Microwave incinerated sugarcane bagasse ash (MISCBA) as a low cost adsorbent for the removal of zinc in aqueous solution

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Abstract

In this particular research, microwave incinerated sugarcane bagasse ash (MISCBA) obtained by incinerating the sugarcane bagasse was utilized as a low cost adsorbent for the removal of $ZnCl_2$ metal ion from synthetic wastewater through the batch adsorption approach. It was realized that the thermal incineration of the sugarcane bagasse changed the morphological structure of the bagasse. In addition, the surface structure of the sugarcane bagasse has changed from non-porous to a porous surface after incineration. The effect of pH and contact time, adsorbent dosage and initial metal concentration was investigated in this study. A pH value of 6 was found to be optimum. Furthermore, the percentage of adsorption improves with an increase in contact time and a contact time of 180 mins was found to be optimum after attaining equilibrium with a removal efficiency of 96.3%. The equilibrium data was well described by Freudlich as well as the Langmuir model with a correlation coefficient of 0.997 and 0.984. The kinetic data fitted well into the pseudo-second order model.
Keywords: microwave incinerated sugarcane bagasse ash (MISCBA), aqueous solution, bagasse, adsorbent, heavy metals.

1 Introduction

With the increase in industrialization and technological advancements, the environment is faced with negative impacts caused by such development. Although, the emergence of such industries contributes to the growth of social and economic status of a nation, release of wastewater laden with heavy metal

contaminants by these industries contributes in the deterioration of the human environment and as well the ecosystem.

The industries discharge their wastewater directly into flowing rivers with or without given proper treatment and this adversely affect the environment especially in places where reuse of surface water is mainly practiced. The contamination of surface water by industrial action has become a major concern to the general public and has been elevating worldwide in the past decades (Meena *et al.* [1]). Their occurrence in the aquatic system has leads to major health issues faced by human, animals and plant as well (Kılıç *et al.* [2]). These metals contaminates not only the earth's water but also the underground water by seeping through the soil when rained or snowed (Mosa [3]). Due to this, regulatory bodies have enacted guidelines to be followed for the treatment of wastewater containing heavy metals before it is discharge into the environment.

Various techniques have been developed for the removal of these metals from wastewater including electrochemical processes, ion-exchange, membrane filtration, adsorption, chemical precipitation, coagulation, vacuum evaporation and floatation (Kılıç *et al.* [2]) etc. Nevertheless, the use of these techniques are not cost effective neither user friendly (Feng *et al.* [4]). Bio-sorption process is among the most suitable technology for the treatment of wastewater laden with heavy metals. It is a promising substitute for the traditional techniques used due to its availability, no nutrient requirement, reduced volume of waste sludge and also found in low cost (Deng and Ting [5]). In view of this, biomaterials have stand out to be an economical and user friendly alternative (Ahluwalia and Goyal [6]). Several biomaterials have been studied as an adsorbent for the removal of heavy metals from aqueous solution. Agricultural by-products have extensively been studied for the removal of heavy metals from solution. These includes, rice husk, peanut, saw dust, orange peel, wool, leaves, banana peel, peat, pine bark, sugarcane bagasse and onion (Wan Ngah and Hanafiah [7]).

Sugarcane bagasse possess some potentiality to be utilized as adsorbent for the removal of heavy metals from aqueous solution, this is because of its high lignin, hemicelluloses, cellulose, and carbon content (Guan *et al.* [8]). The use of raw sugarcane bagasse as an adsorbent has been reported by some authors (Basso *et al.* [9]). However, due to its low adsorption capacity for heavy metals removal, some authors reported to have given different modification for raw sugarcane bagasse waste as a tangible material for an adsorbent, especially by altering its properties in order to enhance its efficiency. In this particular study, the potentiality of utilizing microwave incinerated sugarcane bagasse ash (MISCBA) as a low cost adsorbent for the removal of Zinc from aqueous solution has been investigated.

