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Research Article

Corn Cob-Derived Activated Carbons for Gold Mine Wastewater Treatment in East Cameroon

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Abstract

In East Cameroon, the discharge of untreated effluents, from gold recovery and concentration, into nature poses serious environmental problems. The main aim of this study was to investigate the efficiency of three corn cob-derived activated carbons for gold mine wastewater treatment of East Cameroon. Wastewater samples were collected in three mining sites (Kambele 1, Kambele 2 and Dem) for laboratory analysis. The three activated carbons were produced by chemical and thermal activation with three different chemical reagents ($ZnCl_2$, NaOH, and KH_2PO_4, respectively) meanwhile $Al_2(SO_4)_3$ served as the control. The main results revealed that wastewater from Kambele 2 area was the most contaminated with highest proportion of Fe (3.52 mg/l), Hg (62.7 mg/l), Cd (533.95 mg/l), NO_3^- (103.33 mg/l), SO_4^{2-} (640 mg/l), HCO_3^- (152.5 mg/l), Ca^{2+}(447.12 mg/l), Na^+ (26.8 mg/l), Mg^{2+} (32 mg/l), K^+ (51.05 mg/l). And with low proportion of Ni (0.21 mg/l), Pb (0.41 mg/l), PO_4 (0 mg/l), and Mn (5.66 mg/l), as compared to wastewater from the other sites. Wastewater samples from this site were used to test the efficient of ACs. The wastewater was greatly improved with $ACZnCl_2$ and ACNaOH, but ACNaOH performed better than the control and other activated carbons for cationic extraction, and was the only AC to adsorb almost 100 % of Hg in wastewater. The $ACZnCl_2$ (0.5 mm particle size) was the most efficient in the extraction of major anions: NO_3^- (96.60 %), SO_4^{2-} (81.25 %), HCO_3^- (76 %), compared to the $Ca(OH)_2$ and $Al_2(SO_4)_3$ (control) and ACNaOH. Generally, the $ACZnCl_2$ (0.5 mm particle size) was more efficient compared to $ACKH_2PO_4$ and ACNaOH in adsorption of Fe (94.05 %), Mn (88.51 %), and Ni (99.99 %). The $Al_2(SO_4)_3$ was the only one that reduced the concentration of Pb (24.39 %) and was good for extraction of NO_3^- (96.6 %), Fe (92.6 %), Mn (88.51 %), and Ni (99.99 %). From $ACZnCl_2$, the smaller the particle size of cob-derived AC, the better the extraction of heavy metals and anions and the poorer the extraction of cations (Ca^{2+}, Na^+, Mg^{2+}, K^+). The economic analysis of the different methods enabled to note an additional profit rate of 60 to 160% with the use of the ACs compared to $Al_2(SO_4)_3$. Thus, $ACZnCl_2$ and ACNaOH can either be used alone or combined with $Al_2(SO_4)_3$ for best performance to reduce cost and optimize contaminant removal.

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1. Introduction

Despite the huge mining potential of Cameroon, gold exploitation is still done by artisanal mining practices (Figure 1). However, gold mining whether artisanal or not is inherently disruptive to the environmental ecology [5, 15]. Mine wastes have been generated for several centuries, and mining activity has accelerated significantly during the 20th century [34]. Improper disposal of these wastes can have significant short and long term adverse environmental impacts [10, 11], including: loss of flora and fauna, land degradation, ground and surface water contamination [17, 18]. These impacts generally arise from the high concentrations of potentially toxic metals and metalloids that contaminate waters and soils, and cause negative health impacts such as poisoning and cancers [5, 6]. This emanates from the fact that the recovery and concentration of this precious metal use large proportion of natural resources, hazardous chemicals, and generates large quantities of wastes responsible for environmental damage despite the availability of many processes for wastewater treatment [19], artisanal mining industries still face difficulties. This is mainly due to expensive and unavailability of equipment and chemicals required for this process. Conventionally, the mine drainage as well as the waste itself are treated with alkali to increase pH and precipitate metals [10, 20, 28]. The main drawback of this method is that it has to be repeated activated after use to maintain efficient, meanwhile there may also be negative effects on beneficial microorganisms. Several other treatment methods have been developed to stop weathering processes thereby reducing the environmental impact of mine wastes. In the dynamic and evolving field of wastewater remediation, a diverse array of methods has been developed, each uniquely designed to address different types of pollutants. These methods range from physical to chemical, biological and physico-chemical techniques, each with specific mechanisms and applications [29]. Among these techniques, adsorption is recognized as a suitable tool to overcome water contamination problem of industrial origin [15, 18-22]. Adsorption has been found to be one of the most effective and versatile method due to its simplicity, efficiency and broad range of pollutants it can remove [27]. Nevertheless, high costs of conventional methods to eco-friendly low-cost traditional methods led to the adoption of other forms of adsorbents from plants, microbes (e.g. bacteria, fungi, microalgae), biomaterials (e.g. chitosan, chitin), agricultural wastes, etc [20-24]. Biosorption is a useful technique for industrial wastewater treatment [24, 25, 27, 29]. Although several methods are reported on the sequestration of heavy metals from aqueous solutions, still research is focused on the development of eco-friendly and economic process. Biosorption is a potential process for removal of heavy metals even at the low metal concentration in water [9, 11, 27]. Within the spectrum of adsorbents, activated carbon stands out for its notable efficacy in eliminating organic compounds, chlorinated compounds, and heavy metals from water [6, 22]. Its exceptional adsorption capabilities are attributed to its extensive surface area and porous structure [24, 25, 29]. Activated carbon (or activated charcoal) is a form of carbon commonly used to filter contaminants from water and air, among many other uses [27, 30]. It is processed (activated) to have small, low-volume pores that greatly increase the surface area available for adsorption or chemical reactions. However, generating activated carbon can demand significant energy, and its effectiveness might decline over time, necessitating the need for regeneration or replacement [20]. some of the most often used raw materials of activated carbon are bituminous coals, bones, coconut shells, peach, apricot, olive pits, apricot shells, petrol residues, wood and waste biomass from the agriculture, asphalt, metal carbides, soot, worn out car tyres, incineration products, synthetic polymers, wastes from the paper-cellulose industry, etc [12, 13, 16]. Corn is one of the agricultural commodities that generates a lot of wastes that are often thrown away after harvest [8]. Up to date, works that deal with transformation of corn wastes activated carbon production for water treatment are rare. Such activated carbons could substitute the conventional $Al_2(SO_4)$ [21, 22]. The main objective of this study was to study the level of contaminant removal from mine wastewater using corn cobs-derived activated carbon. The specific objectives were to determine the level of water pollution due to wastewater from gold mine areas in East Cameroon, test the efficiencies of corn cobs-derived activated carbon for the treatment of this waster and to test the economic viability of corn cobs-derived activated carbons compared to $Al_2(SO_4)_3$. This work is important as it enables the economic recovery of corn cobs) for the treatment of wastewater thereby, contributing to sustainable environmental protection.

