



Waste to resource: Utilization of waste bagasse as an alternative adsorbent to remove heavy metals from wastewaters in sub-Saharan Africa: A review

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ABSTRACT

Heavy metals pollution of both surface and groundwater sources of sub-Saharan Africa is alarmingly increased due to unplanned urban populations. Inadequate policies for water management, political commitment, and financial resources forced 65% of rural communities of sub-Saharan Africa to live in economic water stress areas. Sugarcane bagasse (SCB) shows high heavy metals (HMs) adsorption capacity (20–700 mg/g) through chemical entrapments to carbon-oxygen containing functional group and interior pore filling of porous surface. Various modifications like a physical/thermal, chemical, and composite form of bagasse show better adsorption performance for HMs removal. Kinetic and isotherm studies of HMs adsorption equilibrium data over SCB show that both Langmuir and Freundlich adsorption isotherms (cooperative adsorption) as the main adsorption mechanism. In addition, SCB shows potential bio-adsorbent properties for the selective adsorption of target HMs based on their physicochemical properties and shows good repeatability in acid environments. It is believed that information on this review will shed light on the current and future prospects of raw and modified SCB for HMs adsorption removal capacity. Sugarcane bagasse shows a remarkable selectivity for HMs adsorption removals based on their physicochemical properties and shows good potential capability for future utilizations in real wastewaters of developing countries.

Key words: adsorption mechanism, bio-adsorbent, heavy metals, regeneration, sugarcane bagasse

HIGHLIGHTS

- Bio-adsorbent (e.g. sugarcane bagasse) can be regenerated.
- Sugarcane bagasse has high adsorptive capacity for both anion and cation heavy metals.
- Cooperative adsorptive mechanism is well explained by Freundlich and Langmuir isotherms.

INTRODUCTION

The scarcity of fresh water is one of the 21st century's global challenges for developing countries and is increasing alarmingly due to improper disposal of urban and industrial wastes (Anastopoulos *et al.* 2017; Harripersadth *et al.* 2020). Currently, in developing countries such as in sub-Saharan Africa water consumption is increasing substantially to achieve sustainable economic development from different economic sectors in terms of both adequate quantity and acceptable quality for end-users. Reduction of freshwater consumption needs holistic approaches for the effective utilization of existing freshwater and quality enhancement strategies for used water to satisfy global water demands (Jones *et al.* 2021). Currently, water pollution by heavy metals (HMs) is increasing alarmingly day by day due to urban runoff, agricultural activities, mining, and industrial and domestic discharges into the aquatic environment (Agoro *et al.* 2020).

Heavy metals are chemical elements that have an atomic density greater than 4 g/cm³ (Aprile & Bellis 2019; Ayob *et al.* 2021). Among the heavy metals, cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), zinc (Zn), and iron (Fe) are today's primary concerns in the aquatic and terrestrial environment due to their toxicity, high mobility and solubility (Kong *et al.* 2014; Ali *et al.* 2019a). The unique features of heavy metals, such as

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bioaccumulation, non-biodegradability, and biological toxicity, make the existential threat very complex (Dong *et al.* 2016; Tran *et al.* 2017; Nkutha *et al.* 2020; Tejada-Tovar *et al.* 2020). The high concentration of heavy metals can be toxic or carcinogenic in nature and can cause severe problems to humans and aquatic ecosystems (Renu & Singh 2017; Jamshaid *et al.* 2018; Omran *et al.* 2019).

The most challenging issues for sustainable water management in sub-Saharan Africa are mainly rapid population growth (869 million in 2010 to 1.1 billion in 2019) (UN 2018), unplanned urbanization (Gashaye 2020), and inadequate policies and political commitments (Bhari *et al.* 2008; Bishoge 2021). Currently more than 77 million people live under critical water stress around the globe and the majority of them live in sub-Saharan Africa (GIZ 2019; Olagunju *et al.* 2019). In addition, the majority of sub-Saharan Africans exploit only up to 5% of annual renewable water resources due to the low level of investments in conservation, treatment technologies, and other infrastructures (United Nations General Assembly 2016; UN & WHO 2021).

Currently several robust and sophisticated technologies are utilized for heavy metals removal from wastewater such as ion exchange, reverse osmosis, chemical precipitation, electrocoagulation, electro-dialysis and adsorption (Harripersadth *et al.* 2020; Iwuozor *et al.* 2021a; Hamad & Idrus 2022). However, the aforementioned treatment methods are challenged by high initial costs, membrane fouling and high sludge production. In comparison with other processes, adsorption is a potential alternative treatment to existing technologies due to its low cost, simplicity of operation, low energy demand, recovery of heavy metals, good selectivity, and adsorbent regeneration options (Yu *et al.* 2020; Hassan *et al.* 2021; Younas *et al.* 2021).

In recent decades, various adsorbents including activated carbon (AC), biochar, clay, silica gel, zeolite, graphene oxide, nanomaterials, nanocomposites, polymers, and activated alumina have been widely utilized to remove organic and inorganic contaminants including heavy metals ions (Ali *et al.* 2018, 2019b; Hassan *et al.* 2020). Recently, there has been considerable interest in the gradual replacement of conventional materials with green and low-cost adsorbents. Among these adsorbents, biological materials – agricultural by-product residues as adsorbents to remove metals ions from aqueous solution – have had a lot of attention (dos Santos *et al.* 2019; Harripersadth *et al.* 2020; Hamad & Idrus 2022).

