

## Research Paper

# Zinc removal from aqueous solution using novel adsorbent MISCBA

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### ABSTRACT

Pollution caused by heavy metals has become a serious problem to the environment nowadays. The treatment of wastewater containing heavy metals continues to receive attention because of their toxicity and negative impact on the environment. Recently, various types of adsorbents have been prepared for the uptake of heavy metals from wastewater through the batch adsorption technique. This study focused on the removal of zinc from aqueous solution using microwave incinerated sugarcane bagasse ash (MISCBA). MISCBA was produced using microwave technology. The influence of some parameters such as pH, contact time, initial metal concentration and adsorbent dosage on the removal of zinc was investigated. The competition between  $H^+$  and metal ions has affected zinc removal at a low pH value. Optimum conditions for zinc removal were achieved at pH 6.0, contact time 180 min and adsorbent dosage of 10 g/L, respectively. The maximum adsorption capacity for the removal of zinc was found to be 28.6 mg/g. The adsorption process occurred in a multilayered surface of the MISCBA. Chemical reaction was the potential mechanism that regulates the adsorption process. MISCBA can be used as an effective and cheap adsorbent for treatment of wastewater containing zinc metal ions.

**Key words** | adsorption, agitation, aqueous, environment, heavy metals, sugarcane bagasse ash

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### INTRODUCTION

Intensive developments with regard to industries in modern society have led to environmental pollution (Förstner & Wittmann 2012). Pollution of water bodies, mainly caused by the industrial release of wastewater containing toxic heavy metals, continues to be among the major issues of concern for the receiving environment (Fu & Wang 2011). Heavy metals tend to have an antagonistic effect once they enter the environment, causing detrimental effects to human health and other living organisms (Sheng *et al.* 2010; Xiao *et al.* 2012; Huang *et al.* 2013).

Effluents originating from metal bearing industries such as mining operations, metal plating, metallurgical industries, battery manufacturing industries, nuclear power plants and tannery industries tend to contain various toxic heavy

metal ions. Such metal ions include cobalt, lead, zinc, nickel, chromium, cadmium, and mercury (Jiang *et al.* 2015). Heavy metals have the ability to accumulate in the living body, causing different kinds of diseases, such as headache, cancer, and kidney failure; they can distort reproduction and may even lead to death. Accumulation of heavy metals in the living body is a gradual process because of their non-biodegradability coupled with a long half-life.

Zinc is an indispensable trace element required by the body. It is an essential trace element needed by microorganisms, animals, and plants, for their evolution and development (Chasapis *et al.* 2012). Vašák & Hasler (2000) reported that zinc is the second most available transition metal ion discovered in living organisms after iron. Zinc is

considered as a vital component of numerous proteins including transcription factors, cellular signaling proteins and metabolic enzymes (over 300 enzymes) (Beyersmann 2002). This is one of the main reasons for its indispensability. Zinc has been discovered to regulate protein kinase, second messenger metabolism, cellular signal reception and the activities of protein phosphate, and it may also inhibit or activate the DNA of transcription factors (Beyersmann 2002).

However, the release of zinc into water bodies at elevated concentrations can lead to intense toxicological effects on humans and some other living organisms in the aquatic system (Amuda *et al.* 2007). The Minamata episode of mercury poisoning in Japan is a similar experience (Reish & Ruivo 1972). Because of this, it has become necessary to treat zinc from industrial wastewater before discharging into the receiving environment.

Several processes have been employed for the removal of heavy metal from wastewater. Conventionally used methods include chemical precipitation, ion exchange, membrane filtration, coagulation and flocculation, flotation, electrochemical treatment and adsorption (Isa *et al.* 2008; Martín-Lara *et al.* 2014). These treatment techniques have intrinsic advantages and disadvantages.

Chemical precipitation is one of the conventional techniques mainly used for heavy metal removal. Some of the disadvantages of chemical precipitation include poor settling, production of excess sludge that requires additional treatment, long-term sludge disposal impacts and accumulation of metal precipitates. The resins used in ion-exchange processes can be expensive and are not usually available in abundance. The main disadvantage of membrane filtration is the excessive energy consumption. Flocculation/coagulation processes cannot remove heavy metals from wastewater completely. Electrochemical treatment may require excessive energy consumption. Adsorption at industrial scale is usually hindered by the high cost of commercial activated carbon (AC). Commercial AC is the most commonly and effectively used adsorbent for the removal of heavy metals from the liquid phase. Its high cost is a limiting factor in its application on an industrial scale. However, with the emergence of low-cost adsorbents the adsorption process has been acknowledged as an economic and effective method for the treatment of heavy metals in wastewater. There is flexibility in the design and operation

of the process, and in most situations it tends to produce effluent of high quality. Moreover, because of the reversible properties of the adsorption process, regeneration of the spent adsorbent can be achieved through an appropriate process of desorption (Ajmal *et al.* 2003).