2 Materials and method

2.1 Adsorbent

Sugarcane bagasse was obtained from a local juice maker at Botah, Malaysia, after all the cane juice has been extracted. It was then manually cut to an average size

of 10 cm and washed several times with tap water in order to remove all dirt's and impurities from it; the bagasse was further washed with distilled water in order to enhance its purity from any contaminant. It was then dried in oven at 105°C for 24 hours until all its moisture was evaporated and constant weight was achieved. The dried bagasse was then grinded to a size of 6mm using a laboratory grinder. The material was then incinerated at 500°C using a microwave oven incinerator for a complete process of 3 hours. The MISCBA was then grinded in a laboratory still mill and then sieved in the size range of 100–150 μm, the resulting powder was immersed in a week acid (5% sulphuric acid) for 24 hours; the purpose of this procedure is to adjust the pH of the MISCBA into the acidic state to allow the adsorption process to occur. The resulting material was thoroughly washed with distilled water until a ph 4.25 pH was achieved, the washed sample was then dried in an oven at 70°C for 3 hours and was then stored in an airtight container before use.

2.2 Adsorbate

A stock solution of 1000 mg/L of zinc was prepared by dissolving its corresponding salt chloride ($ZnCl_2$) in 1L of ionized water to form an aqueous solution. Further required concentrations were achieved by diluting the stock solution using distilled water. To ensure the homogeneity of both the standard and stock solution, they are stirred for 1hour using magnetic hot plate stirrer at 100 rpm and 30°C. All chemicals employed are of analytical grade, obtained from Merck (Germany).

2.3 Experimentation

Batch adsorption studies were carried out using series of Erlenmeyer flask containing 100 mL of synthetic solution and MISCBA dosage. The flasks were agitated using orbital shaker (Protech model 722) at 150 rpm and at room temperature (27 ± 1°C) until the equilibrium were reached. The final settled solution was then filtered using a Whatsman cellulose acetate membrane filter of 0.45 μm. Filtered solutions are analyzed for its zinc metal content using Atomic Adsorption Spectrometer, AAS (Model AA 6800 Shimadzu). The effect of pH of the initial aqueous solution on the equilibrium uptake of $ZnCl_2$ ion was analyzed upon a pH range from 1 to 8. The pH of the solution was adjusted using 2.0N Hydrochloric acid and 1.5N Sodium hydroxide (NaoH) solutions. 500 mg of MISCBA was placed into each of the flasks. The flasks were clamped in an orbital shaker and agitated at a speed of 150 rpm for a period of 2 hours. The pH of the solution was measured using a pH meter (Model EW 53013, Hach Sension 1). The effect of initial metal ion concentration on the adsorption of zinc was studied by varying the metal concentration from 1 to 200 mg/L. The pH of the solution was adjusted to the optimum pH before the addition of adsorbent. The effect of adsorbent dosage was also varied from 2 to 12 g/L. The batch studies were also conducted as a function of contact time (1, 5, 10, 20 30, 60, 90, 120, 150, 180, 210 and 240min) for maximum adsorption until equilibrium was achieved. The percentage removal (R) of Zinc was calculated by:

$$R = \frac{(Ci - Ce)}{Ci} X 100\% \tag{1}$$

where, Ci and Ce are the initial and equilibrium concentration in (mg/L) in the solution. The adsorptive capacity of the metal ions in (mg/mg) was computed by:

$$q = \frac{(Ci - Ce)V}{W} \tag{2}$$

where q is the capacity of adsorption (mg/mg), Ci and Ce are initial and equilibrium concentration of the metal solution (mg/L), V is the volume of the solution used (L) and W is the weight of adsorbent (g).

The isotherm and kinetics models used in this study are shown in Tables 1 and 2 below.

Table 1: Isotherm equations used in the study.

Isotherm model	Equation	Parameters	Reference
Langmuir	$\frac{x}{m} = \frac{abC_e}{1+bC_e}$	$\frac{x}{m}$ = Amount of adsorbate adsorbed per unit mass of adsorbate (mg/g); C_e= equilibrium concentration of adsorbate in solution after adsorption (mg/L); a and b are constant.	(Isa *et al.* [10])
Freundlich	$\frac{x}{m} = K_f C_e^{1/n}$	Kf = Freundlich constant (mg/g); n is a constant.	(Isa *et al.* [10])

Table 2: Kinetic equations used in the study.

