was necessary to determine the equilibrium time, then the adsorption isotherms according to the Langmuir model, and finally the maximum adsorption capacity Q_m. Knowing Q_m the specific surface area could be calculated using the following formula (6):

$$S_L = Q_m \cdot \delta \cdot \mathcal{N} \tag{6}$$

where, S_L: Specific surface area (m^2/g);

Q_m: Maximum adsorption capacity (mol/g or mg/g);

δ: Area occupied by a molecule (m^2) (the area of methylene blue: 175×10^{-20} m^2);

$\mathcal{N}$: Avogadro number (mol^{-1}).

- **Specific BET surface area**

Knowing V_m helps to determine q_m and consequently the BET surface area (S_{BET}), which is calculated using the following formula Equation (7):

$$S_{BET} = \sigma \cdot q_m \cdot \mathcal{N} \tag{7}$$

With, σ the area occupied by a vapour molecule of N_2;

$\mathcal{N}$ Avogadro's number (6.025×10^{23} mol^{-1}) and at $T = 77$ K, the surface area of a nitrogen molecule is $\sigma = 16.2 \times 10^{-20}$ m^2.

- **Porosity**

Adsorption applies only to microporous adsorbents with small pore sizes. Therefore, it can be concluded that biosorbents prepared from the above methods are predominantly microporous. Specific surface areas are calculated using the BET method [11]. From the basic assumption of BET theory, the BET equation follows Equation (8):

$$\frac{P/P_0}{q_e \cdot (1-P/P_0)} = \frac{1}{q_m \cdot C} + \frac{C-1}{q_m \cdot C} \cdot \frac{P}{P_0} \tag{8}$$

With, q_e: Amount of material adsorbed at equilibrium pressure P per gram of solid;

P_0: Saturated vapor pressure of the adsorbed gas at the experimental temperature;

P: Equilibrium pressure of the adsorbed gas;

q_m: Quantity of material required to completely cover the surface of the solid with a monomolecular layer of adsorbate;

C: Heat of adsorption (Characteristic constant of the gas-solid system).

Where V is the volume adsorbed at pressure P, V_m is the volume of gas required to cover 1 g of adsorbent with a single layer of gas and C is the BET constant. The BET equation is valid for low relative pressures $P/P_0 \leq 0.35$. By plotting $(P/P_0)/[q_e \cdot (1-P/P_0)]$ with respect to P/P_0 we obtain a straight line whose slope is $(C-1)/(q_m \cdot C)$ and intercepting $1/(q_m \cdot C)$ allows us to calculate V_m and C.

Biosorbent characterisation procedure

A mass of 0.1 g of biosorbent was suspended in 50 mL of methylene blue solution with a concentration of C_0 = 5 mg/L contained in different Erlenmeyer flasks. The Erlenmeyer flasks were stirred at a speed of 350 rpm for the entire duration of the experiment. The moment of contact of the biosorbent with the solution was taken as the initial moment t_0. At different time intervals of 5, 10, 20, 30, 45 and 60 min, an Erlenmeyer flask was removed and the contents were filtered. A volume of 10 mL of the filtrate was measured by a Helios OMEGA spectrophotometer at a wavelength of 663 nm in order to determine the residual concentration. The time from which the quantity (C_r) became constant was taken as the equilibrium time for the study of adsorption isotherms. The operating mode of the isotherms is approximately the same as that of the adsorption kinetics. The Erlenmeyer flasks contain a volume (V) of 50 mL of methylene blue solution but at different equilibrium concentrations (C_e). The amount of adsorbed adsorbate (q_e) was determined from equation (9):

$$q_e = \frac{(C_0 - C_r) \cdot V}{m} \tag{9}$$

With, q_e: the amount of species adsorbed per gram of adsorbent in mg/g;

C_r: the concentration of the species in solution at time t in mg/L;

C_0: the initial concentration of the species in mg/L;

V: the volume of solution introduced at the start in L;

m: the mass of the adsorbent in g.

BET surface area, pore volumes and pore dimensions were calculated from nitrogen adsorption isotherms at 77 K. Samples were analyzed using a Quantachrome Autosorb-6B apparatus at the Department of Chemical Engineering, University of Man.

3. Results

3.1. Physicochemical Characterization: Yield and Iodine Index Values

Table 1 shows the impregnation efficiency and iodine value of biosorbents with two different chemical agents. The efficiencies and diode number values of the biosorbents were calculated and reported in this table.

Table 1. Physico-chemical parameters of the biosorbents prepared.