The search for low cost and abundantly available adsorbents for heavy metal removal remains one of the main focuses of research.

Many studies on the use of low cost adsorbents for heavy metal removal from wastewater have been published. Industrial wastes, agricultural by-products, etc. have been investigated as low-cost adsorbents for the removal of heavy metal in wastewater. A number of articles have reviewed the application of low cost methods for heavy metal removal from wastewater, including the adsorption of heavy metals (Cd(II), Pb(II), Cu(II), Hg(II), Cr (VI), Cr(III) and Ni(II)) onto agro-based waste material (Demirbas 2008; Farooq *et al.* 2010), waste biomass adsorbent for copper removal from industrial wastewater (Bilal *et al.* 2013), adsorption of heavy metal (Cd, As, Co, Mn, Zn, Ni, Fe and Cu) on natural and modified kaolinite and montmorillonite (Bhattacharyya & Gupta 2008) and heavy metal (As, Pb, and Hg) uptake by plants through phytoremediation (Tangahu *et al.* 2011).

Many researchers have reported the use of industrial by-products as adsorbents: These include lignite (Mohan & Chander 2006), aragonite shells (Köhler *et al.* 2007), rice husk (Yan *et al.* 2012), natural zeolites (Apiratikul & Pava-sant 2008), kaolinite (Gu & Evans 2008), lignin (Betancur *et al.* 2009), peat (Liu *et al.* 2008), clay (Al-Jilil & Alsewailem 2009) and bagasse (Saad *et al.* 2010). Low-cost adsorbents continue to be investigated by researchers from different perspectives of modification either through chemical, thermal or the combination of both methods in order to enhance their removal efficiencies.

The use of a chemical for the modification of wood sawdust and sugarcane bagasse was reported by Pereira *et al.* (2010). The authors used Ethylenediaminetetraacetic dianhydride as a modifying agent to remove zinc from aqueous solution and electroplating wastewater. The modification was done in order to introduce functional groups of amine and carboxylic acid into the adsorbent materials. The adsorption capacities of the modified materials were higher with a single metal ion solution compared to industrial wastewater. Homagai *et al.* (2010) have used the

xanthation process to enhance the adsorption properties of sugarcane bagasse for the separation of lead, cadmium, zinc and nickel from aqueous solution. The results revealed that the adsorption capacity of the xanthated adsorbent was better than several other adsorbents stated in the literature. Another chemical modification process was also reported by Karnitz *et al.* (2007). The authors used succinic anhydride to introduce carboxylic acid functions to sugarcane bagasse for the removal of cadmium, copper and lead in a single metal solution. The results obtained show that the modified adsorbent indicated a good adsorption capacity for all the heavy metals studied.

Sugarcane bagasse is an abundant and easily accessible agricultural by-product that has the potential to be used as a low cost adsorbent for heavy metal removal from wastewater. Sugarcane is a common plant found in tropical countries, such as Malaysia, Brazil, Nigeria and China. An estimated 1,500 million tons of sugarcane bagasse is produced annually all over the world, out of which 40–45% is the bagasse material generated after the juice has been extracted. The resulting bagasse amounts to about 600 million tons as a waste material generated annually (Hussein *et al.* 2015). Sugarcane bagasse is used widely for pulp and paper production, electricity generation, production of cattle feed, biofuel and other products processed through fermentation (Pandey *et al.* 2000).

Recently, there has been a rapid advancement in thermal technology, including oven modifications and microwave equipment development (Estel *et al.* 2008). Nowadays, microwave heating is a fully developed process that finds broad applications in the field of food processing (Datta 2001), material science (Hasna 2003), polymer synthesis (Zong *et al.* 2002), organic synthesis (Varma 2003), medical waste incineration (Yoshikawa *et al.* 2007), rubber and plastic-treating, curing and preheating of ceramics as well as wood drying (Jones *et al.* 2002). The primary advantage of employing microwave heating is to considerably reduce the treatment time, which in many situations results in a significant reduction in the consumption of energy. Microwave heating has many advantages over the conventional heating method. These advantages include high energy efficiency, less heating time, rapid and volumetric heating, superior restoration of volatile compounds and elements, low levels of contamination, an acceleration effect, additional

reproducible processes and a good working environment (Nüchter *et al.* 2004). With the advancement of AC systems, innovative applications for making ACs using microwave heating are thriving and extending (Zhang *et al.* 2003).

Several studies have reported sugarcane bagasse as a low-cost adsorbent for the elimination of heavy metals from wastewater (Karnitz *et al.* 2007; Gurgel & Gil 2009). However, little information is available on the adsorption potential of microwave incinerated bagasse.

The objective of this study has been to evaluate the ability of a novel adsorbent 'Microwave Incinerated Sugarcane Bagasse Ash' (MISCBA) for the adsorption of zinc (II) from aqueous solution. The effects of pH, contact time, adsorbent dosage and initial metal concentrations on the removal of zinc (II) have been studied. Kinetics of adsorption and isotherm models were also investigated.