Bagasse constitutes the largest amount of solid waste from sugar factories (*Saccharum officinarum*) (Anastopoulos *et al.* 2017; Raza *et al.* 2021) and has huge potential in developing countries. Bagasse is one of the largest agricultural residues and 1,869.7 million tonnes of bagasse was harvested worldwide in 2020 (Faostat 2022). In Ethiopia, annually about 4.6% of total bagasse produced from sugar industries is dumped in the compounds around the factory, posing serious environmental problems, including fire hazards (Getu *et al.* 2021; Adane *et al.* 2022). Despite the Ethiopian government's waste product reduction/reuse policies for sugar processing industries, there are still many unresolved environmental issues that are to be addressed through valorization of waste bagasse in the circular economy.

The circular economy offers various tools for raising awareness of the recovery of waste through mitigation of excessive raw material consumption and reducing the disposal of wastes (Athira *et al.* 2021; Osorio *et al.* 2021). In most sugar industries, bagasse is mainly utilized in boilers to provide heat in the distillation process and ethanol production (Mbohwa & Fukuda 2003; Cueva-Orjuela *et al.* 2017). Although the energy from renewable biomass fuel is carbon neutral, when biomass fuels are burned in unventilated kitchens using smoky and inefficient conventional stoves with poor combustion, this results in a significant concentration of hazardous pollutants, primarily carbon monoxide and particulate matter, as well as nitrogen oxides and poly-aromatic hydrocarbons (Formann *et al.* 2020; Benti *et al.* 2021). Thus, a twofold problem in developing countries will be solved by integrated approaches of converting bagasse waste to value-added adsorbent for heavy metal removal from wastewater. This brings many advantages to bagasse waste management and provides low-cost, locally available alternative adsorbents (Anastopoulos *et al.* 2017; Sarker *et al.* 2017; Ungureanu *et al.* 2022).

The adsorption capacity of sugarcane bagasse (SCB) is due to its high porosity, high surface area, carbon-oxygen containing functional groups, and good stability for reuse (Ighalo *et al.* 2022; Mondal *et al.* 2022). Surface modification methods for bagasse increase its adsorption capacity towards heavy metals (Wang *et al.* 2017; Sarker *et al.* 2017; Tejada-Tovar *et al.* 2020; Irawan *et al.* 2021; Younas *et al.* 2021). The main objective of this review paper is to reveal comprehensive overviews on selective HMs adsorption capability of SCB for its future potential utilization in real wastewaters of low-income countries of sub-Saharan Africa.

WASTE BAGASSE UTILIZATION AND APPLICATIONS

In most developing countries, sugar industries were designed only for production in sugar mills and account for the generation of large quantities of the by-products bagasse (25–30%) after crushing sugarcane, press mud (3–5%) after clarification, and molasses (3.5–5%) after centrifuge (Botkin *et al.* 2012; Formann *et al.* 2020). In a highly competitive environment, the non-utilization of SCB ends up with a loss of resources without generation of revenues. However, most sugar industries burn bagasse in the furnace to produce electric power for the sugar factory (Thangavelu *et al.* 2016; Ajala *et al.* 2021). Open dumping of bagasse as waste is a common practice of sugar industries in most developing countries, including Ethiopia, after fulfillment of hot utilities such as steam and electric power. Thus, bagasse accounts for serious environmental problems including fire hazards (Fito *et al.* 2019; Getu *et al.* 2021).

In contrast to the traditional take-make-use-dispose strategy of a linear economy, a circular economy minimizes waste production, creates wealth from these by-products and maximizes reuse (Hysa *et al.* 2020; Osorio *et al.* 2021). Also, several environmental impact assessment reports show that sugar industries can be considered as zero discharge industries if proper waste conversion technologies are implemented (Sahu 2018). A great deal of research shows that SCB can be used for different applications such as in adsorbent, ion exchange resin, ceramics, concrete, cement and polymer composites (Ajala *et al.* 2021) formations. Consequently, SCB is a biomass with great potential to meet global energy demand and encourage the waste to wealth conversion principle for economic and environmental sustainable development (Ajala *et al.* 2021). Energy security and environmental conservation issues are likely to remain two of the major long-term contradictory challenges facing human existence globally. Therefore, for a sustainable environment and to engage with greener circular economy principles, integrated approaches of renewable resources utilization should be required instead of waste disposal (Formann *et al.* 2020).

Bagasse utilization for energy in sub-saharan Africa sugar industries

The sugar industry makes a great contribution to economic development and is a major source of job creation. According to the information obtained from the Ethiopian Sugar Corporation, about 1.35 million tonnes of sugar (<https://www.ethiosugar.com/>) and more than 893,270 tonnes of SCB are produced on average annually (Mamaye *et al.* 2019). Similarly, 40% of Mauritius electricity total demands was met from bagasse (To *et al.* 2018) and bioelectric generation from bagasse increased by 10% in Malawi, Mozambique, and Zambia (Souza *et al.* 2016). As can be seen in Table 1 and Figure 1 most sub-Saharan African governments are working to boost energy demands from bagasse biomass as the best option for solid waste management (Aleme 2019; Ajala *et al.* 2021). In general, in the sub-Saharan African sugar industry, bagasse by-product management needs a lot of improvement for sustainability and only limited amounts of bagasse are used inefficiently for burning in boilers for electricity generation (Gebrezgabher *et al.* 2018; To *et al.* 2018).