2. Materials and Methods

2.1. Study Site

The study area covers the gold exploitation sites of Kam-

bele 1, Kambele 2 and Dem in the locality of Batouri, in the East Region of Cameroon. Batouri is located in the Kadey Division of Cameroon between latitude 4°24'0''N and 4°30'0''N and longitude 14°22'0''E and 14°28'0''E (Figure 2). It is limited to the North by Kette Subdivision; to the East by the Central African Republic; to the Southeast by the Kentzou Subdivision; to the south by Mbang and Ndelele Subdivision and to the west by the Lom and Djerem Division [29]. Climatically, the region is influenced by subtropical and equatorial climates with two rainy seasons and two dry seasons. The long rainy season extends from August to mid-November and the short rainy season from March to June. The long dry season runs from November to March and the short dry season runs from June to July with sporadic showers. The average annual rainfall at the Batouri station is 1479 mm. The highest temperatures are observed during the long dry season with a maximum average of 32.1 ℃ in February at Batouri. The lowest temperatures are observed in January with a mean of 17.1 ℃ [26]. The region's vegetation comprises savannah and forest types, with a dendritic hydrographic network governed by the Lom and Kadey basins [18]. The hydrographic network consists of many rivers (Belingonga, Mondim, Djengou, Bokoto, Kpwangala, Boungmama, Mama, Bil, Touki, Nol, Dja and Djengue) which all converge on the Kadey River. It is maintained by the Kadey Rivers in the North and Doume in the Southwest, with its main tributaries: Boungmama, Mama, Bil, Touki, Nol, Dja and Djengou. Geologically Batouri belongs to the Central Domain of Pan African Fold Belt in Cameroon. This domain is characterized by multiple major strike slip faults and the wide distributed syn- to post- tectonic granitoids [14]. The granitoids of Pan African ages are the gold-bearing rocks whereby mineralization is diffused within the rock masses and in some segments, gold occurs in hydrothermal quartz veins. From the South towards the North of the Kadey watershed, there are deep red ferrallitic soils with duricrusts and reworked soils with concretions and duricrust debris [28]. The Batouri Gold District has long been subjected to artisanal mining activities mostly by indigenes for livelihood. The mining population compises of persons of the following age ranges: from 15 to 30 (45 %), 31 to 45 (5 %) and 46 to 60 (35 %) [13].

Figure 1. *Some gold mining activities and their environmental impacts in Batouri (East Cameroon); (a) semi-mechanised exploitation (b) artisanal exploitation, (c) ground contamination by tailing disposal (d) deforestation (e) ground disturbance and contaminated artificial lake formation (f) surface water contamination.*

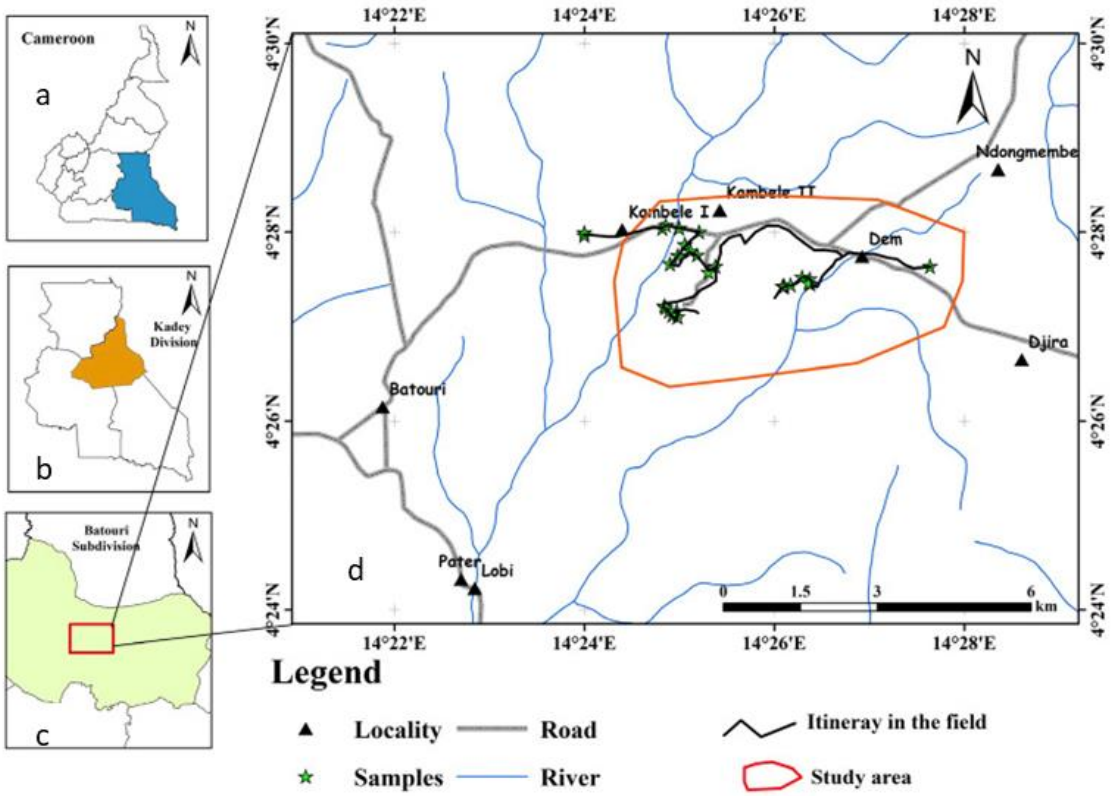


Figure 2. *Location map of the Study area. (a) Location of East Region in Cameroon; (b) location of Kadey Division in the East Region; (c) location of the study site in Batouri Subdivision; d) Study site showing the sampling points.*

2.2. Sampling

In total, three composite wastewater samples were randomly collected from the gold mine sites of Kambele 1, Kambele 2 and Dem. Water sampling was done in the dry season. The sample from Kambele 1 was collected in a semi-mechanised treatment plant (N 4°26'40"N and 14°24'27"E); that from Kambele 2 was taken from an artisanal gold treatment site (4°27'25"N and 14°26'6"E) and that from Dem was collected from an artificial water body (4°27'26"N and 14°26'22"E). In each of these sampling points, 10 water samples were randomly collected and mixed together, to constitute one composite sample from each point. The three composite wastewater samples were stored in clean sterilized polyethylene bottles, in coolers and taken to the laboratory of Soil Science of the Faculty of Agronomy and Environmental Sciences of the University of Dschang (Cameroon) for analysis.

Similarly, 50 kg of corn cobs was collected from a local farmer in Bamenda (North-west Cameroon) for the production of activated carbons for the wastewater treatment.

The chemical reagents $ZnCl_2$, NaOH, KH_2PO_4 and $Al_2(SO_4)_3$) were purchased in ATITEL SARL in Mvog-Mbi (Yaoundé). The choice of this three chemical for impregnation of the carbon material is based on the fact that they are the most commonly used in literature [27]. The chemical most often chosen for impregnation typically consist of an acid, strong base, or a salt (phosphoric acid 25%, KOH 5%, NaOH 5%, K_2CO_3 5%, $CaCl_2$ 25%, and zinc chloride 25%).

2.3. Production of AC

The ACs were produced at MIPROMALO (Local Materials Promotion Authority) in Yaoundé through chemical and thermal activations. Thus, clean and dry corn cobs were crushed between 1 and 2 cm, washed and dried. 25 g of each respective chemical reagent ($ZnCl_2$, NaOH, and KH_2PO_4) was added to 0.5 L of distilled water and stirred. The resulting solutions were poured in three polyethylene sampling bags each containing 250 g of dry crushed corn cobs. The mixtures were allowed to rest for 24 hours. This was to allow the cobs to adsorb the chemical reagents. After this step, each corn cob, now impregnated with the respective chemical reagent, was collected and oven-dried at 70 ℃ for 24 hours. The final product obtained was carbonised in a furnace (without oxygen) between 500-700 ℃ temperatures. The carbon obtained was washed with distilled water (to remove ash) and dried, ready for use. The flowchart of the activation process is show in Figure 3.