Biosorbents	Yield (%)	Iodine value (mg/g)
BA	49.09	444.17
BB	24.37	418.79

From Table 1, it can be seen that the impregnation and magnetisation yields for all the biosorbents prepared are less than 50%. These different yields can be explained by the losses of biosorbents recorded during the various filtrations carried out after impregnation with the activating agent and after neutralisation of their pH by distilled water. To optimise yield, a finer sieve or a white cloth should have been used [12]. In both impregnation cases, the best yield was obtained with the acid agent for BA (49.09%) and the low mass yield obtained with NaOH for BB (24.37%), could be due to the fact that NaOH is a strong, corrosive base. Since the yield is an indicator of the performance of the material preparation method, particularly on an industrial scale, it can be seen that the NaOH activating agent is not more advantageous in terms of biosorbent gain due to its low yield. The difference in yields observed suggests that the nature of the agent used during impregnation for chemical activation could be the cause. Analysis of the results concerning the iodine index reveals that the biosorbents impregnated with the different agents have pores accessible to the iodine molecule. Indeed, these iodine index characterisation tests give values of 444.17 mg/g and 418.79 mg/g for BA and BB respectively. Characterisation of the porosity using the iodine index makes it possible to distinguish between biosorbents with a large number of macropores and mesopores (low iodine index) and biosorbents with a majority of micropores (high iodine index). The increasing order of the iodine values obtained, BB < BA, confirms that chemical activation leads not only to the creation of new pores, but also to the enlargement of available

pores. Of the two biosorbents we prepared, the one impregnated with H_3PO_4 has a greater I_2 adsorption capacity. Similar observations were made by Ousmaila *et al.* [13].

3.2. Chemical Characterisation: Surface Functional Groups and Zero Charge Point pH

Before magnetisation

Table 2 shows the zero charge point pH values of the biosorbents before magnetisation. The pH_{PZC} values are 6.01; 7.16 and 7.34 respectively for BIA (acid-impregnated stalks), BIB (acid-impregnated stalks) and BBT (raw stalks), thus showing that the surface of the biosorbents is almost neutral. These different values confirm the amphoteric nature of BIA, BIB and BBT.

Table 2. Surface chemical groups and zero charge point pH of BIA, BIB and BBT.

Biosorbents	Group (meq/g)					pH_{PZC}
	Acids				Basics	
	Carboxylic	Lactones	Phenols	Total	Total	
BIA	2.90	0	0.50	3.40	0.25	6.90
BIB	2.85	0	0	2.85	1.80	7.16
BBT	2.75	0	0	2.75	1.65	7.34

The pH_{PZC} values in Table 2 were obtained using the curves in Figure 1. The pH_{PZC} is the point where the curve $pH_{final} = f(pH_{initial})$ intercepts the straight line $pH_{final} = pH_{initial}$ (the first bisector).

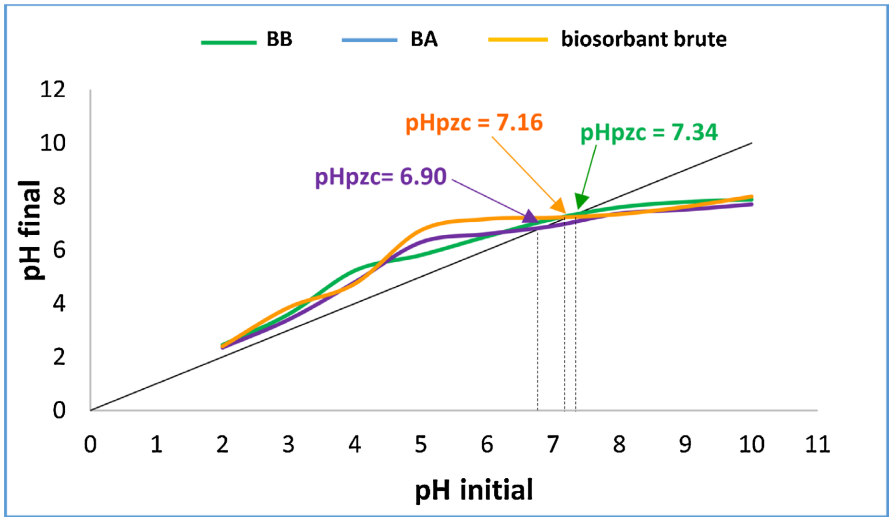

Figure 1. Curves for determining the zero charge point pH of biosorbents before impregnation.