Kinetic Model	Equation	Parameters	Reference
Pseudo first-order	$\ln (q_e-q_t) = \ln q_e - k_1 t$	Q_e (mg/g) = equilibrium adsorption capacity; q_t (mg/g) = amount of adsorbate adsorbed at time t (min); k_1 (min^{-1}) = pseudo first-order constant.	(Ho and McKay [11])
Pseudo second-order	$\frac{t}{q_t} = 1/k_2 q_e^2 + \frac{t}{q_e}$	K_2 (g.mg^{-1}. min^{-1}) = pseudo second-order constant.	(Aharoni and Tompkins [12])

3 Results and discussion

3.1 Effect of pH

Adsorption of metal ion by an adsorbent is greatly influenced by the pH of the adsorbate solution. This is because of the competitive nature between hydrogen ions and positively charged metal ions struggling for an active site of the adsorbent (Rafatullah *et al.* [13]). Figure 1 shows the effect of pH on the adsorption of zinc. It is evident from the plot that the adsorption of zinc by MISCBA is relied upon the pH of the solution. Removal efficiency of zinc increases with an increase in solution pH and attaining a maximum removal efficiency of 96.2% at pH 8. Though, literally for hydroxide precipitation, precipitation of zinc begins at a pH greater than 6 (Metcalf *et al.* [14]). Based on this, a pH of 6 having a removal efficiency of 86.2% is considered to be optimum for further studies. This is comparable to the result obtained by (Peternele *et al.* [15]) on the removal of metal ions by low cost adsorbent from an aqueous solution.
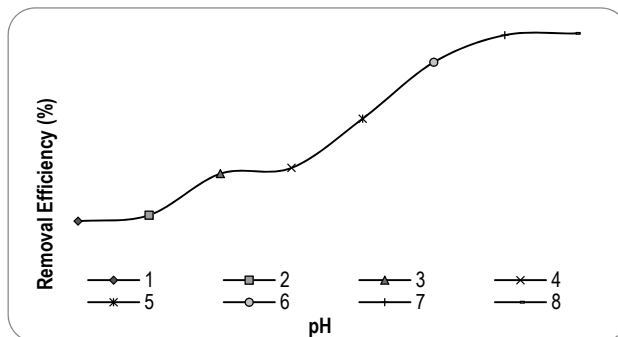

Figure 1:   Effect of pH on the adsorption of metal ion zinc (initial concentration = 100 mg/L, agitation speed = 150rpm, temperature = $27 \pm 1°C$, contact time = 120 mins and adsorbent dosage = 5.0g/L).

3.2 Effect of contact time

Preliminary studies were carried out in order to ascertain the optimum time taken to reach equilibrium adsorption. The results obtained are presented in Figure 2. From the plot it can be seen that higher percentage of removal was noticed in the first 20 mins and there is no substantial removal was realized after 180 mins. The high removal efficiency at the initial contact time is mainly related to the available surface area of MISCBA, as the contact time increase the surface of the adsorbent will be worn out and become lessen, at this stage, the efficiency of removal is controlled by the transport rate from the exterior to the interior sites of the adsorbent material (Rafatullah *et al.* [13]). Contact time of 180 mins is considered to be optimum in this study and maintained for subsequent studies. Similar result was obtained by (Isa *et al.* [10]) in the adsorption of metal ions using low cost sorbent in aqueous solution.
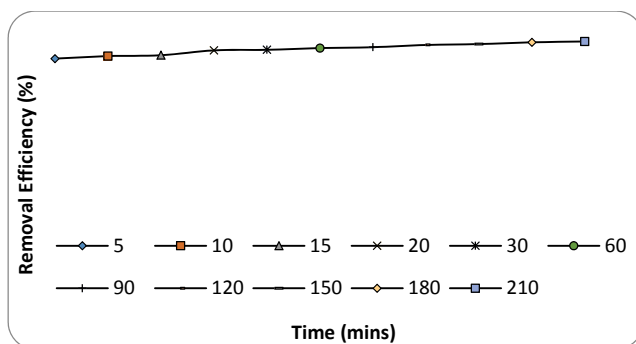
Figure 2:   Effect of contact time on the adsorption of metal ion zinc (initial
              concentration= 100 mg/L, agitation speed = 150rpm, temperature =
              27 ± 1°C, pH = 6.0 and adsorbent dosage = 5.0g/L).

