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ORIGINAL ARTICLE

Pennisetum Purpureum Ash Silica Immobilized Sugarcane Bagasse Bio-Sorbent for Basic Dye Effluent Treatment

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ABSTRACT
A Pennisetum purpureum ash silica immobilized sugarcane bagasse bio-sorbent with improved mechanical properties was prepared. Under optimum conditions a sugarcane bagasseimmobilization of 400 mg/g silica was achieved. The bio-sorbent was used in the removal of methylene blue from aqueous solutions. Removal efficiencies of more than 98 % were achieved at pH 6 with a maximum adsorption capacity of 344.83mg^{-1}g. Experimental data fitted well onto the Langmuir (R^2=0.9839) compared to the Freundlich adsorption isotherm (R^2= 0.9718). Adsorption processes were better described by the pseudo-second order kinetic model with R^2=1. FT-IR spectra revealed typical absorption bands for biomass and silica.
Key words: Methylene blue, Freundlich, Langmuir, bio-sorption, immobilization.

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INTRODUCTION

Synthetic dyes are a persistent class of organic pollutants because of their high resistance to biodegradation [1, 2]. Major sources of dye pollution are industrial effluents from textile manufacturing, printing, and pulp and paper industries [3]. Reports by a number of researchers suggest that synthetic dyes and their degradation products may be toxic to aquatic life and humans [4, 5]. Puvaneswari et al [6] reported that toxic compounds taken up by aquatic organism may end up in the food chain resulting in physiological disorders like hypertension, sporadic fever, renal damage and cramps.A number of dye effluent treatment technologies have been developed but each of these have their own limitations[7-9]. However among these technologies adsorption techniques have proven to be more versatile because of their environmental friendly and low cost nature [10]. One of the major research directionsin adsorption methods is adding value to bio-waste by developing bio-sorption techniques. Some biosorbents based on microorganisms and plant material have poor mechanical properties. To improve on this, immobilization techniques have been developed and these include use of calcium alginate, synthetic polymers and silica [11, 12].

This study focused on developing a bio-sorbent based on sugarcane bagasse immobilized on silica gel matrix for the removal of methylene blue (Figure 4) from aqueous solutions. The source of silica was*Pennisetum purpureum* ash. Sugarcane bagasse and *Pennisetum purpureum* are both renewable. Sugarcane bagasse is a by-product of sugar processing while *Pennisetum purpureum* normally grows widely in most parts of Sub-Saharan Africa and is currently of limited commercial value.

MATERIALS AND METHODS

Sample preparation

Sun dried sugarcane bagasse provided by Hippo Valley Estate in south-eastern Zimbabwe, was oven dried at 80 °C overnight before being pulverized in a laboratory mill. *Pennisetum purpureum* harvested from a nearby farm was cut into smaller pieces, oven dried at 80 °C and finally ground into a fine powder. The powder was refluxed in 2 M HCl solution for one hour to leach out heavy metals. The leached residue was thoroughly washed with distilled water to neutrality and then oven dried at 80 °C overnight. The dried residue was then ignited at 700 °C for three hours. The resultant white ash was used to prepare a sodium silicate rich solution for immobilization through acid precipitation.

Immobilization of sugarcane bagasse

Immobilization method was developed from methods for extraction of silica gel from rice husk ash [13-15].For an optimized approach, *Pennisetum purpureum ash* (10 g) containing 83 %SiO_2 by XRF analysis was refluxed in 50 ml 3 M NaOH solution for three hours. The reaction mixture was allowed to cool and was then filtered off to remove suspended solids. To the clear sodium silicate rich solution, sugarcane bagasse powder (1.4 g)was suspended and under vigorous stirring 1 M HCl solution was gradually added until a pH of 5 was reached. Stirring continued for another five hours and allowed to stand for 48 hours. The resultant silica gel-sugarcane bagasse bio-sorbent was washed with distilledwater to remove NaCl and finally dried at 80°C. The resultant bio-sorbent contained 400 mg sugarcane bagasse per gram silica. An illustration for bio-sorbent preparation is shown in Figure 1 and a picture of immobilized sugarcane bagasse bio-sorbent in Figure 2.