After magnetization

The quantities of surface functional groups and the zero charge point pH of

the biosorbents are grouped together in Table 3. The results of the chemical analysis of pH_{PZC} revealed that the adsorbents have an acidic function estimated at 4.01 and 4.90 for BA and BB respectively, showing that the surface of the biosorbents is acidic synonymous with a high oxygen content, particularly the carboxylic and phenolic functions. This is due to the magnetisation of hydrolysable functional groups in the presence of proton [14].

Table 3. Surface chemical groups and zero charge point pH of biosorbents.

Biosorbents	Group (meq/g)					pH_{PZC}
	Acids				Basics	
	Carboxylic	Lactones	Phenols	Total	Total	
BA	2.65	0.15	2.70	5.50	0	4.01
BB	2.35	0.15	2.65	5.15	0	4.90

The pH_{PZC} values in Table 3 were obtained using the curves in Figure 2.

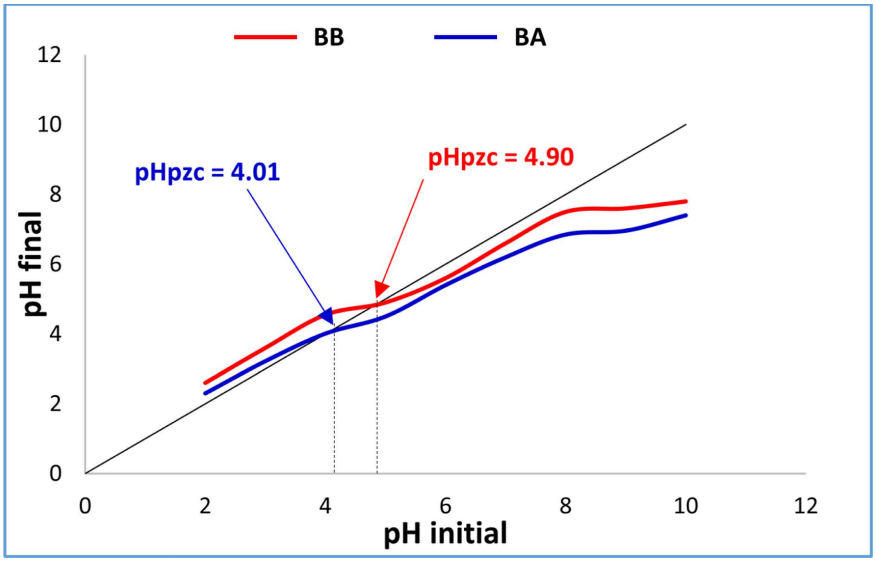

Figure 2. Zero charge point pH determination curves of biosorbents after impregnation.

With regard to the acid functions for BA and BB, the phenol group is superior to the other groups. According to the literature [15], since adsorption is a surface phenomenon, adsorbents with acid groups on the surface will have cationic exchange. The pH_{PZC} value can be used to determine whether biosorbents are acidic or basic and, depending on the pH of the solution, its net surface charge. If both the adsorbent and the pollutant molecule are charged, electrostatic interactions may occur [16]. These values confirm the amphoteric nature of raw maize cobs, impregnated with acid and base, unlike cobs impregnated and then magnetised. A comparison of the pH of the biosorbent surfaces before and after magnetisation, *i.e.* the values in Table 2 and Table 3, shows that magnetisation influenced the zero charge pH (pH drop) of the biosorbents [17]. This drop in

pH is due to magnetisation, which is explained by the release of protons from hydrolysable functional groups. It should be noted that there is a certain consistency between the pH_{pzc} values and the proportions of acidic and basic functions. This result is consistent with that obtained by Khelifi *et al.* [18] and Daoud *et al.* [19].

3.3. Measuring Specific Surface Areas

Determination of the equilibrium adsorption time of methylene blue on the different biosorbents

The study of methylene blue adsorption was carried out on the BA and BB biosorbent samples.The results of the experiments relating to the effect of contact time are shown in **Figure 3**. These results were obtained for the same initial concentration of 5 mg/L of methylene blue.