Table 1 | Bagasse utilization for energies in sugar factories of sub-Saharan Africa

Factory	Energy production (MW)	Sub-Saharan Africa countries	References
Fincha	31	Ethiopia	Habte <i>et al.</i> (2018)
Wonji	20		
Metahara	9		
Tendaho (2 factories)	60		
Kesem	26		
Omo-Kuraz (4 factories)	415		
Mumias Sugar company	34	Kenya	Gebrezgabher <i>et al.</i> (2018)
Mauritius sugar factories	600,000	Mauritius	To <i>et al.</i> (2018)

Bio-adsorption application of bagasse

Bio-adsorption is a physicochemical process in which the concentration of heavy metals is adsorbed on the metabolically passive biological materials or surface of materials derived from biological sources (Michalak *et al.*

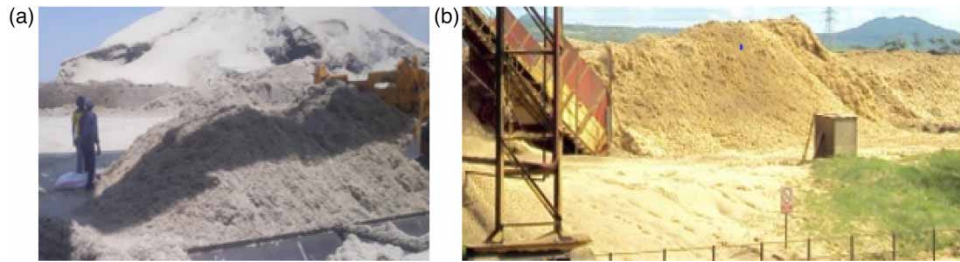


Figure 1 | Waste bagasse open dumping (a) Wonji sugar factory in Ethiopia (b) Bagasse storage facility in Mauritius (To *et al.* 2018).

2013; González *et al.* 2017). However, bio-adsorption terms are not well understood and sometimes used interchangeably with bioaccumulation (bio-absorption). Bioaccumulation refers to heavy metals accumulation in the cell wall and is a biologically active process. The advantages of the bio-adsorption process are due to multiple functional groups for heavy metal binding sites, abundance, efficiency for large volumes of wastewater, easy synthesis procedure, high adsorption rate and low treatment cost (Tofan *et al.* 2022). Based on biological sources, bio-adsorbents are classified into three (see Figure 2) as reported by Chakraborty *et al.* (2020).

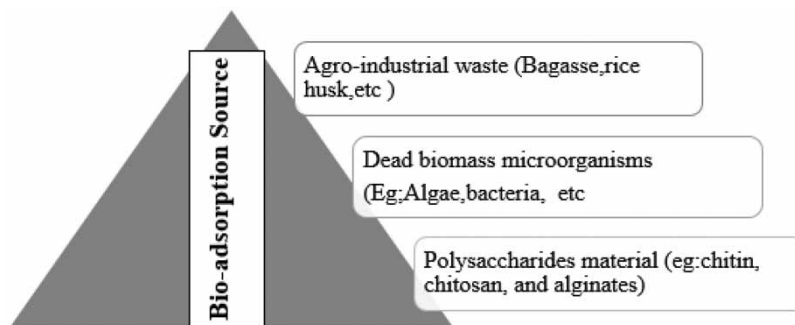


Figure 2 | Classification of bio-adsorbents (Chakraborty *et al.* 2020).

Among sources of bio-adsorbents, agro-industrial waste and polysaccharides materials are the most widely reported types for adsorptive removal of heavy metals. In contrast to conventional adsorbents that contain single types of binding sites, the multi-electron density functional groups of bio-sorbents have good potential for metal ion binding by a variety of adsorption mechanisms. The effective removal of heavy metals from wastewater using bio-adsorbents such as bagasse depends on its unique surface chemistry and functional groups (Hamad & Idrus 2022). Among agro-industrial wastes, bagasse has carbon-oxygen containing functional groups like carboxyl, ketone, ester, aromatic rings and hydroxyl that have good capacity for metal ion adsorption (Anastopoulos *et al.* 2017; Siqueira *et al.* 2020).

Heavy metals bio-adsorption removal potentials of waste bagasse

The main potential heavy metal adsorption capacity of SCB is due to its highly porous nature and presence of carbon-oxygen, which account for pore filling and/or binding heavy metals by changing their hydrogen ions for metal ions or giving an electron pair to form complexes with the metal ions (Shah *et al.* 2018; Ambaye *et al.* 2021). However, raw sugarcane bagasse and its main functional components show good adsorption capacity towards heavy metals; they can satisfy the water quality need for low concentrations of heavy metals (Ighalo *et al.* 2022). Thus, to meet water quality need at high pollutant loads and to enhance selectivity towards the target adsorbent, further modification of bagasse was needed (Irawan *et al.* 2021). Various modification techniques such as chemical modification by addition of functional groups, acid hydrolysis, carbonization of SCB to derive activated carbon are among those widely reported (Xavier *et al.* 2018).

Surface modification of bagasse increases its heavy metals adsorption capacity (Yu *et al.* 2015; Wang & Wang 2018). In addition, surface modification of SCB based bio-adsorbents is easy due to the abundant hydroxyl,

phenolic and carboxylic functional groups of cellulose and hemicellulose (Ighalo *et al.* 2022). Chemical modification of SCB enhanced HMs bio-adsorption capacity; this may be attributed to the increase in functional properties and binding sites of the bio-adsorbent by the modifying agent and therefore, higher sorption affinity (Li *et al.* 2013; Romero-Cano *et al.* 2017; Irawan *et al.* 2021). As presented in Table 2, SCB chemical modification with EDTA di-anhydride and pyromellitic di-anhydride provides additional carbonyl functional groups on the bagasse surface that account for enhanced Pb(II) removal capacity (Moyo *et al.* 2017; Tang *et al.* 2018). In another study by Shah *et al.* (2018) and Al-Saidi *et al.* (2022) acid modifications of SCB surface hydrolysis ester functional groups converted them to carboxylate groups, which accounts for the highly coordinated interaction with HMs through electrostatic interaction as shown in Table 2.