## MATERIAL AND METHODS

### Preparation of adsorbent material

Sugarcane bagasse was obtained from a local outlet at Bandar Seri Iskandar, Malaysia. The bagasse was cut manually to an average size of 10 cm and washed with tap water to remove dirt and lignin impurities. It was later washed with distilled water to further enhance its purity. The bagasse was dried in an oven at 105 °C for 24 hours until all moisture evaporated and a constant weight was achieved. The dried bagasse was then ground down to an average size of 6 mm using a mechanical grinder. The ground bagasse was incinerated at 500 °C using a microwave oven incinerator for a complete heating and cooling process of 3 hours. The resulting MISCBA was made into powder and then sieved in the size range of 100–150 µm. The MISCBA was immersed in a weak acid (0.5% H<sub>2</sub>SO<sub>4</sub>, pH 4.25) for 24 hours. Afterwards, the ash was filtered, washed with deionized water and dried at 70 °C. The prepared ash MISCBA was stored in a tight container until use.

### Characterization of adsorbent

The surface morphology of natural and used MISCBA was analyzed with a supra 55 VP Scanning Electron

Microscope (Carl-Zeiss AG, Germany). Determination of the element constituents in the adsorbents was undertaken using X-ray fluorescent (XRF) spectrometry (Tiger, S8).

### Preparations of adsorbate solutions

A stock solution of 1,000 mg/L zinc ions was prepared by dissolving its equivalent salt chloride ( $ZnCl_2$ ) in 1 L of ionized water to form an aqueous solution. The stock solution was diluted appropriately to prepare the working solutions. All chemicals employed were of analytical grade, obtained from Merck (Germany).

### Experimental procedures

Batch experiments were conducted using a series of Erlenmeyer flasks containing 100 mL of synthetic solution and 0.5 g of MISCBA dosage. An orbital shaker (Protech model 722) was used to agitate the flasks at 150 rpm at room temperature ( $27 \pm 1^\circ C$ ). At the end of the scheduled agitation time, the mixtures were separated using a Whatman cellulose acetate membrane filter (GF/C). The filtered solution was analyzed for residual zinc concentration using an Atomic Adsorption Spectrophotometer (Model AA 6800 Shimadzu).

The effect of initial pH on the adsorption of zinc was studied by varying the pH of the solution over a range of pH 1–8. The pH of the solution was adjusted using either 2.0 N hydrochloric acid or 1.5 N sodium hydroxide; 0.5 g of MISCBA was put into each flask. The flasks were clamped in an orbital shaker and agitated at a speed of 150 rpm for 2 hours. A pH meter (Model EW 53013, Hach Sension 1) was used in measuring the pH of the solution.

Experiments were conducted to investigate the effect of contact time on the adsorption of zinc. Erlenmeyer Flasks of 250 mL containing 100 mL of aqueous zinc solution with initial zinc concentrations of 100 mg/L adjusted to the optimum pH and 0.5 g of MISCBA were agitated at 150 rpm. At the end of predetermined times, (1, 5, 10, 20, 30, 60, 90, 120, 150, 180, 210 and 240 minutes) samples were removed from the shaker and analyzed for the residual zinc concentration.

Batch adsorption experiments were conducted by varying the MISCBA dosage as a functional parameter. The dosage was varied from 2 to 12 g/L while the pH and the time remained at their optimum values. An experiment on the effect of initial metal concentrations on the adsorption was also conducted. One hundred mL of aqueous zinc solution with initial concentrations of 1, 5, 10, 25, 50, 100, 150 and 200 mg/L adjusted to the optimum pH, and an added optimum dosage of MISCBA, were agitated at 150 rpm. The agitation time remained at the optimum value. At the end of the agitation time, samples were removed from the shaker and analyzed for residual zinc concentration. Equations (1) and (2) were used to compute the metal removal efficiency and the adsorption capacity of the MISCBA, respectively:

$$R = \frac{(C_i - C_e)}{C_i} \times 100\% \quad (1)$$

where  $R$  is the zinc removal efficiency (%),  $C_i$  is the initial and  $C_e$  is the residual concentration of zinc at the equilibrium point (mg/L);

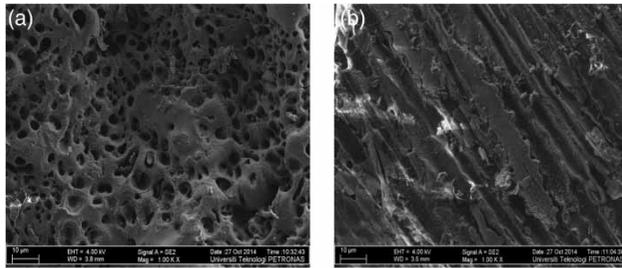
$$Q_c = \frac{(C_i - C_e)V}{W} \quad (2)$$

where  $Q_c$  is the adsorbent adsorption capacity (mg/g),  $C_i$  is the initial concentration and  $C_e$  the residual concentration of zinc (mg/L) at equilibrium,  $V$  is the volume of aqueous zinc solution (L) and  $W$  is the weight of MISCBA dosage (g).