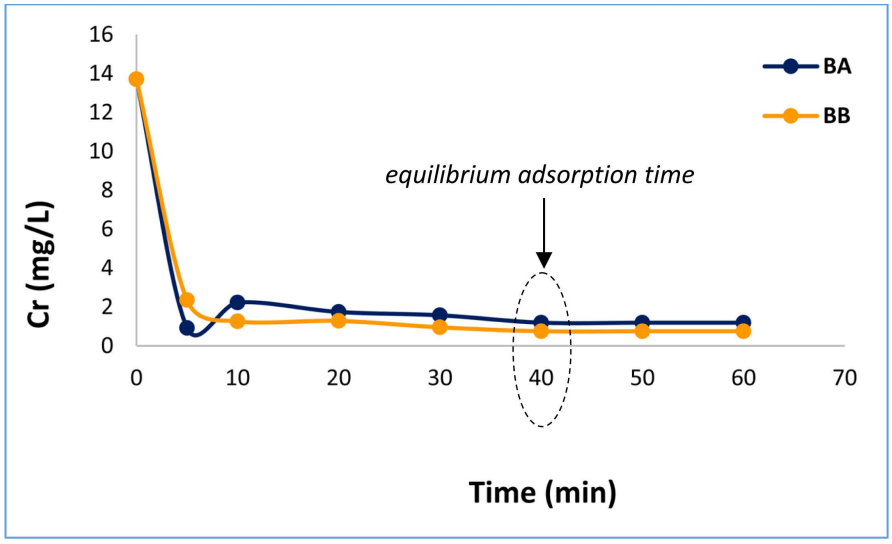

Figure 3. Residual concentration of BM in aqueous medium as a function of time.

Figure 3 shows the adsorption kinetics of methylene blue on the different types of biosorbent. The residual concentration decreases over time until it reaches an approximately constant value. This decrease in residual concentration is synonymous with adsorption of methylene blue. The adsorption kinetics of methylene blue on BA and BB show that after 40 minutes of contact time, almost all the BM has been adsorbed.

Specific surface bound to methylene blue (S_{MB})

The graphical representation of the adsorption isotherm of methylene blue (MB) according to Langmuir is presented in **Figure 4**.

Figure 4 shows that the correlation coefficients (R^2) are close to 1. The adsorption of methylene blue on all the biosorbents can therefore be described by the Langmuir model.

The maximum adsorption capacity Q_m of each adsorbent was determined by applying the Langmuir isotherm model. A high Q_m value implies good adsorp-

tion. The specific surface area offered by each adsorbent was calculated using Q_m and summarised in Table 4.

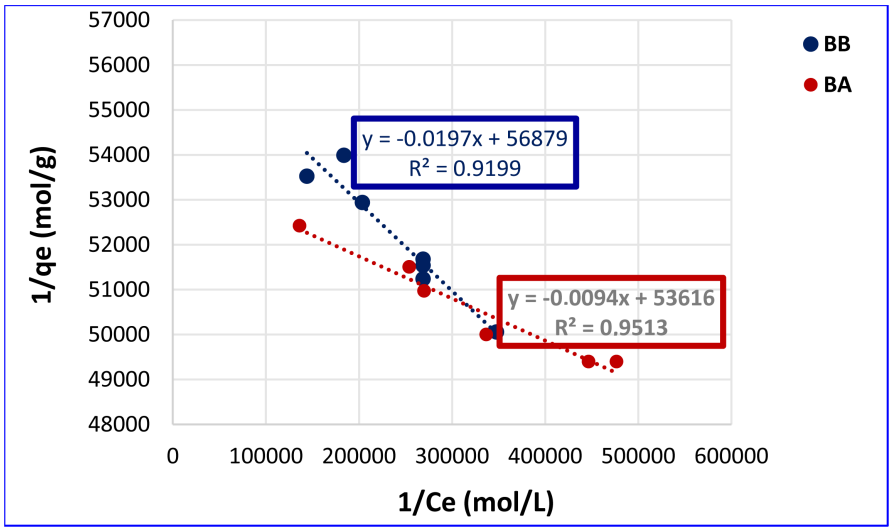

Figure 4. Langmuir modelling of BM adsorption isotherms.

Table 4. Parameters of the Langmuir model for the adsorption of BM.

Biosorbents	R^2	K_L	Q_m (10^{-6} mol/g)	S_{MB} (m^2/g)
BA	0.9513	−5703.787	18.7	19.70
BB	0.9199	−2887.258	17.6	18.54

The methylene blue specific surface areas obtained in this study show that the adsorptions decrease in both cases in the following order: S_{MB}(BA) > S_{MB}(BB). It seems clear that BA is the best biosorbent prepared due to its high methylene blue specific surface area, indicating mesoporous adsorption. The BET method is a very accurate method of surface area determination and was therefore used to verify the results obtained previously.

Specific surface area and BET porosity

- **Specific surface area**

Data on the adsorption of N_2 were obtained from the Department of Chemical Engineering at the University of Man. However, the N_2 adsorption isotherms at 77 K of biosorbents prepared with different activating agents are shown in Figure 5 and the pore properties are given in Table 5.