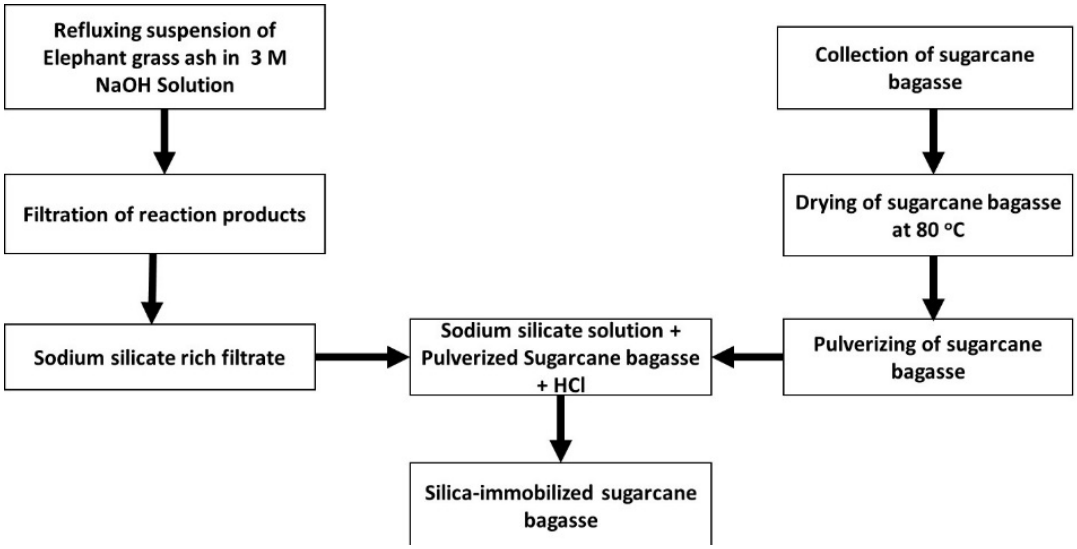

Figure 1: Illustration for preparation steps for the silica gel-sugarcane bagasse bio-sorbent

Figure 2: Picture of granules of silica gel immobilized sugarcane bagasse bio-sorbent

Instrumental characterization

A double-beam Thermo Fisher Scientific Genesy 10S UV/Vis spectrophotometer was used to determine the concentration of methylene blue before and after adsorption. IR spectra of samples were recorded in mid-IR range 4000-400 cm^{-1}on a Thermo Fisher Scientific Nicolet iS5 MIR FT-IR spectrophotometer with an ATR iD7 accessory and OMNIC software.

Adsorption experiments

Methylene blue solutions of 25, 50, 100 and 200 $mg{\cdot}L^{-1}$ were prepared by serial dilution of a 1000 $mg{\cdot}L^{-1}$stock solution. Methylene blue solution (50 ml) in which 0.8 gadsorbent was suspended was agitated at 125 rpm. The concentration of methylene blue before and after agitation was determined UV/Vis spectrophotometrically at λ_{max}=662 nm under specific experimental conditions. Adsorption experiments

were optimized in terms of contact time, pH, and adsorbent dosage. The removal efficiency (RE) was calculated using equation 1.

$$RE = \frac{C_o - C_t}{C_0} \times 100 \qquad (1)$$

whereC_o is the initial dye concentration and $C_t$dye concentration at time t. The dye adsorption capacity was calculated using equation 2 and 3.

$$q_t = \frac{(C_o - C_t)V}{m} \qquad (2)$$

$$q_e = \frac{(C_o - C_e)V}{m} \qquad (3)$$

whereq_t is the adsorption capacity in mg·g^{-1}at time t, q_e adsorption capacity at equilibrium, m the mass of the adsorbent in g, C_e equilibrium concentration mg·L^{-1}and V volume of the dye solution.

Results and Discussion

FT-IR Spectra

FT-IR spectra were recorded in order to ascertain functional groups on the adsorbent surface. Typical FT-IR spectra for sugarcane bagasse and silica are shown in Figure 3. From the spectra, one can observe -NH stretching vibrations between 3500 and 3000 cm^{-1} for both samples. A strong absorption band at about 1000 cm^{-1} is attributed to overlapping of C-O-C stretching vibrations of the cellulose and hemi-cellulose in the bagasse and Si-O-Si of the silica gel matrix. Another typical absorption bands are the –OH bending vibrations at 1600 cm^{-1} in both samples. Similar IR absorption band for silica [16, 17] and bio-based adsorbents [18, 19] has been reported by other researchers.