## RESULTS AND DISCUSSION

### Characterization of MISCBA adsorbent

The images obtained through scanning electron microscopy (SEM) of MISCBA and zinc loaded MISCBA are shown in Figure 1. SEM discovered that thermally treated MISCBA shows the existence of heterogeneous and vastly porous openings in excess on the honeycomb surface of the MISCBA, showing a good probability of the adsorption of pollutants (Figure 1(a)). After adsorption, the pores are not visible, indicating the binding of zinc on MISCBA.



**Figure 1** | SEM micrograph of MISCBA (a) before and (b) after adsorption.

The chemical compositions of the MISCBA based on XRF analysis are presented in Table 1. From the result, it can be seen that silicon dioxide is the predominant element in the MISCBA. The high silicon value of 72.6% in the MISCBA is due to the thermal treatment the material undergoes. The quality of a produced AC is mainly judged by its high silicon content (Usman *et al.* 2014). The predominance of silica content in the MISCBA might be the major constituent element involved in the adsorption process of heavy metals. The results obtained are similar to the results reported by Manyà & Arauzo (2008) on describing the isothermal pyrolysis of micro-particles of sugarcane bagasse replacement of sugarcane bagasse as quartz in red ceramic (Teixeira *et al.* 2008) and analysis of sugarcane bagasse ash under thermal gasification (Fredericci *et al.* 2014).

### Effect of pH

The adsorption of the metal ion by an adsorbent is influenced greatly by the initial pH of the solution. This is because of the competition between the hydrogen ion and the metal ions for an active site on the adsorbent (Rafatullah *et al.* 2009). Figure 2 shows the plot of removal efficiency against the initial pH of the solution. It can be observed that zinc removal efficiency was low at a lower pH value. This was because of the presence of a higher concentration of hydrogen ions compared to the metal ions. At a low pH

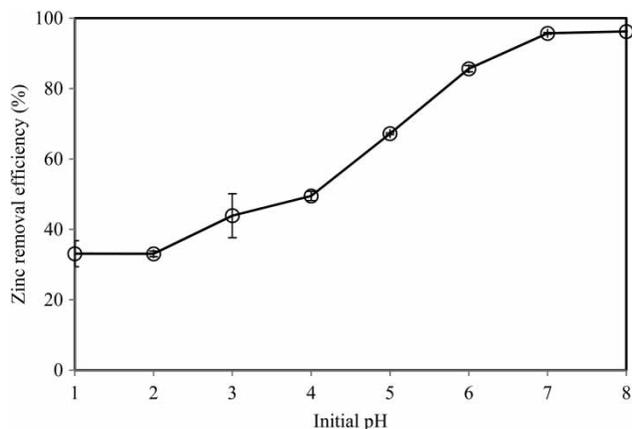
value, the two different ions struggle for the same active sites on the adsorbent. As the pH was increased, zinc removal efficiency also increased. The increase in the zinc removal efficiency was because more active sites having negative sites are uncovered. This, therefore, may likely increase the electrostatic attraction between the positively charged metal ions and the MISCBA surface. Further significant removal was not obtained after a pH value of 7.0. There is the possibility that zinc ions may precipitate as hydroxide when the pH is above 7.0 (Pereira *et al.* 2010). Therefore, the pH value of 6.0 with a removal efficiency 82.6% was selected to be optimum and was used in further studies.

### Effect of contact time

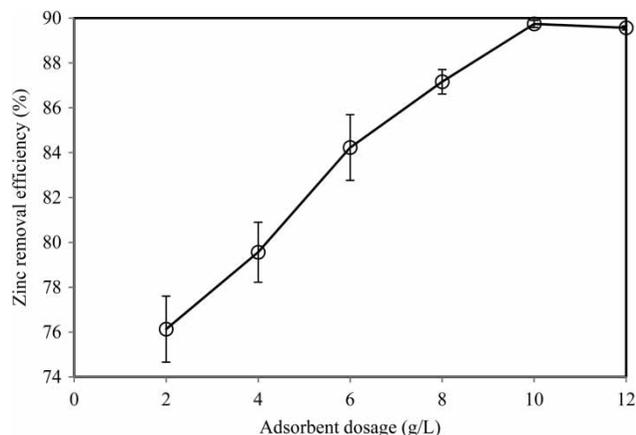
An experiment into the effect of contact time was carried out to find the optimum equilibrium time required for the removal of zinc from aqueous solution. The graph of removal efficiency against contact time is shown in Figure 3. Generally, it can be observed that as the contact time was increased there was a gradual increase in the removal efficiency of zinc. At the first 20 minutes, it was observed that the rate of zinc removal was high and then continued to decrease steadily until equilibrium was achieved. The high removal at the initial contact time was due to the presence of a more available larger surface area of the MISCBA. As the contact time was increased, the surface of the adsorbent become exhausted and the removal efficiency decreased. The equilibrium contact time was attained at an agitation time of 180 minutes. Further significant removal was not observed above a contact time of 180 minutes. The contact time of 180 minutes was considered to be optimum and was used in subsequent studies. The result obtained is in accordance with the result reported on the biosorption of zinc (II) from aqueous solution by dried activated sludge (Yang *et al.* 2010).