3.3 Effect of adsorbent dosage

Effect of MISCBA on the adsorption of Zinc was investigated by varying the
adsorbent dosage from 2 to 12 g/L. Other parameters such as pH, contact time
were set to the optimum value obtained; initial metal concentration of the metal
ion was kept constant in its initial value. Figure 3 shows the plot of the effect of
adsorbent dosage on the removal efficiency of zinc. It is evident from the plot that
rate of removal increases with an increase in MISCBA dosage, literally this is
attributed to the availability of more adsorption sites at increased attentiveness of
the adsorbent material with regard to complexation of metal ions (Ahmad *et al.*
[16]). Removal percentage of zinc increased from 73.5% to 91.1% with an increase
in MISCBA adsorbent at equilibrium condition.

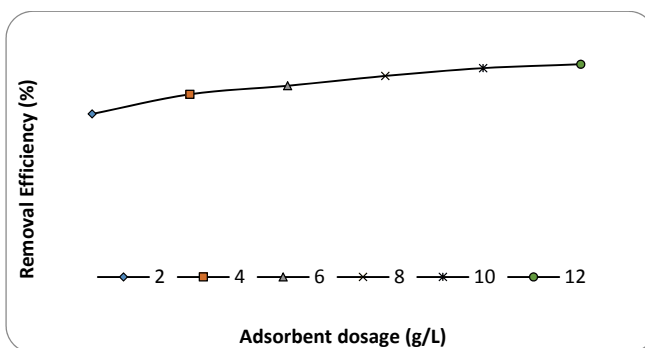
Figure 3:   Figure 3:   Effect of adsorbent dosage on the adsorption of metal
              ions (initial concentration= 100 mg/L, agitation speed= 150rpm,
              contact time = 180 mins, temperature= 27 ± 1°C, pH=6.0 and
              adsorbent dosage = 5.0g/L).

3.4 Effect of initial metal ion concentration

Concentration of metal ion in the solution plays a vital role in the adsorption process as a major steering force to outweigh the mass transport resistance involving the solution as well as solid stages (Rafatullah *et al.* [13]). At lower concentration it is expected that the adsorption rate will be higher and vice versa. Figure 4. Show that percentage of removal decreases with increasing metal ion concentration in the aqueous solution. Adsorption of zinc by MISCBA is found to be relied on the initial concentration of the adsorbate to a greater extent.
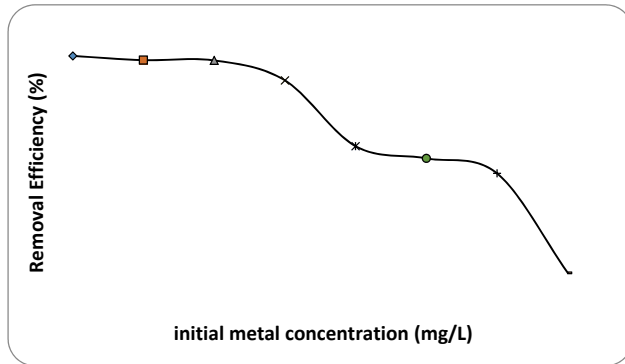

Figure 4: Effect of initial metal ion concentration on the adsorption of metal ion zinc (agitation speed = 150rpm, contact time = 180 mins, temperature= 27 ± 1°C, pH = 6.0 and adsorbent dosage = 5.0g/L).

3.5 Adsorption isotherms

In the modeling process for the analysis and design of an adsorption system, an adsorption isotherm tends to be an essential tool in understanding the adsorption behavior between the adsorbent and the adsorbate. Freundlich and Langmuir equations were employed in order to relate the isotherm upon the adsorption of Zinc. The isotherm constants obtained graphically for both Langmuir and Freundlich are presented in Table 3 below.

Table 3: Constants of isotherm and correlation coefficients.