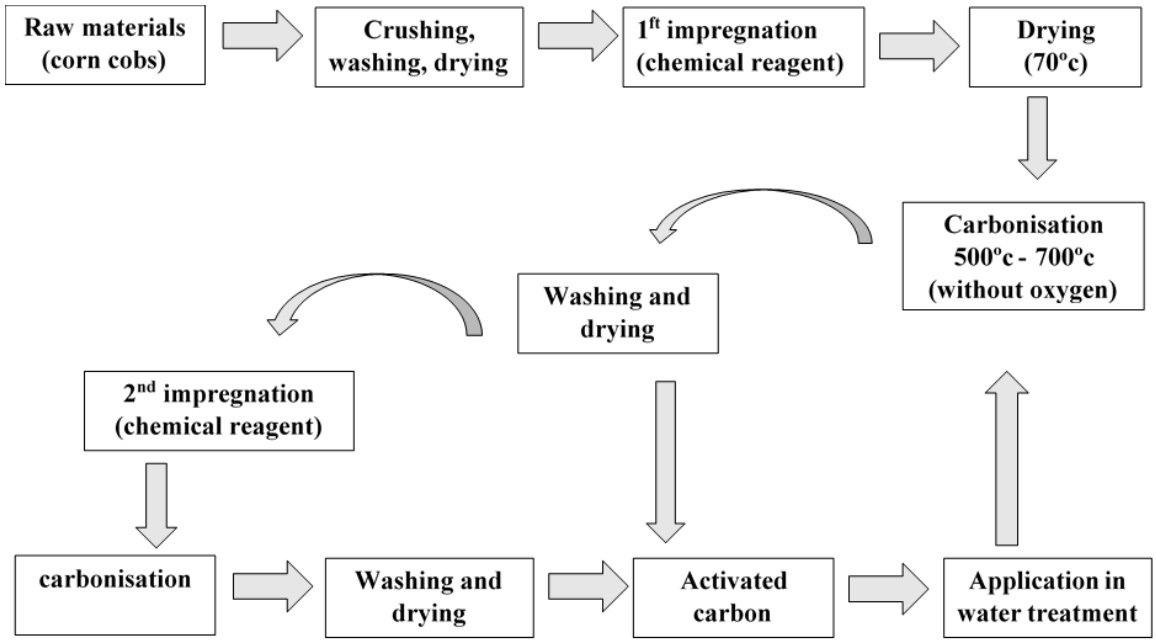


Figure 3. *Flowchart of the activated carbon production process.*

2.4. Laboratory Analysis of Water

The wastewater analysis was done in Laboratory of Soil Science of the Faculty of Agronomy and Agricultural Science of the University of Dschang (Cameroon). Major ions (sodium, potassium, calcium, magnesium, chloride, bicarbonate, sulphate and nitrate) were determined using standard techniques already approved by the American Public Health Association [3]. Thus, flame photometry was used to analyse Na^+ and K^+; colorimetry was used for Ca^{2+} and Mg^{2+} and heavy metals [34]. Volumetric methods enabled to determine bicarbonate (HCO_3^-), phosphate (PO_4^{3-}) and sulphate (SO_4^{2-}) [3]. The physico-chemical properties (conductivity, turbidity, pH) were done by screening and sedimentation [3]. The total hardness (TH) was deduced from equation (1):

$$TH = 2.5Ca + 4.1Mg \quad (1)$$

To determine the suitability of the studied groundwater for irrigational purpose, equations (2) and (3) were used to compute for the values of Na% and SAR [34].

$$\text{Sodium Percentage (Na\%)} = \frac{Na+K}{Ca+Mg+K+Na} \times 100 \quad (2)$$

$$\text{Sodium adsorption ratio (SAR)} = \frac{Na}{\sqrt{Ca+Mg/2}} \times 100 \quad (3)$$

2.5. Wastewater Treatment Using ACs from Corn Cobs

After production, each AC was crushed to a specific particles size: AC with $ZnCl_2$ (500 µm; 1 mm), AC with NaOH (1 mm), AC with KH_2PO_4 (2 mm). AC$ZnCl_2$ was crushed to two sizes so as to determine the ideal particle size for optimum efficiency of the AC. Wastewater was treated in a very simple way using five principal steps consisting of screening, sedimentation, impregnation of ACs, agitation and filtration. Only the water from the most contaminated site was used. This step started with screening using a 500 µm sieve mesh and sedimentation, to remove part of suspended and floating materials and also to allow the heavy materials to settle at the bottom. Thus, three samples of 0.5 L of wastewater from these first stages were collected at temperature between 20 ℃ and 23 ℃ and 25 g of each specific AC was added to each of them. The mixtures were then stirred for 15 minutes and allowed to rest for 45 minutes to allow the ACs to physically and chemically react with the contaminants. After resting, each mixture was filtered using a 0.5 mm thick filter paper of 10 µm pore size (Figure 4 (a), (b), (c), (d)). The final AC-treated waters were taken for chemical and physical characterisation.

Figure 4. *Various steps of the mine wastewater treatment using activated carbons (a) impregnation of activated carbon, (b) filtration of treated water, (c) resulting activated carbons ready for reactivation, (d) resulting treated water with activated carbons); using the $Al_2(SO_4)_3$ (e) sedimentation after reaction with $Al_2(SO_4)_3$), (f) filtration of treated water, (g) resulting treated water with the $Al_2(SO_4)_3$ ($Al_2(SO_4)_3$), (h) resulting $CaSO_4$ (tailing).*

2.6. Wastewater Treatment Using $Al_2(SO_4)_3$ (Control)

As stated above, the treatment of wastewater from the most contaminated site (Kambele 2) started by screening with 500 µm sieve aperture and sedimentation, to remove part of suspended and floating materials, and allowed heavy materials to settle at the bottom. A sample of 0.5 L of wastewater from these first stages was collected at temperature between 20 ℃ and 23 ℃ and 0.5 g of $Ca(OH)_2$ added to it. The solution was slowly agitated for 20 minutes, after which, 0.5 g of $Al_2(SO_4)_3$ was added and the overall solution gently stirred for 20 minutes (coagulation and flocculation). The solution was allowed to rest for 10 hours (secondary sedimentation) and treated water was filtered using a filter paper of 0.5 mm thickness and 10 µm pore size (Figure 4 (e), (f), (g), (h)). The treated sample was taken with the three others for laboratory analysis.

2.7. Characterisation of Measurements

Chemical reagents concentration

$$C = m/MV \quad (4)$$

Where: C is the reagent concentration; m is the mass of reagent used; M is the molar mass of reagent; and V is the volume of distilled water used in solution.

Contaminant absorption percentage

$$\Omega = \mu \times 100/ C_o \quad (5)$$

$$\mu = C_f - C_o \quad (6)$$

Where: Ω is the % Contaminant absorption; µ the concentration difference (mg/l); Co the initial concentration of contaminant (mg/l); and Cf is the final concentration of contaminant after treatment (mg/l).