**Table 1** | Elemental constituents of MISCBA by percentage

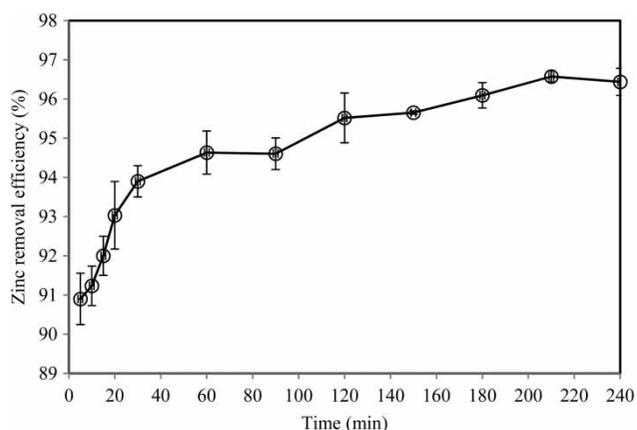
Elements	Oxides											
	SiO <sub>2</sub>	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	CaO	SO <sub>3</sub>	MgO	Fe <sub>2</sub> O <sub>3</sub>	MnO	Al <sub>2</sub> O <sub>3</sub>	ZnO	CuO	Rb <sub>2</sub> O
%	72.6	12.1	6.17	3.69	2.43	0.69	0.608	0.22	0.19	0.15	0.22	0.07



**Figure 2** | pH effect on the removal of metal ion zinc (initial metal concentration: 100 mg/L; contact time: 120 min; shaking speed: 150 rpm; adsorbent dosage: 5.0 g/L and temperature:  $27 \pm 1$  °C).



**Figure 4** | Adsorbent dosage effect on the removal of metal ions (initial metal concentration: 100 mg/L; pH: 6; contact time: 180 min; adsorbent dosage: 5.0 g/L; shaking speed: 150 rpm and temperature:  $27 \pm 1$  °C).



**Figure 3** | Contact time effect on the removal of metal ion zinc (initial metal concentration: 100 mg/L; shaking speed: 150 rpm; adsorbent dosage: 5.0 g/L, pH = 6.0 and temperature:  $27 \pm 1$  °C).

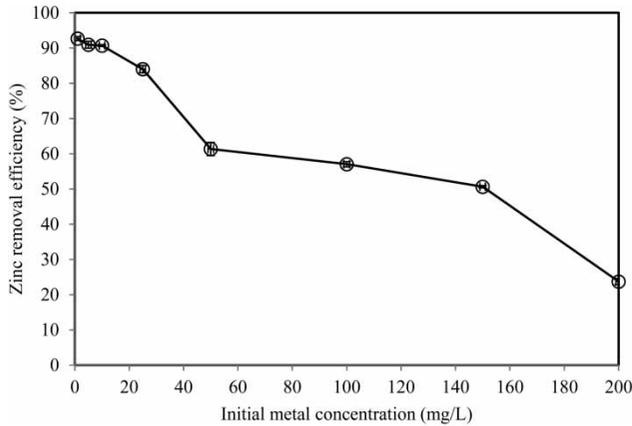
### Effect of adsorbent dosage

This study was carried out to investigate the effect of varying MISCBA dosage on the removal of zinc from aqueous solution. MISCBA dosage was varied in the range of 2–12 g/L until a steady state was achieved. The initial zinc concentration was fixed at 100 mg/L. The pH of the solution was adjusted to the optimum value obtained earlier, and the contact time was set at 180 minutes. The graph of zinc removal efficiency against adsorbent dosage is shown in Figure 4. It can be observed that zinc removal increased with the increase in the dosage of MISCBA. This was because of the presence of a number of active sites of the adsorbent

therefore making it easier for the metal ions to penetrate to the sorption sites. The optimum removal efficiency was found to be 89.7% at a MISCBA dosage of 10 g/L. Further significant removal was not observed as the MISCBA dosage was increased. This indicates that after a certain dose of MISCBA, the maximum zinc removal sets in. Thus, even with the further addition of adsorbent dosage, the quantity of free ions and the ions bound to the adsorbent will remain the same (Singanan & Peters 2013). The principal mechanism for the adsorption can be ion exchange between the hydrogen ions and the metal ions. The result obtained is in accordance with the result reported on the adsorption of zinc from aqueous solution using different adsorbents (Bhattacharya et al. 2006).