Langmuir isotherm			Freundlich isotherm coefficients		
a	b	R^2	K_f	R^2	n
28.57	0.984	0.9210	8.76	0.997	1.17

The Freundlich isotherm model fitted well into the experiment data with a higher correlation coefficient near unity. With n > 1 adsorption is a physical process and also represents a favourable adsorption condition with heterogeneous activated carbon surface and is the most common value usually obtained which

can be link to other factors that lessens the relationship between adsorbent and adsorbate while enhancing the surface density (Reed and Matsumoto [17]). Higher value of correlation coefficient was also obtained for Langmuir isotherm, which is the main factor that is used to describe the capability of the adsorption process and which indicates that the adsorption data fitted well into the model with a maximum adsorption capacity for Zinc of 28.57 mg/g.

3.6 Adsorption kinetics

Adsorption data were analyzed using two different kinetic models namely pseudo first-order and pseudo second-order models in order to establish the adsorption mechanism that is responsible for the removal of Zinc. Figure 5 and 6 display the linear plots of the kinetic models (Pseudo first-order and Pseudo second-order). Kinetic constants obtained are shown in Table 4. Pseudo first-order with $R^2 = 0.825$ indicates that the model has no satisfactory value to be predicted as a suitable model while a value $R^2 > 0.99$ shows a very much ideal correlation value to be perfect model. Hence, it can be established that the adsorption of Zinc onto MISCBA perfectly follows the pseudo-second-order kinetic model. Indicating a chemisorptions process (Izanloo and Nasseri [18]).
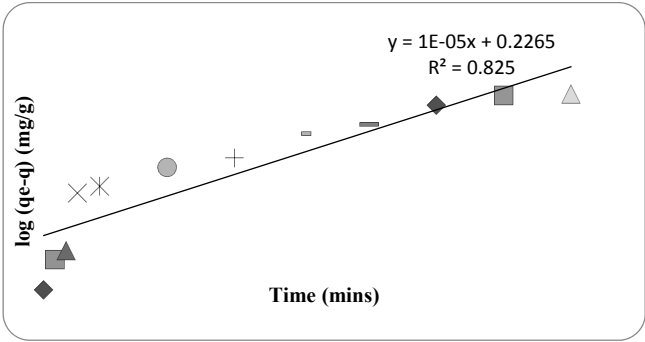

$$y = 1E\text{-}05x + 0.2265$$
$$R^2 = 0.825$$

Figure 5: Pseudo first-order kinetic plot for the adsorption of metal ion zinc.

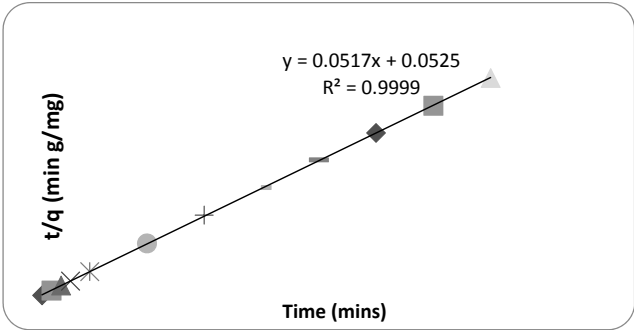$$y = 0.0517x + 0.0525$$
$$R^2 = 0.9999$$

Figure 6: Pseudo second-order kinetic plot for the adsorption of metal ion zinc.

Table 4: Kinetic models reaction rate constants for zinc adsorption.

Kinetic model	R^2	K	Equation
Pseudo first-order	0.825	0.007	$y = 1e^{-05}x + 0.2226$
Pseudo second-order	0.999	0.051	$y = 0.051x + 0.052$

4 Conclusion

The study indicates that MISCBA have the capability to adsorb Zinc from aqueous solution. The removal efficiency is depended upon the solution pH and contact time with an optimum pH 6 and an equilibrium contact time 3 hours. Maximum adsorption capacity was found to be 28.57 mg/g. The adsorption isotherm of the removal is described by both Freundlich and Langmuir isotherm models. Pseudo second-order fitted well into the adsorption data which implies a chemisorptions process between the adsorbent and the adsorbate.

Acknowledgements

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