Table 5. Summary of the different surfaces of the biosorbents obtained.

Biosorbents	Correlation coefficient (R^2)		Q_m (mmol/g)		S (m^2/g)	
	MB	N_2	MB	N_2	S_{MB}	S_{BET}
BA	0.9513	0.9998	0.0187	0.1980	19.7000	72.0126
BB	0.9199	0.9994	0.0176	0.0003	18.5400	63.1026

Figure 5 shows the N_2 adsorption-desorption isotherms at 77 K for the BA and BB adsorptions. The isotherms in this figure are of type IV according to the IUPAC classification, each with a type H3 hysteresis loop. This type of isotherm characterises the simultaneous presence of micropores (pore diameter less than 20 Å) and mesopores (pore diameter between 20 and 500 Å), suggesting that the biosorbents used would all be both microporous and mesoporous. The hysteresis loop is less pronounced for BB than for BA, which would mean that the mesoporous volume of BB is smaller than that of BA [20]. The type IV isotherm is characteristic of the mesoporous adsorbents widely used by several industrial structures [21].

Figure 6 shows the linear representation of the BET equation for the two biosorbents prepared. The linear fit curves obtained seem to confirm our previous results (R^2 close to unity).

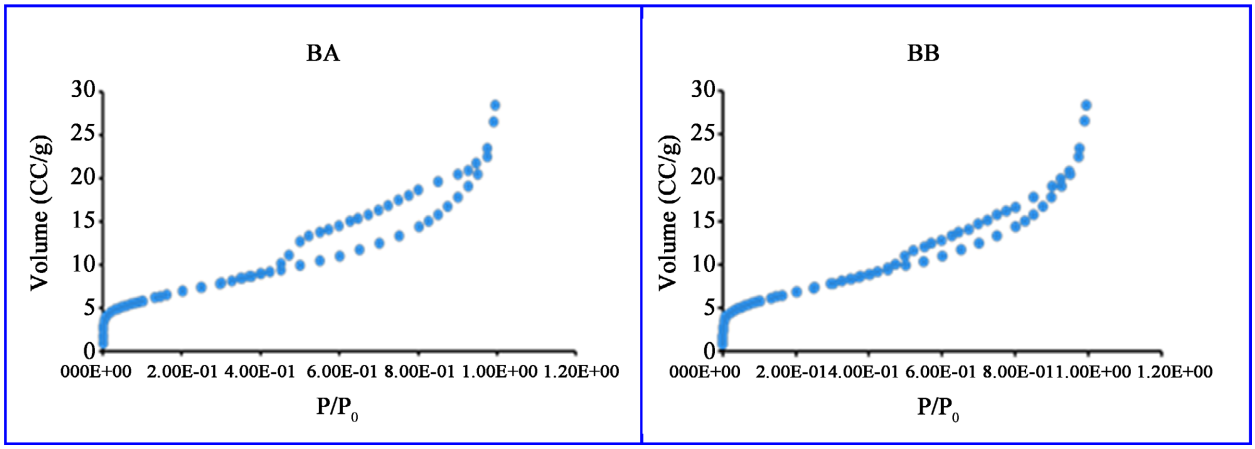

Figure 5. N_2 adsorption-desorption isotherms at 77 K for BA and BB adsorptions.