Extraction efficiency of chemical contaminants based on particle size of AC $ZnCl_2$

A comparative diagram of extraction capacity was drawn based on concentration difference of contaminants before and after treatment with AC $ZnCl_2$, and carbon particle size:

$$\partial = C_f - C_o / X \quad (7)$$

Where: ∂ is the extraction capacity; X is the particle size of $ZnCl_2$; Co the initial concentration of contaminant (mg/l); and C_f the final concentration of contaminant after treatment (mg/l).

2.8. Characterisation of Treated Water

Treated water from each AC and $Al_2(SO_4)_3$ was characterised while taking into consideration their physical and chemical properties, and especially their chemical contaminants concentration.

During laboratory analysis of wastewater, a control sample (distilled water) and a known proportion of a targeted contaminant was prepared under each characterization method. Before, during and after each water treatment, the temperature was maintained between 20 ℃ and 23 ℃ so as to reduce the influence of temperature on results outcomes. During the entire process all the equipment were washed with distilled water of known pH after every step of treatment so as to avoid contamination or any other chemical that could impact the sample integrity. Each experiment was replicated thrice and the mean value was recorded.

3. Results

3.1. Characteristics of Wastewater from the Gold Mining Areas in Batouri

Wastewater from Kambele 2 was the most contaminated by major anions (NO_3^-, PO_4^{3-} and HCO_3^-) with concentrations all above WHO [37] and national values (Table 1), with high potential of acid generation as shoen in Table 2. This was followed by wastewater from Dem, and the one from Kambele 1 was the least contaminated by major anions. However, the concentration of PO_4^{3-} was within national norm for all the three sites and would not trigger the process of eutrophication. The wastewater from Kambele 1 and Kambele 2 were highly contaminated with heavy metals such as Pb, Mn, Ni, Fe, Hg and Cd respectively all 20 to 500 times above International and National recommended values (Table 1). This was followed by wastewater from Dem, with the lowest heavy metal concentrations, but still out of WHO [37] and national norms. Only Pb and Ni in Kambele 2 had acceptable concentrations within the WHO norms [37]. All physico-chemical properties of wastewater from all the three sites (Table 2) where within acceptable levels [37]. The wastewaters of Kambele 2 and Dem were very hard (1249 and 1383.16 mg/l) while that of Kambele1 is hard [3]. The sodium percentage is highest for Kambele 1 (22.24 %), followed by Kambele 2 (13.66 %) and lowest for Dem (10.98 %). The sodium adsorption ratio was very high for Kambele 2 and Dem but very low for Kambele 1.

Table 1. Chemical characteristics of the wastewaters raw wastewater and acceptable norms.

Parameter Chemicals		WHO norm permissible limit	National norm permissible limit	Kambele 1	Kambele 2	Dem
Major Cations (mg/l)	Ca^{2+}	/	270	4.72	447.12	508
	Mg^{2+}	/	/	2.62	32	27.6
	K^{+}	/	/	2.04	51.05	42.7
	Na^{+}	200	/	0.06	26.8	23.4
Major anions (mg/l)	NO_3^{-}	50	30	46	103.33	68.3
	PO_4^{3-}	0.3	10	7.02	0	9.6
	SO_4^{2-}	200	250	0.79	640	432.2
	HCO_3	500	/	24	152.5	108
(mg/l)	Fe	0.03	0.2	1.71	3.53	3.33
	Pb	0.01	1	646.88	0.41	7.8
	Hg	0.01	0.01	21.03	62.67	37.04
	Cd	0.03	1	35.97	533.95	219
	Mn	0.01	1	20.24	5.66	3.52
	Ni	0.07	1	23.45	0.21	7.19

3.2. Characteristics of Kambele 2 Wastewater After Treatment with ACs and $Al_2(SO_4)_3$

Concerning major cations, the concentration of Ca^{2+} in the wastewater was highly reduced to an acceptable value within national norm after treatment with ACNaOH, and $ACKH_2PO_4$. However, this Ca^{2+} concentration vividly increased with the $Al_2(SO_4)_3$ treatment. Despite the fact that there is no restriction for Mg^{2+}, K^{+}, and Na^{+}, the concentration of Mg^{2+} was reduced by ACNaOH, but increased with all other treatments. K^{+} level remained constant after treatment with $Al_2(SO_4)_3$, reduced with ACNaOH treatment, but increased drastically after treatment with $ACZnCl_2$ and $ACKH_2PO_4$. The Na^{+} content in wastewater was increased after $ACZnCl_2$ and $ACKH_2PO_4$ treatment (Table 3).

Table 2. Physio-chemical properties of the wastewaters raw wastewater and acceptable norms.

Parameter	WHO norm permissible limit	National norm permissible limit	Kambele 1	Kambele 2	Dem
pH	6.5 - 8.5	6.5 - 8.5	7.7	8.5	8.0
Electrical conductivity (µS/cm)	/	2	0.17	0.56	0.41
Turbidity (UTN)	/	/	57.2	23.4	22.0
Total hardness (mg/l)	/	200	128.72	1249.0	1383.16
Sodium percentage (Na %)	/	50	22.24	13.66	10.98
Sodium adsorption ratio (SAR)	/	2	3.13	178.72	142.99

Table 3. *Characteristics of wastewater from the most contaminated gold exploitation site (Kambele 2).*

Treatments methods	Particle size of ACs	Major cations (mg/l)				Major anions (mg/l)			
		Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	NO_3^{-}	PO_4^{3-}	SO_4^{2-}	HCO_3^{-}
Wastewater (Kambele 2)	/	447.12	32	51.05	26.8	103.33	0	640	152.5
WHO norm	/	/	/	/	200	50	0.03	200	500
National norm (permissible level	/	270	/	/	/	≤ 30	≤ 10	≤250	/
$Al_2(SO_4)_3$	/	1792	116.64	51.05	20.29	3.51	0	1160	164.7
$ACZnCl_2$	0.5mm	880	388.8	2449.11	168.19	3.51	0	120	36.6
	1mm	642	183	1761	93.08	7.41	0	203	64
ACNaOH	1mm	32	9.72	26.84	26.8	3.51	0	680	122
$ACKH_2PO_4$	2mm	256	58.32	1123.65	82.92	60.55	97.32	1400	213.5

Table 3. *Continued.*

Treatments methods	Particle size of ACs	Heavy metals (mg/l)						Physicochemical parameters	
		Fe	Pb	Hg	Cd	Mn	Ni	pH	EC (µS/cm)	Turb (UTN)
Wastewater (Kambele 2)	/	3.53	0.42	62.67	533.95	5.66	0.21	8.5	0.56	23.4
WHO norm	/	0.3	0.01	0.01	0.03	0.01	0.07	6.5-8.5	2	/
National norm (permissible level	/	≤0.2	≤ 1	≤0.01	≤ 1	≤ 1	≤ 1	/	/	/
$Al_2(SO_4)_3$	/	0.28	0.31	135.6	646.36	0.65	0	11.1	1.35	21
$ACZnCl_2$	0.5mm	0.21	0.93	16.77	758.77	0.65	0	6.7	4.75	37.5
	1mm	0.32	0.97	27.3	529	0.55	0	7.3	5.04	26
ACNaOH	1mm	0.28	10.35	0	562.05	0.68	1.02	11.12	8.45	29
$ACKH_2PO_4$	2mm	2.12	0.72	24.91	477.74	2.89	1.25	8.1	1.26	74