Table 2 | Effect of SCB modification on adsorption removal of heavy metals

Modification	Heavy metals	Enhanced adsorption capacity (mg heavy metal/g adsorbent)	Reference
EDTA di-anhydride	Pb ²⁺	59.25–306.33	Moyo <i>et al.</i> (2017)
Pyromellitic di-anhydride	Pb ²⁺	60.5–241.7	Tang <i>et al.</i> (2018)
Acid pyrolysis	Pb ²⁺	21–31	Shah <i>et al.</i> (2018)
Sulfuric acid modifies SCB	Pb ²⁺	2.42–3.704	Al-Saidi <i>et al.</i> (2022)
Alkali modified hydrochar SCB	Pb ²⁺	92.4	Malool <i>et al.</i> (2021)

EDTA: ethylenediaminetetraacetic acid.

Sugarcane bagasse based adsorption removal shows selectivity based on physicochemical properties of HMs (Homagai *et al.* 2010; Saxena *et al.* 2017; Hassan *et al.* 2021; Mondal *et al.* 2022). Also, the literature shows that SCB adsorption removal of different heavy metals under similar experimental setups, shows different adsorption capacity (Kong *et al.* 2014; Tran *et al.* 2017; Ighalo *et al.* 2022). Recently, Harripersadth *et al.* (2020) reported in the same working environment that at 1.0 g of SCB adsorbent dose and solution pH = 5.5, the adsorption capacity of bagasse for two different heavy metals ions, namely Pb²⁺ and Cd²⁺, are different, 31.45 and 19.49 mg/g respectively. Higher adsorption capacity of Pb²⁺ than Cd²⁺ in the same working environment was due to high ionic radius (0.118 nm) and electron negativity (1.8) of Pb²⁺. Whereas, Cd²⁺ has relatively smaller ionic radius and electronegativity, 0.097 nm and 1.7.

In general, highly electronegative metal ions show relatively high affinity to attract electrons and are thereby adsorbed at surface of bagasse or trapped by surface pores. As shown in Table 3, Ighalo *et al.* (2022) reported low-density polyethylene hybrid bagasse biochar for adsorption removal of four heavy metals, Cu²⁺, Pb²⁺, Zn²⁺ and Fe²⁺. The bagasse biochar low-density polyethylene hybrid adsorbent shows higher adsorption capacity for Zn²⁺ than other heavy metals (Pb²⁺, Cu²⁺, and Fe²⁺) because of its greater hydrolysis constant, higher ionic radius, and larger softness for inner-sphere surface complexation or adsorption reaction mechanisms. Heavy metals with greater hydrolysis constant, electronegativity, higher ionic radius, and larger softness value show greater tendency for adsorption at bagasse bio-adsorbents surface (Ighalo *et al.* 2022). Similarly, most literature reported that chemical modification of SCB enhances adsorption capacity. This may be explained as addition of further functional groups and binding sites that accounts for better adsorption tendency towards target heavy metals.

However, in some instances, the adsorption capacity of the unmodified sugarcane bagasse appeared to be significantly higher than that of the modified bagasse. As shown in Table 3, Ighalo *et al.* (2022) reported 17.83 mg/g Pb²⁺ adsorption of low density polyethylene hybrid biochar modified SCB and Tran *et al.* (2017) reported 19.3 mg/g of Pb²⁺ removal capacity of ZnCl₂ derived activated carbons from SCB at 500 °C carbonization temperature. Whereas, Harripersadth *et al.* (2020) reported 31.45 mg/g of Pb²⁺ adsorption removal of unmodified bagasse. Similarly, Tejada-Tovar *et al.* (2020) reported 37.88 mg/g of Pb²⁺ adsorption removal of unmodified bagasse. This may be due to differences in growth of SCB with different climatic conditions that may affect its chemical composition, and SCB bio-adsorbent preparation techniques may account for variable percentages of functional groups and surface chemistry nature. In addition, a plausible reason for low adsorption capacity of modified bagasse as reported by Tran *et al.* (2017) and Ighalo *et al.* (2022) may be the high temperature carbonization methods that account for removal of functional groups and pore volume of bagasse.

Table 3 | Heavy metal adsorption capacity of unmodified and modified bagasse

Sugarcane bagasse modifications	Metals	Adsorption equilibrium time (min.)	Q_{max} (mg/g)	Adsorption isotherm	Kinetic model	Reference
Unmodified	Pb ²⁺	30	31.45	–	–	Harripersadth <i>et al.</i> (2020)
	Cd ²⁺	60	19.49	–	–	
Unmodified	Pb ²⁺	–	37.88	Langmuir	PFO	Tejada-Tovar <i>et al.</i> (2020)
Unmodified	Pb ²⁺	90	1.61	Freundlich	PSO	Ezeonuegbu <i>et al.</i> (2021)
	Ni ²⁺	90	123.46			
Biochar	Ni ²⁺	180	38.15	Redlich Peterson	PSO	Lyu <i>et al.</i> (2018)
ZnCl ₂ derived activated carbon	Ni ²⁺	–	2.99	–	–	Tran <i>et al.</i> (2017)
	Cu ²⁺	–	13.24	–	–	
	Pb ²⁺	–	19.3	–	–	
SCB-Low density polyethylene hybrid biochar	Cu ²⁺	–	16.23	Langmuir	PFO	Ighalo <i>et al.</i> (2022)
	Pb ²⁺	–	17.83			
	Zn ²⁺	–	61.73			
	Fe ²⁺	–	8.772			
Acrylic acid and acrylamide using N,N-methylene-bis-acrylamide cross linker	Pb ²⁺	60	700	Langmuir	PSO	Kong <i>et al.</i> (2014)
	Cd ²⁺	90	320			
	Cu ²⁺	180	268			
Nitric acid SCB Facial carboxylation	Cd ²⁺	3 h	119.3	Langmuir	PSO	Ai <i>et al.</i> (2020)
Citric acid	Cu ²⁺	24 h	31.53	Langmuir	PSO	dos Santos <i>et al.</i> (2019)