### Effect of initial metal concentration

Adsorbate initial concentration is one of the major steering powers in overcoming the resistance to movement between the adsorbate and the adsorbent (Rafatullah et al. 2009). As such, it was expected that at lower initial concentration the metal removal would be higher and vice versa. Figure 5 shows the graph of zinc removal efficiency against initial metal concentration. The percentage of zinc removal decreased with the increase in the initial concentration of zinc ions in the solution. This is because at a higher initial metal concentration there is resistance to movement of the metal ions from the outer to the inner side of the adsorbent,



**Figure 5** | Effect of initial metal ion concentration on the removal of metal zinc (contact time: 180 min; pH: 6.0; shaking speed: 150 rpm; dosage: 10.0 g/L and temperature:  $27 \pm 1^\circ\text{C}$ ).

and the resistance may be less at a lower initial metal concentration. Removal of zinc by the MISCBA was found to rely on the metal concentration of the adsorbate to a greater extent. This can further be explained as follows: higher energy sites are involved in the adsorption of metal ions when the initial concentration is low. However, as the concentration of metal ions increases, the higher energy sites will be overloaded and the adsorption commences on the lesser energy sites, resulting in a reduction of the efficiency of adsorption (Kadirvelu & Namasivayam 2003). The high performance of the MISCBA at a lower initial concentration is its potential to be used at the industrial level. This is because most industrial effluents contain lower concentrations of heavy metals.

### Adsorption isotherm studies

The adsorption isotherm model is an indispensable tool for the design and analysis of the adsorption process. Isotherm models play a vital role in understanding the adsorption behavior between adsorbent and adsorbate. In this study, Freundlich and Langmuir isotherm models were employed to interpret zinc adsorption using MISCBA.

### Freundlich isotherm model

The Freundlich isotherm model is among the most widely used models to determine the equilibrium relation between an adsorbate and adsorbent. The Freundlich isotherm

model is an empirical equation. It is mainly used in describing the adsorption of organic or inorganic elements over a wide range of adsorbents. The non-linear form of the Freundlich equation is shown in Equation (3) (Jonathan et al. 2009):

$$q_e = K_F C_e^{1/n} \quad (3)$$

The linear form of the Freundlich isotherm model can be written in the form of Equation (4):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where  $q_e$  is the amount of solute adsorbed (mg/g),  $K_F$  is the Freundlich constant related to the adsorption capacity,  $n$  is an empirical parameter that reflects the adsorption intensity and  $C_e$  is the equilibrium concentration (mg/L). The plot of  $\log C_e$  against  $\log q_e$  will give a straight line with  $1/n$  as its slope and  $\log K_F$  as the intercept. Adsorption is said to be favorable if the value of  $1/n$  is less than unity; there is an increase in the adsorption capacity with the appearance of new adsorption sites. The interaction between the adsorbent and adsorbate is stronger with a smaller value of  $1/n$  (larger value of  $n$ ). A value of  $1/n$  equals unity suggests that the adsorption is linear, resulting in the same energy of adsorption for all adsorbent sites. If the value of  $1/n$  is greater than unity, the adsorption is said to be unfavourable; the capacity of the adsorption decreases and the adsorption bonds will become weak (Hasnain Isa et al. 2007).

The Freundlich isotherm model relates to the adsorption of the substance on a multilayer surface. The Freundlich isotherm constants obtained graphically are shown in Table 2. The adsorption intensity value of 1.17 indicates that the adsorption process is favorable; new adsorption sites appeared and the adsorption capacity also increased. With the Freundlich isotherm as a desirable model, this suggests that the adsorption occurred at the multilayer surface of

**Table 2** | Freundlich and Langmuir isotherm constants

Langmuir isotherm				Freundlich isotherm coefficients		
$k$	$b$	$R^2$	$R_L$	$K_F$	$R^2$	$n$
28.6	0.09	0.92	0.1	8.76	0.99	1.17

the MISCBA. The larger value of  $n$  (smaller value of  $1/n$ ) indicates that there is a strong interaction between the zinc ions and the MISCBA. The high correlation value of 0.99 explains that the MISCBA has a heterogeneous surface (Figure 1(a)). This is the common value usually obtained, and can be linked to other factors that lessen the relationship between the adsorbent and adsorbate while enhancing the surface density (Reed & Matsumoto 1993).