For Major anions, the concentration of PO_4^{3-} was 0 mg/l in both raw and treated water, except for $ACKH_2PO_4$ treated water where PO_4^{3-} increased from 0 to 97.32 mg/l, above WHO and national norms. The concentration of NO_3^{-} in wastewater was highly reduced below the highest national recommended value and through all the treatment methods; except $ACKH_2PO_4$ that enabled reduction of value but not till the norm. The SO_4^{2-} concentration increased with $ACKH_2PO_4$ and $Al_2(SO_4)_3$, but HCO_3^{-} was reduced only with $ACZnCl_2$ treatment even if no restriction on its concentration in environmental water was found (Table 3). For heavy metals, none of the treatment methods has a meaningful impact on Cd removal. The small quantity of Ni present in the wastewater was completely removed by the $Al_2(SO_4)_3$ and $ACZnCl_2$, but the concentration of the same Ni increased after treatment with ACNaOH, although still within acceptable limit (≤ 1 mg/l). On other hand, Ni concentration was above the norm after treatment with $ACKH_2PO_4$. Hg was significantly removed by $ACKH_2PO_4$ and $ACZnCl_2$, but the concentration in treated water was still 10 to 20 times above WHO and national recommended values. Treatment with the $Al_2(SO_4)_3$ instead raised the level of Hg, meanwhile ACNaOH alone removed

100% of Hg from the wastewater. The concentrations of Fe, Pb, and Mn in the wastewater were consistently reduced to the national norm (≤ 1 mg/l) using $ACZnCl_2$ and the $Al_2(SO_4)_3$ treatments. ACNaOH also reduced Fe and Mn concentrations relative to the norm but Pb increased tremendously (Table 3). Similar results have been reported by [23].

The electrical conductivity and turbidity of water treated with ACs and $Al_2(SO_4)_3$ were within acceptable level of WHO. Only the pH of water treated by $Al_2(SO_4)_3$ and ACNaOH were too high and above acceptable values (Table 3).

3.3. Evaluation and Comparison of Treatment Methods

3.3.1. Based on Contaminant Concentration Difference After Treatment and Chemical Reagent Used

The concentration of Ca^{2+} in initial wastewater considerably dropped upon treatment with $ACKH_2PO_4$ and ACNaOH, but increased with $ACZnCl_2$ and the $Al_2(SO_4)_3$. The ACNaOH was the only agent to reduce the concentration of Mg^{2+} in wastewater (-22.28 mg/l), compared to the other methods that instead increased it; especially $ACZnCl_2$ that increased the value with 356.8 mg/l. The $ACKH_2PO_4$ and $ACZnCl_2$ increased the concentration of K^+ in the water compared to the other methods. The ACNaOH slightly reduced the concentration of K^+ in wastewater, and the $Al_2(SO_4)_3$ did not show any effect on K^+. The concentration of Na^+ in the wastewater was principally increased through treatment with $ACKH_2PO_4$ and $ACZnCl_2$. The $Al_2(SO_4)_3$ was more efficient than the other methods for sodium extraction (- 6.51 mg/l) (Table 4).

As for major anions, removal of NO_3^- from wastewater was efficient with all the methods, but $ACZnCl_2$, ACNaOH and the $Al_2(SO_4)_3$ were more efficient relative to $ACKH_2PO_4$ that only removed (- 44.78 mg/l). Since PO_4^{3-} was not detected in wastewater, no trace of it was found after treatment using all the methods, except with $ACKH_2PO_4$ that led to concentration increase from 0 to 97.32 mg/l. The concentration of SO_4^{2-} in the wastewater increased upon treatment with ACNaOH, $ACKH_2PO_4$ and the $Al_2(SO_4)_3$. Only treatment with $ACZnCl_2$ enabled to strongly eliminate SO_4^{2-} (- 520 mg/l). Same as SO_4^{2-}, $ACZnCl_2$ was highly efficient in the extraction of HCO_3^-, followed by ACNaOH. The other methods instead increased the concentration: 12.2 mg/l for the $Al_2(SO_4)_3$ and 61 mg/l for AC KH_2PO_4 (Table 4).

Table 4. Efficiency evaluation treatment methods and comparison for chemical contaminant extraction.

Treatment method	Chemical concentration difference (μ) (mg/l)													
	Major cations				Major anions				Heavy metals					
	Ca^{2+}	Mg^{2+}	K^+	Na^+	NO_3^-	PO_4^{3-}	SO_4^{2-}	HCO_3^-	Fe	Pb	Hg	Cd	Mn	Ni
$Al_2(SO_4)_3$	1314.88	84.64	0	-6.51	-99.82	0	520	12.2	-3.25	-0.11	72.93	112.41	-5.01	-0.21
AC $ZnCl_2$ (0.5 mm)	432.88	356.8	2398.06	141.39	-99.82	0	-520	-115.9	-3.32	0.51	-45.9	224.82	-5.01	-0.21
AC $ZnCl_2$ (1 mm)	194.88	151	1709.95	66.28	-95.92	0	-437	-88.5	-3.21	0.55	-35.37	-4.94	-5.11	-0.21
AC NaOH (1 mm)	-415.12	-22.28	-24.21	0	-99.82	0	40	-30.5	-3.25	9.93	-62.67	28.1	-4.98	0.81
AC KH_2PO_4 (2 mm)	-191.12	26.32	1072.6	56.12	-42.78	97.32	760	61	-1.41	0.3	-37.76	-56.21	-2.77	1.04

Concerning heavy metals, all the treatment methods were efficient for Fe removal in wastewater, especially $ACZnCl_2$ with (-3.32 mg/l), followed by the $Al_2(SO_4)_3$ with (-3.25 mg/l). Pb removal was only effective with the $Al_2(SO_4)_3$ (- 0.11 mg/l), meanwhile $ACKH_2PO_4$ and $ACZnCl_2$ treatments led to a slight increase in its concentration to 0.3 mg/l and 0.51 mg/l, respectively. Pb concentration increased by nine folds (9.93 mg/l) the initial level in the effluent following treatment with ACNaOH. ACNaOH was also the only AC to totally eliminate Hg (-62.67 mg/l), followed by $ACZnCl_2$ and $ACKH_2PO_4$. The $Al_2(SO_4)_3$ instead led to an increase in the Hg concentration in the water by 72.93 mg/l. The Cd levels in the wastewater reduced by -56.21 mg/l following $ACKH_2PO_4$ treatment, meanwhile the other methods were inefficient and instead stepped up Cd levels in the water. Mn was considerably removed with all treatment methods, but $ACZnCl_2$ and the $Al_2(SO_4)_3$ similarly performed better than the others. Ni concentration in water increased with $ACKH_2PO_4$ treatment

(0.81 mg/l) and ACNaOH (1.04 mg/l); ACZnCl$_2$ and the Al$_2$(SO$_4$)$_3$ removed 100% of Ni in the wastewater.

The physico-chemical properties revealed that ttreatment with Al$_2$(SO$_4$)$_3$ did not have any physical damage on water quality, but instead made the water clearer, just as ACZnCl$_2$. However, the Al$_2$(SO$_4$)$_3$ increased the water pH from 8.5 to 11.1, same as ACNaOH from 8.5 to 11.2 (Figure 5).