Pseudo first order (PFO), Pseudo second order (PSO), maximum adsorption capacity in milligrams of adsorbate/grams of adsorbent (Q_{max}).

Heavy metal adsorption removal mechanisms of bagasse

It is worth mentioning that bagasse adsorption removal of heavy metals happens through physical processes (pore filling, hydrogen bonding, Van der Waals force, etc.), chemical processes (inner-sphere complexation (–OH) and surface complexation (–COOH)), and electrostatic interaction (Hamad & Idrus 2022). Adsorption capacity of SCB is not only charge dependent but it also shows adsorption at the positive adsorbent surface (acidic medium) due to the pore nature of bagasse, and physical adsorption has a significant role in HMs adsorption removal capacity. In addition, the main chemisorption adsorption mechanisms of bagasse are surface complexation, inner sphere complexation and electrostatic attraction (Kumar *et al.* 2014; Harripersadth *et al.* 2020).

Surface adsorption

Surface adsorption is a physical process that involves formation of covalent bonds with relatively weak forces through diffusion of metal ions into pores of the adsorbent surface (Madelá & Skuza 2021). The pore volume and surface area of adsorbent depends on methods of bagasse synthesis. Different literature reports acid treatment of bagasse for adsorbent shrinks the SCB cell wall, largely reducing the specific surface area and pore volume (Ighalo *et al.* 2022).

Electrostatic interaction of metals on bagasse

The electrostatic interaction mechanism involves the electrostatic interaction between the negatively charged bagasse functional groups and positively charged heavy metal ions. Such types of adsorption mechanism play a dominant role in effective removal of heavy metal ions (Madelá & Skuza 2021). The electrostatic adsorption mechanism depends on solution pH and point of zero charge of bagasse. The molecular level studies of density function theory (DFT) calculation results demonstrated that hydroxymethyl (–COOH) on the bagasse surface is converted into –COONa ligands in the presence of sodium salt, which was coordinated with Cd²⁺ through the chelation effect (–COO–) and Cd²⁺ could spontaneously bond with –COO– through coordination bonds as reported by Ai *et al.* (2020). However, exchange of proton (H⁺) of the –COOH functional group with Cd²⁺ did not occur because the replacement would cause an increase in total energy and Gibbs free energy as

shown in Table 4. These carboxylate groups can interact with Cd^{2+} ions through the chelation or the coordination adsorption process involving electrons as shown in Figure 3. Thus, detailed molecular level studies were needed to understand the clear adsorption mechanism of target heavy metals. DFT study for Cd^{2+} confirms adsorptions happens through electrostatic interaction rather than ion-exchange as presented in Table 4 and Figure 3.

Table 4 | Bagasse functional groups facial carboxylation total energy and Gibbs free energy (Ai *et al.* 2020)

Metal	Functional groups	Change in total energy (kJ/mol)	Change in Gibbs free energy (kJ/mol)
Cd^{2+}	-COONa	-23.1	-66.7
	-COOH	54.9	15.1

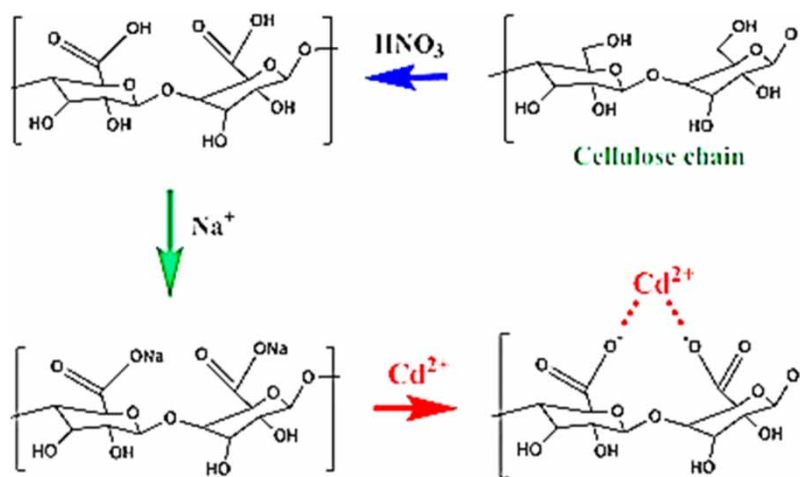


Figure 3 | Schematic diagram for conversion of hydroxymethyl into carboxylate group in the presence of nitric acid for Cd^{2+} adsorption removal mechanism (Ai *et al.* 2020).