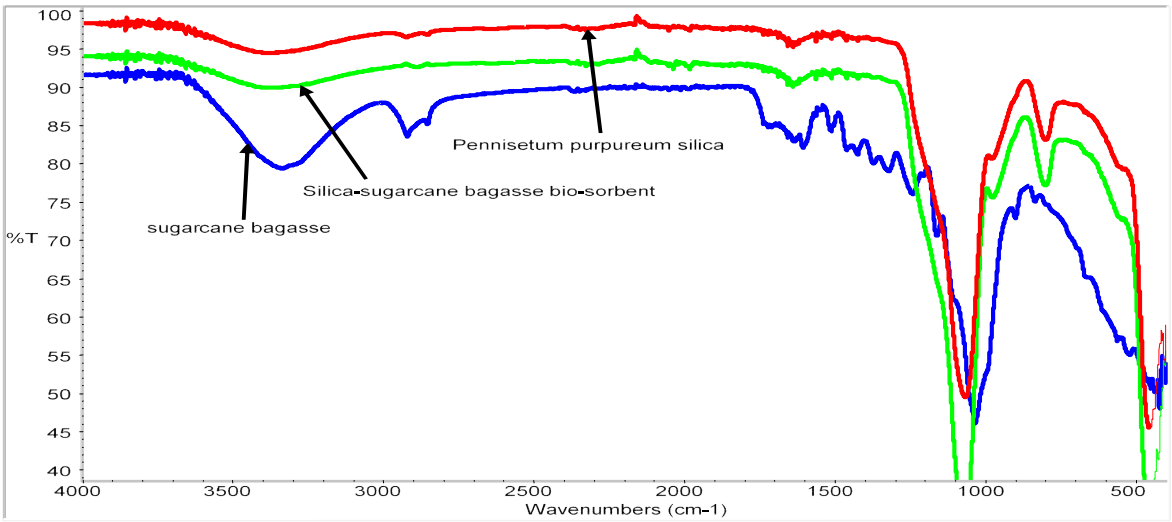

Figure 3: FT-IR spectra of silica gel and silica-sugarcane bagasse adsorbent

Effect of experimental conditions on removal efficiency

Most adsorption processes are pH dependent. The effect of pH on methylene blue removal efficiency was tested over the pH range 2-8. Experiments at higher pH were not conducted as silica dissolves in alkaline pH above 8.5. The result as illustrated in Figure 5 shows that optimum pH conditions are in the range 6-8. Lower removal efficiencies at lower pH are due to positively charged amine groups which promotes repulsion cationic dye molecules (see Figure 4). Vansanth et al [20] also attributed lower removal efficiencies to higher concentration of H^+ ions competing with methylene blue for bio-sorption sites.

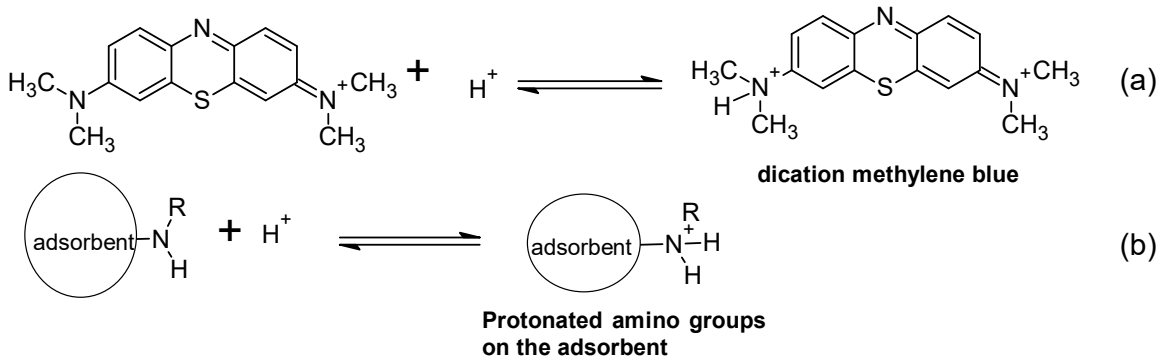

Figure 4: Protonation of amine groups of methylene blue (a) and bio-sorbent (b).