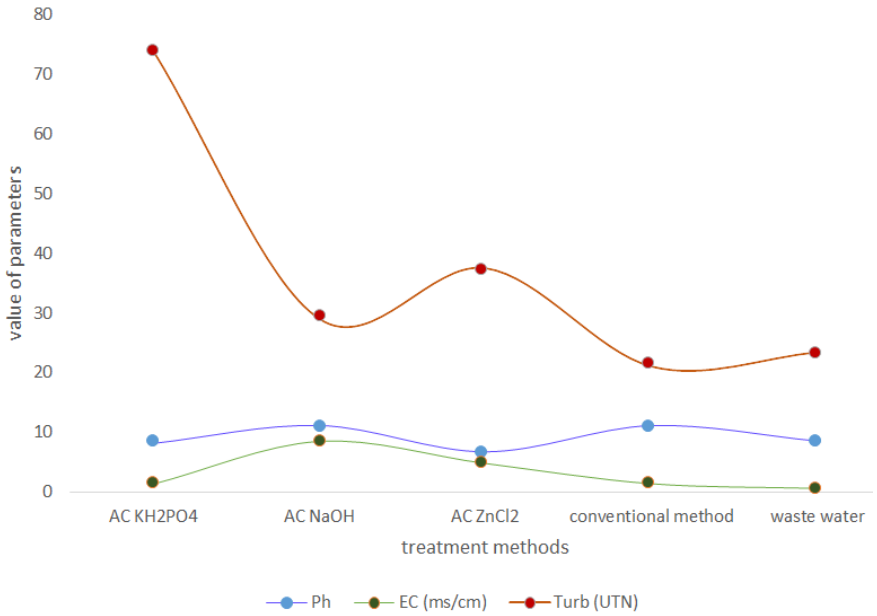


Figure 5. *Variation of pH (Ph), electrical conductivity (EC) and turbidity (Turb) of the mine wastewater after treatment according on treatment methods.*

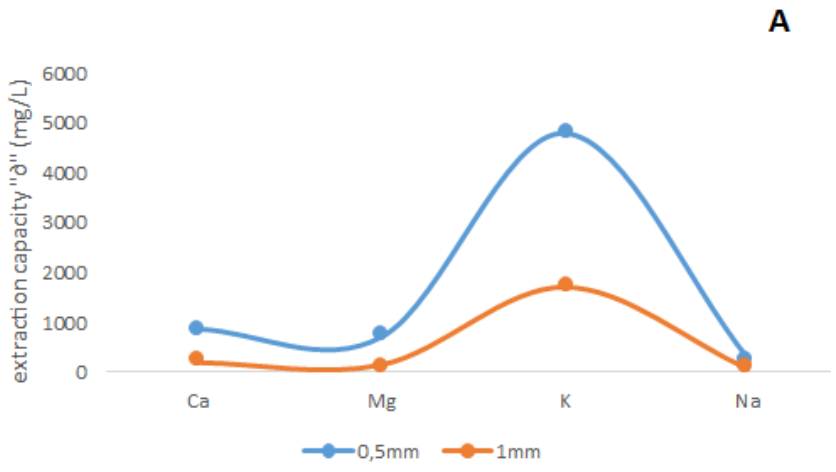
3.3.2. Effect of Particle Size on Capacity of AC: Case of AC ZnCl$_2$

Wastewater was treated with two different particle sizes of AC ZnCl$_2$ (0.5 mm and 1 mm), so as to identify and evaluate the ideal size for each major contaminant extraction.

For major cations, both 0.5 and 1 mm AC ZnCl$_2$ were inefficient for removal of major cations. Their concentration (Ca^{2+}, Mg^{2+}, K^+, and Na^+) instead increased after treatment (Table 4). However, 1 mm AC ZnCl$_2$ was less damaging than 0.5 mm, since it did not increase contaminants at the same rate (Figure 6a).

For major anions, 0.5 mm AC ZnCl$_2$ was more efficient than 1 mm grain size in the removal of all major inions and especially NO_3^-, HCO_3^-, and SO_4^{2-} (Figure 6b).

Finally, for heavy metals, 0.5 mm AC ZnCl$_2$ was more efficient than 1 mm in removal of Fe, Hg, and Mn. The concentration of Ni remained unchanged. Both 0.5 and 1 mm AC ZnCl$_2$ were inefficient for Pb extraction, but its value remained within international norms (Figure 6c).



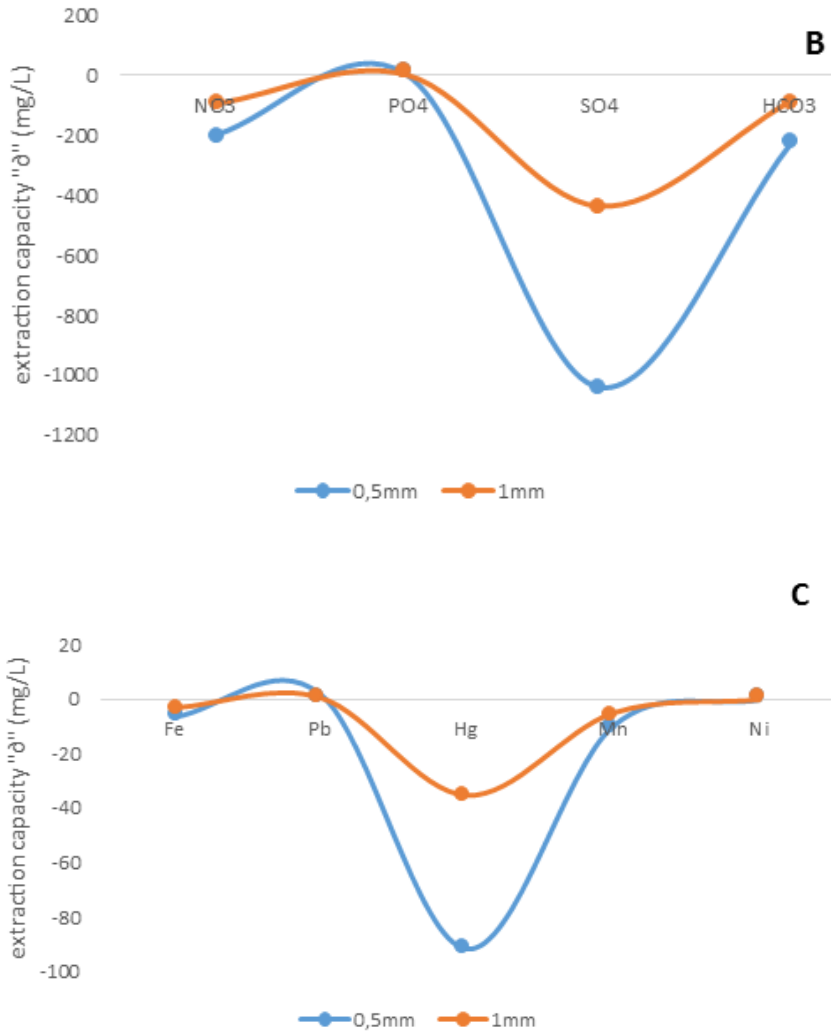


Figure 6. *Extraction capacity of major cations (A), major anions (B) and heavy metal (C) contaminants present in the mine wastewater as a function of particle size of* $ACZnCl_2$.