### Langmuir isotherm model

The Langmuir model is another isotherm model that is used widely for describing the sorption of heavy metals by biosorbents. The Langmuir model relates the concentration of the adsorbate above the solid to the number of molecules on the solid surface at a given temperature. The Langmuir isotherm was established based on three assumptions: the adsorption is restricted to monolayer coverage, all surface sites are the same and can only support a single adsorbed atom, and the ability of an atom to be adsorbed on a particular site is independent of the occupancy of its neighboring sites. These assumptions indicate that adsorption and desorption rates are equal. The non-linear form of the Langmuir model can be written in the form of Equation (5) (Ho 2006):

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (5)$$

The linear form of the Langmuir isotherm model can be written in the form of Equation (6):

$$\frac{C_e}{A_m} = \left(\frac{1}{k}\right) \left(\frac{1}{b}\right) + \left(\frac{1}{b}\right) (C_e) \quad (6)$$

where  $C_e$  is the remaining concentration of the metal in the solution at the equilibrium point (mg/L),  $A_m$  is the adsorbate adsorbed per given amount of adsorbent (mg/g),  $k$  is the constant for equilibrium and  $b$  is the quantity of adsorbate required to form a monolayer adsorption. The plot  $C_e/A_m$  against  $C_e$  will be a straight line with  $1/b$  as the slope and  $1/kb$  as the intercept. The Langmuir equilibrium parameter ( $R_L$ ) can be used to further explain the important characteristics of the Langmuir isotherm. The parameter  $R_L$  is defined in Equation (7) (Amin 2008):

$$R_L = \frac{1}{1 + b(C_0)} \quad (7)$$

where  $b$  is the Langmuir constant and  $C_0$  is the initial concentration of the the metal ion (mg/L). The  $R_L$  value describes the bisorption nature as linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ), unfavorable ( $R_L > 1$ ), irreversible ( $R_L = 0$ ). The Langmuir isotherm constants obtained graphically are shown in Table 2.

The coefficient of determination obtained from the plot of the Langmuir isotherm model (graph not shown) indicates a value of 0.92, which is less compared with the value obtained from the Freundlich isotherm model. The large value of  $b$  indicates that there is a strong bonding between zinc and the MISCBA adsorbent. The  $R_L$  value of 0.1 obtained shows that the adsorption of zinc ions into the MISCBA is favorable. The maximum adsorption capacity of the adsorbent was found to be 28.6 mg/g, which was better than some ACs prepared from low cost materials as reported in the literature (Table 3).

The Freundlich and Langmuir expressions for zinc removal by MISCBA can appear as in Equations (8) and (9).

**Table 3** | Comparison of zinc removal by MISCBA with other adsorbents

S/n	Adsorbents	Operational conditions			Adsorption Capacity (mg/g)	Removal efficiency (%)	Reference
		pH	Time (h)	Dosage (g/L)			
1	Phaseolus aureus hulls	7.0	0.5	6.5	21.2	99.2	Rao et al. (2009)
2	MISCBA	6.0	3	10	28.6	89.7	This study
3	Van apple pulp	5.0	–	4	11.72	78	Depci et al. (2012)
5	Low cost adsorbents	6.0	3	20	11.24	–	Mishra & Patel (2009)
6	Moringa oleifera	6.0	4	7	10.94	63.9	Helen Kalavathy & Miranda (2010)
7	Dried activated sludge	5.0	3	3	17.86	43.7	Yang et al. (2010)

Freundlich equation:

$$q_e = 8.76C_e^{0.85} \quad (8)$$

Langmuir equation:

$$q_e = \frac{2.80C_e}{1 + 0.09C_e} \quad (9)$$

### Adsorption kinetics

The experimental data obtained was tested using pseudo first and second-order kinetic models. The two models are used to investigate the adsorption mechanisms and the potential rates regulating the steps involved, such as chemical reaction and mass transport processes. The adsorbents, physical and chemical characteristics play a vital role in determining its adsorption mechanism. The pseudo first-order kinetic model can be expressed in the form of Equation (10) (Taty-Costodes *et al.* 2003):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (10)$$

where  $q_e$  is the amount of metal adsorbed at equilibrium (mg/g),  $q_t$  is the amount of metal adsorbed at a given time  $t$  and  $k_1$  is the first-order adsorption rate constant ( $\text{min}^{-1}$ ). The plot of  $\log(q_e - q_t)$  against time is a straight line with a slope of  $k_1/2.303$  and intercept  $\log q_e$ . Figure 6 shows the plot of the pseudo first-order linear model for zinc

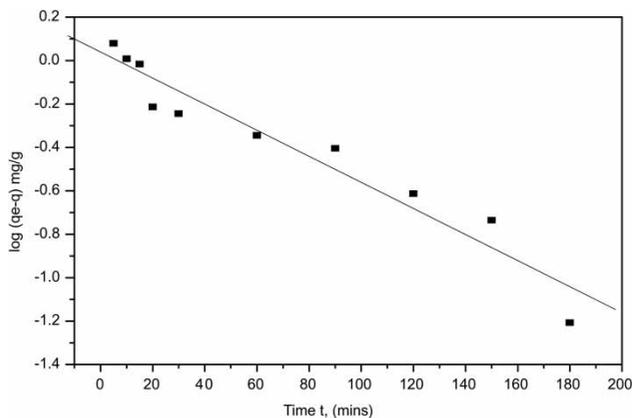


Figure 6 | Pseudo first-order kinetic plot for the adsorption of metal ion zinc.