Ion exchange

Ion exchange takes place because of the electrostatic interaction between positive cations and the negatively charged groups in the bio-sorbent (Saxena *et al.* 2017). In SCB adsorbents, the functional groups carboxyl (-COOH) or hydroxyl (-OH) emit protons (H^+) that can participate in ion exchange reactions with heavy metals (M^{+n}) (Sarker *et al.* 2017). This can account for the decrease in electron density around carbon-oxygen bonds with ion exchangeable functional groups like $(\text{COO})_2 \text{Cd}$ and $(\text{CO})_2 \text{Pb}$ for each specific heavy metal as shown in Figure 4, and improve its stability (Younas *et al.* 2021).

Complexation

The mechanisms of metal complexation include the arrangement of multi-atom formation through the interaction of specific metal ligands to form a complex (Madelá & Skuza 2021). Sugarcane bagasse functional groups, which contain carbon-oxygen in their structure, such as phenolic (lignin), hemicellulose, and cellulose, bind with heavy metals. Thus, carbon-oxygen content can increase surface oxidation of the SCB leading to enhanced metal complexation (Ambaye *et al.* 2021). Consequently, heavy metal ions can be removed by inner-sphere complexation (by interaction with -OH) or by surface complexation (interaction with -COOH) of bagasse functional groups (Sarker *et al.* 2017).

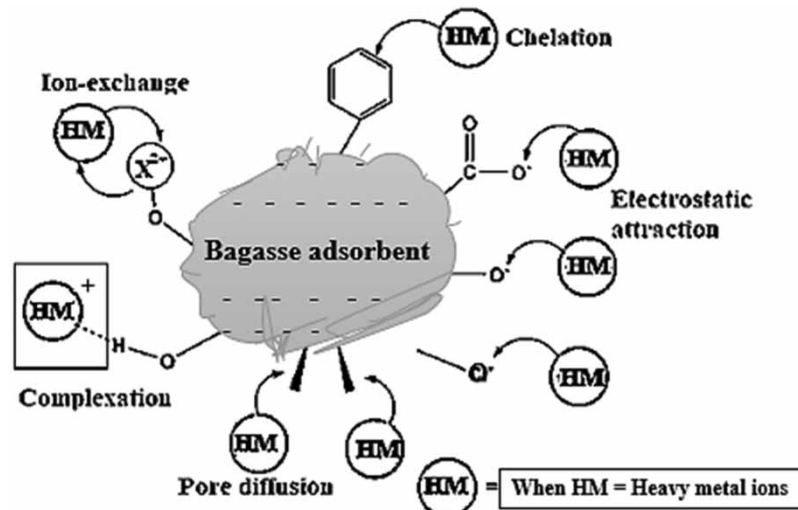


Figure 4 | Heavy metal (HM) adsorption mechanism of bio-adsorbent bagasse.

ADSORPTION ISOTHERM AND ADSORPTION KINETIC STUDY

Adsorption isotherm studies

Adsorption is a two-way process, where adsorption and desorption equilibrium occurs simultaneously. An adsorption isotherm is the equilibrium relationship between the concentration of adsorbate in solution and the adsorbate retained in the adsorbent at a given temperature (Iwuozor *et al.* 2021b). The adsorption isotherm is more concerned with how the adsorbate molecules are distributed between the liquid and solid phase when the sorption process attains equilibrium (Hashem *et al.* 2010; Abonyi *et al.* 2019; Al-Ghouti & Da'ana 2020). Analysis of isotherm data by fitting different isotherm models is a crucial step to find an appropriate model that represents adsorbate molecules at equilibrium. Most literature reports that Langmuir and Freundlich are the most appropriate isotherm models to describe heavy metal ion adsorption by bagasse (Ezeonuegbu *et al.* 2021; Iwuozor *et al.* 2021a). Hence, these isotherm models give detailed information about the nature of adsorption of HMs on bagasse surface. Adsorption could happen either through monolayer adsorption with affinities over homogeneous surface or multilayer adsorption with high affinities over heterogeneous surface. The Langmuir model assumes all forces that act on adsorption processes are similar to chemical reactions and there is no interaction among adsorbed species only between adsorbate and adsorbent (Langmuir 1918). In addition, the Langmuir isotherm confirms the positive interaction between the adsorbate and SCB, which is valid proof for an ion-exchange type adsorption mechanism (Çelebi *et al.* 2020; Shafiq *et al.* 2021). On the other hand, the Freundlich isotherm model assumes adsorption on a heterogeneous surface with various adsorption sites, which can hold more than one metal ion at a time; the strong binding sites are occupied first and the amount of adsorption is the summation on all surface sites (Freundlich 1907).

As most literature reports, the adsorption isotherm of SCB fits Langmuir and/or Freundlich, which refers to Langmuir at low concentration and Freundlich at high concentration of HMs (Ighalo *et al.* 2022). In fact, such empirical isotherm models may often not give insights on the mechanism of sorption when multiple models based on different assumed adsorption mechanisms can fit the same experimental data as shown in Table 5. Thus, the goodness of the fit alone cannot be used to conclude the superior mechanism of one model over the other. However, as presented in Table 5, the adsorption isotherm parameters of Langmuir such as separation factor (R_L), in the range of $0 < R_L < 1$, shows favorability of the adsorption process, while $R_L > 1$ shows unfavorability of the Langmuir adsorption isotherm and $R_L > 1$ shows the physical nature of adsorption (Hashem *et al.* 2021; Ragadhita & Nandiyanto 2021). Sugarcane bagasse shows different adsorption isotherm models as shown in Table 3; this variation may be due to different concentrations of heavy metals, adsorbent synthesis and the nature of surface modification (Tejada-Tovar *et al.* 2020; Ezeonuegbu *et al.* 2021). Similarly, from the Freundlich isotherm, the slope was also reported as in the range of $0 < 1/n < 1$ and shows normal adsorption process (Salman *et al.* 2016). In addition, most literature reported both the Langmuir parameter (R_L) and