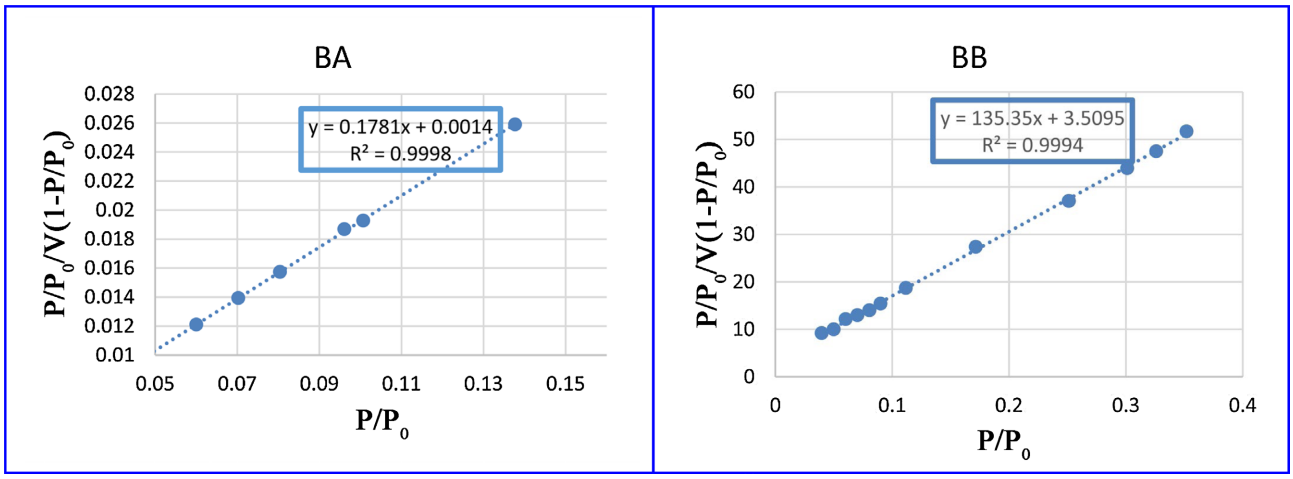

Figure 6. Linear form of the BET adsorption isotherm for N_2 on BA and BB biosorbents for the $0.05 < P/P_0 < 0.4$ branch.

- **BET porosity**

Table 6 shows that sample BA has a higher specific surface area than sample BB and the same order is followed for the amount of N_2 adsorbed. This would be attributed to the nature of the activating agent used.

Table 6. Porous characteristics of impregnated adsorbents.

Biosorbents	Cumulative pore volume (cm^3/g)	Pore width (nm)	S_{BET} (m^2/g)
BA	0.9100	1.9300	72.0126
BB	0.9300	1.6900	63.1030

We can deduce from this table that the specific surface area calculated using the BET method shows that the BA sample has a higher specific surface area (72.0126 m^2/g) than the BB samples (63.1030 m^2/g); similarly, the quantity of N_2 adsorbed for the BA (0.198 mmol/g) is greater than that for the other BB samples (0.0003 mmol/g). This could be due to the nature of the activating agent used during chemical activation. The decreasing order of BET specific surface areas of our different sorbents ($S_{AB} > S_{BB}$) was in good agreement with those found in methylene blue adsorption studies. A comparative study of the values of the specific surface areas obtained according to the adsorbate used leads us to reveal that the BET method seems to be the most suitable for determining the specific surface area of a porous solid. Nitrogen adsorption isotherms also provide information on pore volume and pore diameter (Table 6).

Scanning electron microscope analysis

Scanning electron microscope analysis of biosorbents from maize cobs yielded Figure 7. The iodine value results obtained during the physicochemical characterisation carried out in our study are confirmed once again by the scanning electron microscope (SEM) analysis shown in Figure 7. The surface morphologies