4. Discussions

4.1. Water Quality in Batouri (Kambele 1, Kambele 2, and Dem)

The increase of industrial activities and water consumption has been causing environmental problems leading to an environmental imbalance, necessitating wastewater quality assessment and improvement [2]. In gold mining areas of Batouri, sample of wastewater from Kambele 2 collected from an artisanal gold treatment site was the most contaminated by cations (Mg^{2+}, K^{+}, Na^{+}) and anions (NO_3^{-}, SO_4^{2-}, HCO_3^{-}). This was followed by wastewater from Dem collected from an artificial lake. Heavy metal content in different water bodies has recently become a prime concern [14, 16, 26]. Kambele 1 and Kambele 2 were the most contaminated by heavy metals (Pb, Mn, Ni and Hg, Cd, Fe respectively). The presence of these heavy metals and major ions in wastewater from these areas is principally due to chemicals from excavated ground during gravity separation of gold and those used for gold concentration. Similar results have already been documented [15, 26, 28, 29]. According to [4], weathering of geological units, mining activities and seasons have a major influence on the water quality. Therefore, it appears that decision-makers must take immediate action to decrease pollution and adopt suitable and sustainable remedial solutions. All the waters are recommendable for irrigation based on Na% but the SAR is above acceptable limits for irrigation water based on WHO [37].

4.2. Effect of Different Treatments on Water Quality

The concentration Ca^{2+} dramatically increased with the $Al_2(SO_4)_3$ of water treatment due to the use of $Ca(OH)_2$ in the treatment process. The concentration K^{+} also increased after treatment with $ACZnCl_2$ and $ACKH_2PO_4$ probably because of presence of K in the chemical reagents used [20]. The concentration of PO_4^{3-} in water increased from 0 mg/l to

97.32 mg/l after treatment with $ACKH_2PO_4$ due to the presence of phosphate within the chemical reagent used for carbon activation. The concentration of SO_4^{2-} increased when using the $Al_2(SO_4)_3$ probably because of inappropriate quantity of $Al_2(SO_4)_3$ used in the treatment. Similar results were reported by [2, 3]. The 100% absorption of Fe with AC size of 60 mesh, and at a temperature of 45 ℃ and the maximum absorption of Mn was 11.91 % in the treatment with an AC size of 60 mesh and at the temperature of 55 ℃. While in this study, the extraction of 3.53 mg/l Fe(II) and 5.66 mg/l Mn(II) from 0.5 L of gold mine wastewater using 25 g of corn cobs AC grain size of 0.5 mm, and chemically activated with 25 % $ZnCl_2$ and 25% NaOH solutions respectively, resulted in 94.05 % Fe(II) and 88.51% Mn(II) extraction with AC $ZnCl_2$, and 92.06 % Fe(II) and 87.98 % Mn(II) extraction with ACNaOH. The high rates of Mn(II) absorption in this work might have been due to the porosity and absorption capacity of the corn cobs used for AC production. [27, 31-36] reduced heavy metals concentration in mine wastewater with ACs prepared from coconut shells enabled to reduce Fe, Mn, and Pb ions of 3.242 mg/l, 1.62 mg/l, and 0.002 mg/l, respectively, to environmentally acceptable limits. However, in the present study, only $ACKH_2PO_4$ was inefficient in Fe and Mn removal to acceptable limits, and the $Al_2(SO_4)_3$ treatment led to drastic removal of Pb. Thus, depending on the initial raw materials and chemicals used, different types of AC are obtained with different performances [1]. Author [7] reported removal of Pb^{2+} (1.56 mg/l), Cu^{2+} (87 mg/l), and Cd^{2+} (0.69 mg/l) from mine wastewater using 25 g AC prepared from coconut husk; This AC also reduced the concentration of heavy metals below Ghana environmental protection agency standard as 0.10 mg/l, 1.30 mg/l, and 0.03 mg/l, respectively). The results of the present work also agree with those of [36], whereby AC from seeds of *Albizia lebbeck* and *Melia azedarach* trees enabled removed of 75 and 62 % Pb and 77 and 66 % Cd from wastewater. In the present study, none of the corn cobs AC was efficient in Cd removal. According to [8], addition of 1 g corn cob AC decreased level of Fe, Cu and Pb as much as 60%; 59 % and 59% respectively, meanwhile 1.5 g corn cob AC increased efficiency by removing as much as 80 %, 79 % and 79 % respectively for those three metals. Concerning physico-chemical parameters, the pH of water treated with AC NaOH and the $Al_2(SO_4)_3$ were relatively high probably due to the presence of NaOH and $Ca(OH)_2$ respectively, which are actually basic elements.

4.3. Influence of AC Particle Size on Contaminant Extraction Capacity

This work revealed that 0.5 mm particles of $ACZnCl_2$ was more efficient in removal of major anions and heavy metals than 1 mm particles of the same AC as already reported by [22]. This is probably due to the fact that with 0.5 mm, larger surface area of $ACZnCl_2$ is more exposed to adsorb the chemical contaminants. However, 0.5 mm $ACZnCl_2$ was inefficient in extraction of major cations than 1 mm, showing that particle size is an important parameter to consider when using ACs for water purification.

4.4. Economic Implications of the Different Treatments

All the ACs were cheaper in term of production compared to the control ($Al_2(SO_4)_3$) (Table 5). The cheapest AC in terms of production were $ACZnCl_2$ and ACNAOH with benefic-to-cost ratio of 2.6 each. These two AC enables to have an extra benefit of 160 % over the conventional $Al_2(SO_4)_3$. This two ACs are therefore recommendable, especial as they also showed higher performance in terms of removal of pollutants from water compared to the $Al_2(SO_4)_3$.

Table 5. *Economic implications of the different treatments.*

Treatments	Cost of 10 kg (FCFA)	MR (FCFA)	II (4.25%)	OC (FCFA)	BCR	PR (%)
$Al_2(SO_4)_3$	11 468	0	468	11468	0	0
$ACZnCl_2$	3000	8000	128	3128	2.6	160
ACNaOH	3000	8000	128	3128	2.6	160
$ACKH_2PO_4$	4500	7500	191	4691	1.6	60

MR=Marginal return; II= Interest on investment; PR=profit rate; BCR=benefit-to-cost-ratio; OC=operation cost; 1 USD is about 600 FCFA.

4.5. Limitations of Activated Carbons and Specific Future Research Areas

Activated carbon is crucial for cleaning water because it can remove numerous types of pollutants [20-25, 27, 36]. However, the search for better, cheaper, and more eco-friendly cleaning materials needs to continue. This is because wastewater is getting more complicated and environmental laws are becoming stricter, pushing for new and improved methods beyond the usual ones [17, 21, 27]. The advent of nanotechnology marks a significant change in the development of materials used for adsorbent development. This technology allows for the manipulation of materials at a molecular scale, leading to higher efficiency in capturing pollutants. Innovations such as carbon nanotubes, graphene, metal-organic frameworks, and nano-structured polymers are at the forefront, offering better performance, specificity, and reusability than older methods. These nano-scale materials demonstrate the possibility of precisely removing specific pollutants, such as heavy metals, organic compounds, and new threats like drugs and hormone disruptors, establishing a new standard for water purification technology [29]. The production cost of AC can be high depending on the method of production. Production of ACs require High energy consumption, necessitating sustainable production and disposal methods. The results of the SWOT analysis are summarised in Table 6. A comparison between AC and some adsorbents is shown in Table 7.