removal. The values of  $R^2$ ,  $K_1$ , and  $q_e$  deduced from the straight line plot are shown in Table 4. The model correlation of determination ( $R^2$ ) was found to be 0.82. This shows that the model has a poor correlation value to fit the data best. It can also be seen that the experimental value of  $q_e$  did not go along with the computed value obtained from the plot. Thus, it could be resolved that the first-order kinetic model does not have an adequate value to be projected as an appropriate model. Mishra & Patel (2009) have reported a similar phenomenon on the removal of lead and zinc ions from water by low cost adsorbents.

The pseudo second-order kinetic plot for the analysis of adsorption data can be expressed in the form of Equation (11) (Ho *et al.* 2000):

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e} \quad (11)$$

where  $q_t$  is the amount of metal adsorbed at a given time  $t$  (mg/L),  $q_e$  is the amount of metal adsorbed at equilibrium (mg/g), and  $k_2$  is the second-order adsorption rate constant ( $\text{g}/\text{min mg}$ ). The plot of  $t/q_t$  against time will yield a straight line. The second order rate constant  $k_2$  and the equilibrium adsorption  $q_e$  can be obtained from the slope and intercept of the plot. Figure 7 shows the plot of the pseudo second-order linear model for zinc removal.

Table 4 shows the values of  $R^2$ ,  $K_2$  and  $q_e$  deduced from the straight line plot of the second order model. It can be observed that the  $R^2$  value of 0.99 was greater than 0.82 (obtained for the first-order kinetic plot), and the computed value of  $q_e$  also agreed well with the experimental value (Table 4). Therefore, it can be deduced that the adsorption of zinc followed the pseudo second-order kinetic model, and the potential rate regulating the adsorption step could be a chemical reaction (chemisorption) between the adsorbate and the surface of the adsorbent (Ho & McKay 1998, 2000).

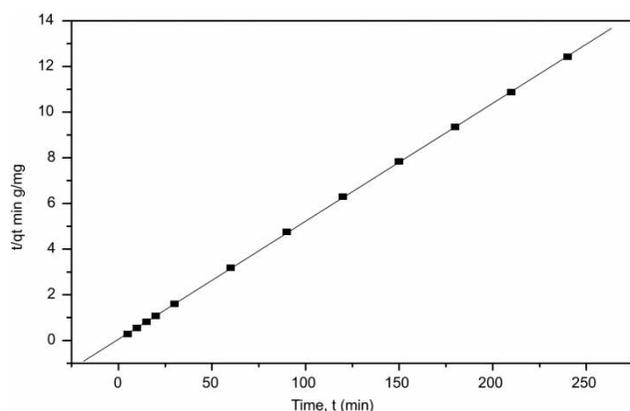
### CONCLUSIONS

A low cost adsorbent from sugarcane bagasse was successfully prepared using microwave technology. The high adsorption capacity of 28.6 mg/g obtained from this study

**Table 4** | Pseudo first and second-order reaction rate constants values for zinc adsorption

Zinc initial concentration (mg/L)	Pseudo first-order model				Pseudo second-order model		
	$q_{e, \text{exp}}$ (mg/g)	$k_1$ ( $\text{min}^{-1}$ )	$q_{e, \text{cal}}$ (mg/g)	$R^2$	$k^2$ (g /min mg)	$q_{e, \text{cal}}$ (mg/g)	$R^2$
100	19.14	0.007	4.42	0.82	0.0523	19.12	0.99

$q_{e, \text{cal}}$  = calculated value from model,  $q_{e, \text{exp}}$  = experimental value.

**Figure 7** | Pseudo second-order kinetic plot for the adsorption of metal ion zinc.

was better than a number of AC prepared from other low cost materials using different methods. The study revealed that the competition between the hydrogen ions and the metal ions at low pH values were the main factors that affect the adsorption characteristics of the MISCBA. The optimum removal efficiency was achieved at a pH of 6.0. The optimum equilibrium time required for the adsorption of zinc was found to be 180 min. As the MISCBA dosage was increased, the number of active sites for adsorption of zinc ions also increased. An optimum removal efficiency of 89.7% was achieved at a MISCBA dosage of 10 g/L. MISCBA has demonstrated that it can be used as a low cost adsorbent for the removal of metal ions from aqueous solution. More adsorption sites appeared and the adsorption capacity also increased, as revealed by the Freundlich isotherm model. Annually, about 1,500 million tons of sugarcane is produced globally, out of which 40–45% is the waste bagasse produced after the juice has been extracted. Based on the findings of this study, when the appropriate processes are carried out, wet bagasse can be used as an efficacious and cheap biosorbent for zinc (II) removal from aqueous solutions.

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