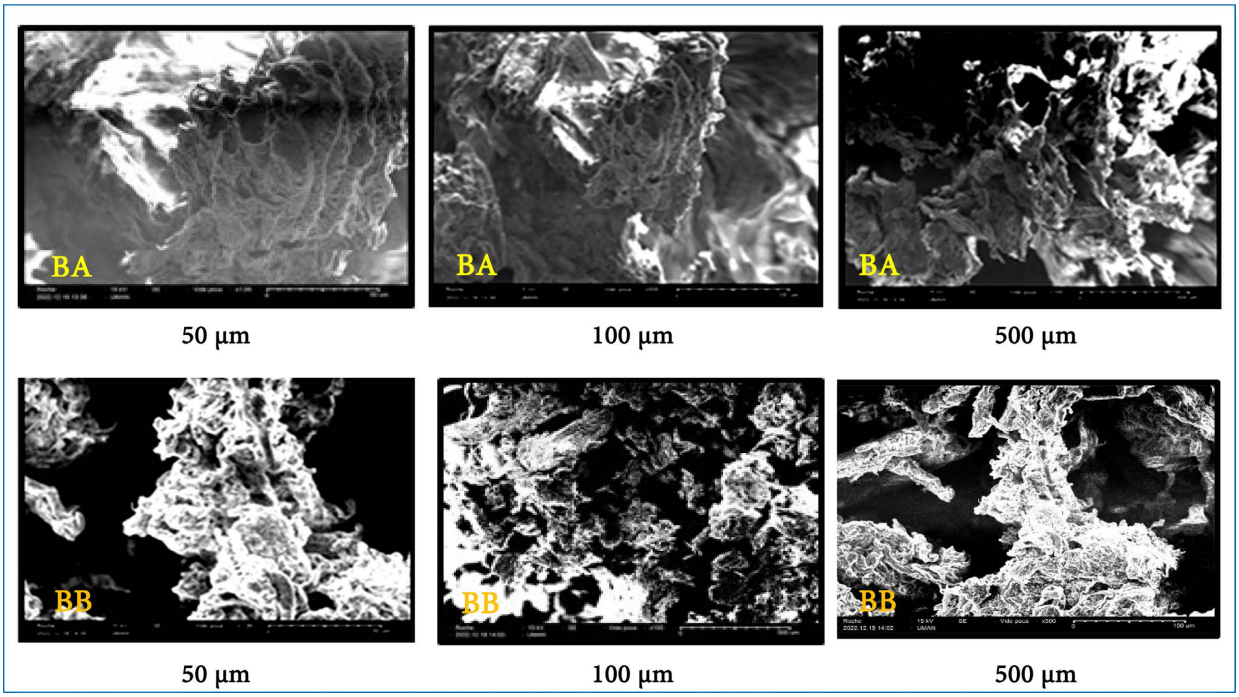

Figure 7. Morphology of BA and BB samples at different magnifications using HIROX SEM model SH-4000 M: 50 µm; 100 µm and 500 µm.

of the prepared materials are quite different. SEM images of BA and BB at different magnifications (50 µm, 100 µm and 500 µm) showed that the adsorbents had different morphologies, confirming that the nature of the impregnating agent influenced activation and, consequently, pore creation. The difference in texture between BA and BB could be attributed to the type of activating agent used during their synthesis. These observations indicate once again that the activating agent has effects during activation and therefore on pore creation.

In the context of this study, the results of the specific surface areas indicate that the biosorbents manufactured all have mesopores and micropores. Specifically, the BA and BB adsorbents have the same number of mesopores, but BA has more micropores than BB. A comparison of the specific surface areas obtained during nitrogen and methylene blue adsorption shows that the value determined is low in the case of methylene blue adsorption. This can be explained by the fact that the methylene blue molecule being larger (air 175 $Å^2$) is accessible mainly to the mesopores, unlike that of nitrogen (16 $Å^2$) which is more accessible to the micropores. According to the literature, the diameter of BM could be in the mesopore diameter range (2 - 50 nm) and therefore the molecule cannot enter the micropores (diameter < 2 nm). Consequently, its adsorption would be limited to the mesopores, which reduces the specific surface area. Our work is in agreement with that of certain authors such as Bonnetain [22] who assert that if the diameter of the adsorbent pores is smaller than that of the adsorbate molecules, these molecules cannot penetrate the pores and the surface area of the pore walls is not taken into account in the evaluation of the adsorbent surface area. By using an adsorbent with smaller molecules, it will then be possible to reach the pores. With the ranking S_{BET}(BB) < S_{BET}(BA) obtained, the BET method supports the thesis that BA is the adsorbent with more micropores than BB. These results confirm those obtained in the case of the iodine index study, where BA is more microporous than BB (**Figure 8**).

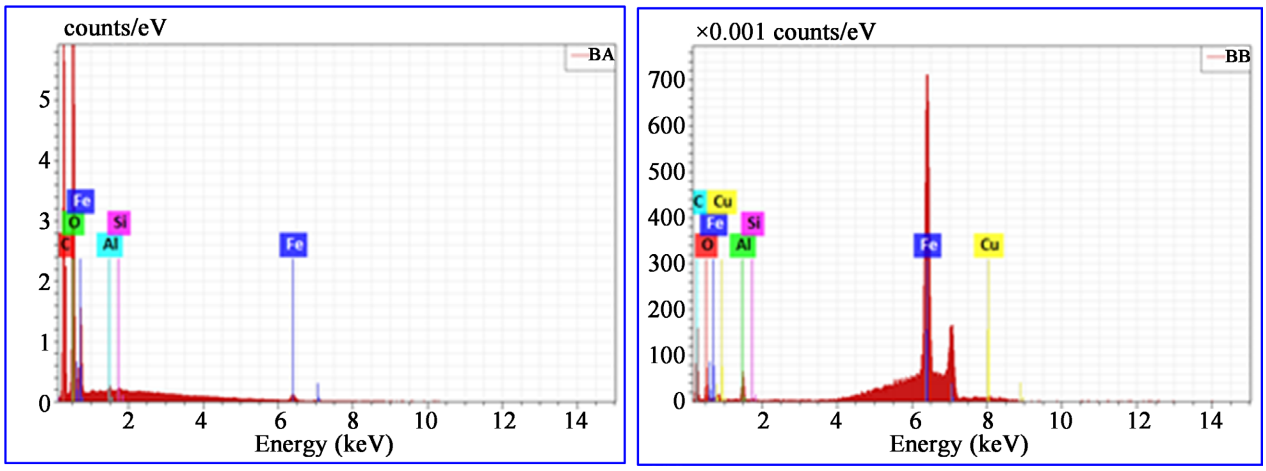

Figure 8. Spectra from energy dispersive spectrometry (EDS) analysis of adsorbents.