Table 5 | Adsorption isotherm parameters of adsorption data

Adsorbent	Pollutant heavy metals	Isotherm parameters					Reference
		Langmuir ($q_e = \frac{q_{max} K_L C_{eq}}{1 + K_L C_{eq}}$)		Freundlich ($q_e = K_F C_{eq}^{1/n}$)			
		R_L	R^2	n	$\frac{1}{n}$	R^2	
SCB	Pb ²⁺	0.001146	0.9692	2.6462	0.378	0.991	Hashem <i>et al.</i> (2021)
SCB	Pb ²⁺	1.035	0.9819	2.3050	0.434	0.9401	Ezeonuegbu <i>et al.</i> (2021)
SCB	Pb ²⁺	1.604	0.974	6.410	0.156	0.964	Tejada-Tovar <i>et al.</i> (2020)
SCB	Cd ²⁺	0.029	0.9904	1.34	0.746	0.9902	Harripersadth <i>et al.</i> (2020)
Citric acid modified SCB	Cr ³⁺	–	0.994	1.580	0.633	0.965	dos Santos <i>et al.</i> (2019)
Acrylic modified SCB	Pb ²⁺	0.07289	0.995	1.105	0.905	0.956	Kong <i>et al.</i> (2014)
Acid assisted pyrolyzed SCB	Pb ²⁺	–	0.9006	1.257	0.795	0.999	Shah <i>et al.</i> (2018)

Langmuir parameter (K_L), adsorption capacity at equilibrium (q_e), equilibrium concentration (C_e), Freundlich constant (K_F), Freundlich adsorption isotherm slope ($1/n$), and linear regression coefficient (R^2).

Freundlich isotherm parameter ($1/n$), showing favorability of Langmuir ($R^2 = 96.9\text{--}99.4\%$) and Freundlich ($R^2 = 95.6\text{--}99.9\%$) for the same adsorption data as shown in Table 5.

Similarly, the Freundlich adsorption isotherm slope ($1/n$) gives some hints that the isotherm process is more favorable in cooperative adsorption (physi-sorption and chemisorption) (Ragadhita & Nandiyanto 2021). The chemisorption occurs at the first layer occupation of all functional group active sites on the SCB surface (Chaiwon *et al.* 2017). After all chemically active sites of adsorbent are saturated with heavy metal, a multi-molecular layer of HMs is formed by physical adsorption such as pore filling, and intermolecular Van der Waals forces result in attraction on the SCB surface (Wang *et al.* 2017). Also, the equilibrium adsorption capacity (q_e) increases with increasing initial pollutants (HMs) which refers to multilayer adsorption (Freundlich) at high pollutants concentration.

In addition, cooperative adsorption is applicable to both specific and non-specific interactions between sorbate and interface (Shimizu & Matubayasi 2021). Furthermore, some literature reports have been supported with chemical instrumentation from scanning electron microscopy (SEM) analysis: the adsorbed heavy metals ions on the surface of bagasse are uniformly distributed on bagasse surface and interior of the pores (Akanni *et al.* 2019) and this may suggest chemical and physical adsorption mechanisms of bagasse for heavy metals adsorption removals.

Adsorption kinetics of bagasse adsorbent

Adsorption kinetics is one of the adsorption processes used to understand the rate at which metal ions are transferred from bulk solution to the adsorbent surface (dos Santos *et al.* 2019). In general, adsorption kinetics occurs through two steps. The first step assumes the transfer of the adsorbate from the bulky solution to surface of the adsorbent through the solid–fluid boundary layer known as film. Such surface diffusion adsorption kinetics is governed by hydrodynamic effects such as agitation speed and fluid flow rates. It is fast and results in chemical entrapment of HMs on the bagasse functional groups (Iwuozor *et al.* 2021a). However, the second step of adsorption kinetics assumes pore diffusion of the adsorbate into the porous adsorbent. In particular, such adsorption kinetics occurs at high concentration of pollutant dose after saturation equilibrium of chemically active sites. However, pseudo second order kinetics of initial rapid adsorption is due to the large binding sites of bagasse functional groups. In contrast, slow adsorption onto residual binding sites and diffusion of heavy metals into the porous surface follows pseudo first order kinetic models (Hassan *et al.* 2021). Most adsorption kinetics of modified and unmodified SCB for metal ion removal have been reported as pseudo first and pseudo second order kinetic models (Irawan *et al.* 2021; Iwuozor *et al.* 2021a). Pseudo first order kinetics assumes that the adsorption kinetics is directly proportional to the available number of unoccupied sites and governed by a physical adsorption process that is diffusion-controlled; this can occur at high concentration of pollutant dose after all the chemically active adsorption sites are occupied (Shah *et al.* 2019). However, in pseudo second order adsorption kinetics it is assumed that adsorption rate and reaction mechanism are controlled by chemical entrapment processes including ion-exchange between adsorbate and functional groups of adsorbent or inter-valence force

(Liu *et al.* 2018; Irawan *et al.* 2021). The pseudo second order kinetics model may be the rate-dominating mechanism at appropriate ratios of SCB chemically active sites to pollutant heavy metals dose. Adsorption kinetics deals with the uptake rate of unmodified and/or modified bagasse with time and rate constant calculated with pseudo first and pseudo second order kinetics (Hashem *et al.* 2021) as shown in Table 6.