4.6. Future Research Areas

The transition from conventional to advanced methods has been strongly supported by ground-breaking developments in material science and environmental engineering. Traditional approaches, primarily centred on activated carbon and zeolites, have set the stage for the emergence of sophisticated techniques employing novel materials like carbon nanotubes, metal-organic frameworks and graphene-based structures [27, 29]. This evolution reflects a dynamic interplay of factors such as efficacy, cost-effectiveness, environmental sustainability and technological feasibility [22, 23]. The future of adsorption technology holds exciting possibilities for further breakthroughs in water purification and environmental sustainability. Some potential areas of advancement that could revolutionize adsorption technology include: development of highly selective and efficient adsorbents, incorporation of advanced materials, design of integrated adsorption systems, application of machine learning and artificial intelligence, development of sustainable and cost-effective adsorbents, in-situ remediation and point-of-use systems, tailoring adsorbents for emerging pollutants, regeneration and reuse of adsorbents, understanding adsorption mechanisms at the molecular level and the integration of adsorption technology with circular economy principles.

Table 6. *SWOT analysis of activated carbon from corn cobs in wastewater treatment.*

Factors	Activated carbons from corn cobs
Strengths	Good in extraction of Ni, Hg, Fe, Pb, Mn, NO_3^- and HCO_3 Almost no need of electrical energy; Easy and fast to operate even to non-experts; Possibility of regeneration after use; Waste carbon can be used as charcoal for thermal energy; High availability of corn cobs as raw material for AC production; Can be used for both water and air purification; wide field of application; More efficient than $Al_2(SO_4)_3$) as it can be designed to adsorb a specific element; Relatively Cheaper than $Al_2(SO_4)_3$).
Weaknesses	Poor in Cd extraction; The pH of water might vary depending on chemical reagent used for activation; Require larger surface area than $Al_2(SO_4)_3$ for water treatment; High cost of activated carbon compered to chemicals used in the $Al_2(SO_4)_3$.
Opportunities	Constant growing market demand; Applicable in health, cosmetics, environmental management, etc for specific toxins adsorption.
Threats	Possibility to increase electrical conductivity; Possibility of carbonic acid generation; Rick of diseases due to poor handling.

Table 7. Comparison between the activated carbon and some common adsorbents in literature [20-22, 29].

S/N	Parameter	Activated Carbon	Bentonite Clay, Biochar	Nanoadsorbents
1	Synthesis Technique	Physical/Chemical Activation (Activated Carbon)	Natural Formation/Modification (Bentonite Clay), Pyrolysis of Biomass (Biochar)	Nanofabrication (Graphene Oxide-ZnO), Chemical Synthesis/Nanofabrication (Metal Oxides), Polymerization Techniques (Dendritic Polymers)
2	Principle	Surface Adsorption	Ion Exchange (Bentonite Clay), surface activation (biochar)	Enhanced Surface Adsorption, Chemical Interaction, Molecular Recognition
3	Adsorption Limit	Moderate, limited by surface area and pore structure	Moderate, limited by surface area and pore structure	High, enhanced by engineered surface areas, functional groups, and nanostructures
4	Advantages	Simplicity, natural availability, cost-effectiveness	Simplicity, natural availability, cost-effectiveness	Higher efficiency, specificity for contaminants, reusability, advanced control over adsorption properties
5	Some applications	General water purification, removal of common pollutants	General water purification, removal of common pollutants	Targeted removal of specific contaminants, complex wastewater streams, heavy metal, and organic pollutant removal
6	Specific pollutants targeted	Organic compounds, Chlorinated compounds, Heavy metals	Cations (e.g., Na+, K+), Heavy metals (e.g., Pb, Cd) (Bentonite), Organic pollutants, Heavy metals, Phosphates (biochar)	Trace pollutants, Heavy metals, Organic compounds;
7	Efficiency (%)	High (up to 90-100 % removal of some heavy metals)	Moderate to high (bentonite), moderate (biochar)	Very High (efficient even at low concentrations)
8	Environmental impact	Moderate (requires energy-intensive production, but low waste generation	Low (natural and synthetic varieties with minimal environmental impact) (bentonite), Low (sustainable and environmentally friendly, but with variable efficiency) (biochar)	High (concerns about stability and nano-particle release into the environment, Potential ecological risks
9	Sustainable consideration	Requires sustainable production and disposal methods	Often involves natural, abundant materials (bentonite), Utilizes waste materials, reduces greenhouse gases (biochar)	Requires careful assessment of lifecycle impacts
10	Ease of synthesis	Moderate (energy- intensive process)	Moderate, less energy- intensive than activated carbon (bentonite), High (relatively simple production from biomass (biochar)	Low (complex and costly synthesis)
11	Regeneration Capability	High generation capacity	Moderate (ion-exchange capacity can diminish over time)(Bentonite), Low (limited regeneration capability) (biochar)	Varies (some can be regenerated, others are single-use)
12	Economic aspect	Good (can be regenerated but Moderate-High production and regeneration	Moderate (cost-effective for specific applications) (bentonite), Low (cost-effective, especially when produced from waste biomass) (biochar)	High (due to advanced technology and materials used)

5. Conclusions

This study aimed to test the efficiency of three types of AC from corn cobs for treatment of mining wastewater. The main results revealed that the mining site of Kambele 2 is the most contaminated with major ions and heavy metals compared to those of Kambele 1 and Dem. The wastewater was

highly improved using $ACZnCl_2$, ACNaOH and the $Al_2(SO_4)_3$) (control). The ACNaOH treatment was more efficient than the $Al_2(SO_4)_3$ (control) and other ACs for cations extraction, and was the only treatment to adsorb 100% of Hg in the wastewater. $ACKH_2PO_4$ was inefficient in the extraction of major ions and heavy metals. $ACZnCl_2$ was most efficient for the removal of major anions among the three ACs and the control. Looking at ACs in general, AC $ZnCl_2$ was more efficient than $ACKH_2PO_4$ and ACNaOH in adsorption of Fe, Mn and Ni. Only the control enabled to reduce the concentration of Pb, NO_3^-, Fe and Mn. Based on particle size, the smaller the particle size of the AC, the better the adsorption capacity in terms of heavy metals and anions, but the lower the removal capacity of major cations. All three ACs were cheaper in terms of production compared to $Al_2(SO_4)_3$). Also, $ACZnCl_2$ (BCR=2.6) and ACNaOH (BCR=2.6) were more economical in terms of production cost than $ACKH_2PO_4$ (BCR=1.6). $ACZnCl_2$ and ACNaOH can therefore be recommended for popularization. The work thus finds its interest in environmental management and the promotion of the use of local material.

Abbreviations

AC	Activated Carbon
AC $ZnCl_2$	Activated Carbon Using $ZnCl_2$
AC NaOH	Activated Carbon Using NaOH
AC KH_2PO_4	Activated Carbon Using KH_2PO_4
BCR	Benefit-to-cost ratio
EC	Electrical Conductivity
FASA	Faculty of Agronomic Science
GPS	Global Position System Receiver
II	Marginal Return
MR	Interest on Investment
MINEPDED	Ministry of Environment, Natural Protection, and Sustainable Development
MIPROMALO	Local Materials Promotion Authority
OC	Operation Cost
PR	Profit Rate
NTU	Nephelometric Turbidity Unit
SWOT	Strengths, Weaknesses, Opportunities and Threats
WHO	World Health Organization

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Conflicts of Interest

The authors declare no conflicts of interest.

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