3.4. Elemental Analysis of Biosorbents

Figure 8 shows the spectrum and quantification of the BA and BB samples at 20 µm using a BRUCKER EDS, model XFlash 30/100. The elemental analysis of the biosorbents carried out by this analysis mainly revealed carbon, oxygen and iron, but also other elements such as aluminium, silicon and copper.

The contents (in percentage) of the constituent elements of the various adsorbents were generated automatically by the device and grouped together in Table 7.

Table 7. Centesimal mass composition of chemical elements present in biosorbents.

BA		BB	
Elements	**Content (%)**	**Elements**	**Content (%)**
C	51.52	C	62.25
O	48.29	O	9.47
Fe	0.15	Fe	10.11
Al	0.03	Al	15.75
Si	0.01	Si	1.05
-	-	Cu	1.37

Analysis of Table 7 shows that the adsorbents obtained have a good carbon content (51.52% and 62.25% respectively for BA and BB). This carbon content shows that maize cobs are rich in lignite. According to Danish *et al.* [23], when the carbon content of a precursor is between 50% and 90%, it is considered to be rich in lignite and therefore suitable for activated carbon production. In addition, the various rates obtained are much higher than those found by Aloko *et al.* [24], who obtained 29.24% from mango skins, and Kouadio *et al.* [6], who found a rate of 37.43% using coconut shells. These carbon contents suggest that maize cobs can be considered suitable for producing quality activated carbon. If this is the case, we will continue our research by preparing activated carbons from corn cobs in order to compare the results obtained with those of our work here.

3.5. Comparative Study of Biosorbents Obtained from Corn Cobs

Table 8 shows the comparative results of the BET surface area with one author.

In our study, the biosorbents were obtained under the same conditions as those of Allou *et al.* [3], but the results in terms of pore volume and BET surface area of the biosorbent activated with NaOH are higher than those obtained by Allou *et al.* [3], as shown in Table 8. This difference could be explained by the fact that 1 hour after magnetisation, the reaction had to continue by oxidation since, while waiting for the reaction temperature to drop in order to proceed to washing to neutralise the pH of the solution, the flat-bottomed flask in which the magnetisation was carried out was open and therefore exposure to the open air allowed this oxidation to take place. This should have given better results than

those obtained by Allou *et al.* [3]. Similar observations were made by Atheba *et al.* [25].

Table 8. Comparative results for BET surface area with one author.

Biosorbent source	Activating agent	Magnetization condition		Cumulative pore volume (cm^3/g)	S_{BET} (m^2/g)	Reference
		Temperature (°C)	Time (hour)			
Corn	NaOH	100	1	0.147	35.22	Allou *et al,* 2023
Corn	NaOH	100	1	0.93	63.10	Our study
Corn	H_3PO_4	100	1	0.91	72.01	Our study

This difference could also be explained by the difference in the variety of maize species used in this study. The same observations were made by Kra *et al.* [26] when preparing activated carbons from two varieties of acacia wood.

4. Conclusion

Biosorbents derived from maize cobs (local biomass) activated with H_3PO_4 acid and NaOH base were prepared and characterised. Compared with the two methods (BM and BET) used to determine surface area, the BET method was found to give the best results. The biosorbents prepared had specific surface areas ranging from 63.10 to 72.01 m^2/g and pore volumes of between 0.91 and 0.93 cm^3/g. These specific surface areas confirm the orders of iodine adsorption capacity ranging from 418.79 to 444.17 mg/g. Chemical activation of this material provided active microporous sites (type isotherm I). Boehm's chemical analysis and determination of the charge pH at zero point showed the presence of various functional groups on the surface of the biosorbents and some uniformity between the pH_{PZC} values and the proportions of acidic functional groups. At the end of this work, it is clear that the biosorbent activated with phosphoric acid seems better than the other, as it gives a high yield (49.09%), high specific surface (72.01 m^2/g) and large pore volume (0.91 cm^3/g). However, future work will be devoted to studying the adsorption capacity of this biosorbent in the elimination of various metal pollutants in order to assess its effectiveness in water treatment.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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