Table 6 | Kinetic adsorption model equation and parameters

Model	Equation	Parameters
Pseudo first order	$\ln(q_e - q_t) = \ln q_e - k_1 t$	q_e (mg/g): adsorption capacity at equilibrium q_t (mg/g): adsorption capacity in a time t K_1 (1/min): adsorption rate constant for pseudo first order
Pseudo second order	$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2}$	K_2 ($\text{g}^{-1}\text{min}^{-1}$): adsorption rate constant for pseudo second order

Reusability of SCB adsorbents

Reusing the adsorbent is one of the important criteria for application of the adsorbent in water and wastewater adsorptive industries (Koopal *et al.* 2019; Tofan 2022). Thus, selection of stable bio-adsorbent has viable advantages for re-utilization of used adsorbents for new adsorption phase after several adsorption–desorption cycles (dos Santos *et al.* 2019; Alaqarbeh 2021). Shiralipour *et al.* (2018) reported acid desorbing (HNO_3) for desorbing Pb^{2+} from SCB and found excellent stability after four adsorption processes without a considerable loss (>95%) of its adsorption efficiency, as presented in Table 7. In another study, Okoronkwo & Olusegun (2013) reported the Ni^{2+} desorption from bio-adsorbent (lignin) using distilled water, EDTA and HCl de-sorbents; HCl showed better desorption performance over distilled water and EDTA de-sorbents as presented in Table 7. In general, heavy metals desorption from bio-adsorbents using acids causes protonation of the sorbent surface which allows desorption of positively charged metal ions from the adsorbent (Kong *et al.* 2014; Akanni *et al.* 2019). The percentage desorption efficiency was calculated using Equation (1) (Ezeonuegbu *et al.* 2021):

$$\text{Desorption efficiency (\%)} = \frac{\text{Amount metal ion desorbed}}{\text{Amount metal ion adsorbed}} \times 100 \quad (1)$$

The effective adsorbents should have good adsorption potentials for the removal of HMs and also a good recovery capacity of metal ions and reusability (Kołodynska *et al.* 2017; Ezeonuegbu *et al.* 2021).

Table 7 | Recovery efficiency of sugar cane bagasse using different acids and bases after adsorption

Adsorbents	Heavy metals adsorbed	Desorbing agents	Efficiency	Reference
SCB	Pb^{2+}	HNO_3	~95% efficiency to reuse for four cycles	Shiralipour <i>et al.</i> (2018)
SCB	Pb^{2+} and Ni^{2+}	Acids (HNO_3)	~90% metal recovery	Ezeonuegbu <i>et al.</i> (2021)
SCB	Pb^{2+} and Ni^{2+}	Base (NaOH)	~45–55% metal recovery rate	Ezeonuegbu <i>et al.</i> (2021)
Acrylic-modified SCB	Pb^{2+} , Cd^{2+} , Cu^{2+}	Acid (HCl)	95, 96 and 92% respectively for recovery after five cycles	Kong <i>et al.</i> (2014)
SCB	Fe^{2+}	Acid (HCl, HNO_3 and H_2SO_4)	Used four times without significant losses in dilute acids	Akanni <i>et al.</i> (2019)

Challenges in heavy metal adsorption removals and future perspectives

Most literature reports show batch adsorption is a dominant process for SCB bio-adsorption; there are only limited reports on dynamic adsorption, column and pilot-scales. This review may provide some hints for the dynamic adsorption possibilities of SCB-based bio-adsorbents for practical uses. In addition, research on SCB-based adsorbent for removal of HMs has failed to report the effect of coexisting ions and a disposal strategy for used

adsorbent for a truly sustainable approach. Moreover, the current literature lacks reports on the treatment cost analysis of SCB. Thus, a cost analysis should be undertaken to show the real cost effectiveness of SCB for initial and running costs for wastewater treatment. In addition, several researchers have tried to explain the HMs adsorption mechanisms of SCB. However, detailed understanding of SCB for HMs adsorption removal needs knowledge of molecular level study such as DFT of Gaussian view and/or other molecular level study such as Monte Carlo simulations.

CONCLUSION

Global water pollution is increasing alarmingly. Most sub-Saharan African countries are forced to live under economic water stress due to lack of finance and skilled staff to reuse the abundant renewable water resources. The agricultural bio-waste sugarcane bagasse is eco-friendly, locally available and has a large surface area, high porosity and carbon–oxygen containing functional groups that account for heavy metal adsorption capacity. The HMs adsorption mechanism of both modified and unmodified bagasse involves inner sphere complexation, surface adsorption, pore filling, electrostatic interaction, ion exchange and precipitation. This review paper has revealed that adsorbent bagasse showed great adsorption potential towards heavy metals with high electronegativity, hydrolysis constant, higher ionic radius, and larger softness. It was inferred that cooperative (physical and chemical) adsorption processes are appropriately represented by Langmuir and/or Freundlich adsorption isotherms for HMs adsorption removal over SCB-based bio-adsorbents. The kinetic adsorption equilibrium explained by pseudo-first and pseudo-second-order kinetic models depends on initial HMs concentrations. The short adsorption equilibrium nature of bagasse at low concentration of HMs follows pseudo second order kinetics with chemical adsorption and first order kinetics through pore filling and other physical adsorption processes at high HMs concentrations. The bio-adsorbent SCB-based adsorption process is promising in terms of economic viability and easy regeneration for practical applications in real wastewater in developing countries such as in sub-Saharan Africa.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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