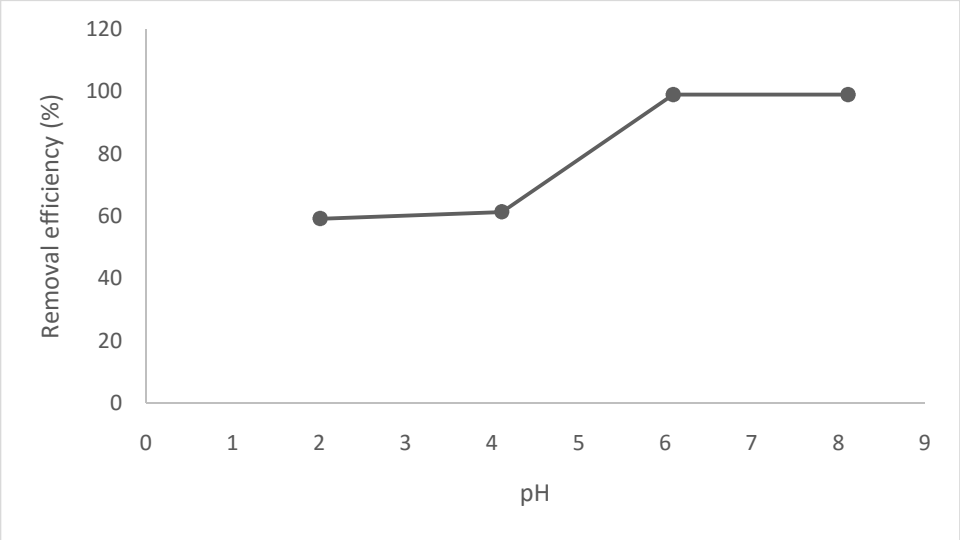

Figure 5: Effect of pH on adsorbent removal efficiency (C_o=200 mg·L^{-1}, adsorbent dosage = 0.8 g, agitation = 125 rpm, T = 25 ^oC)

The effect of contact time is very important in optimizing adsorption processes. As illustrated in Figure 6, the removal efficiency quickly rose in the first 30 minutes reaching 94 % and reached 98 % in 120 minutes. According to Khatee et al [21], the steep rise in the removal efficiency in the first 30 minutes can be attributed to large number of adsorption sites on the bio-sorbent. A similar trend has also been reported by Mahamadi & Mawere [22].

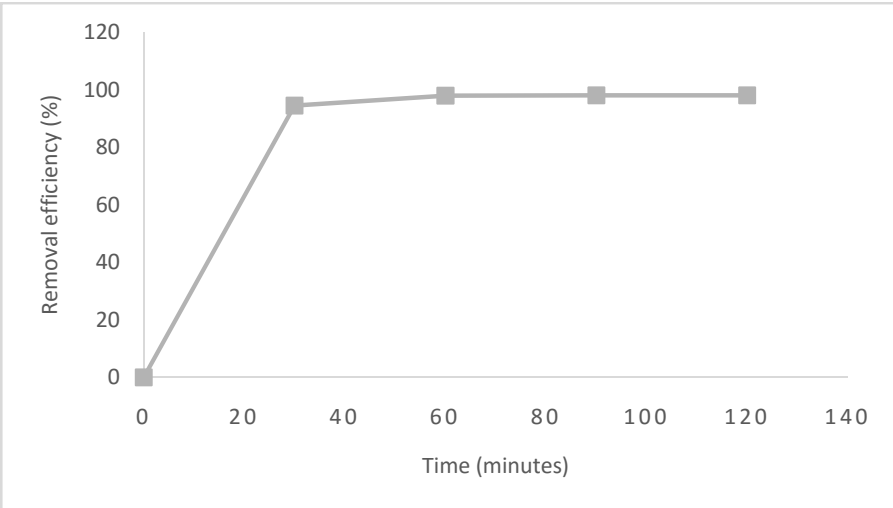

Figure 6: Effect of contact time on removal efficiency(C_o = 50 mg·L^{-1}, pH = 6, bio-sorbent dosage = 0.8 g, agitation speed = 125 rpm, T= 25 ^oC).

The effect of bio-sorbent dosage is illustrated in Figure 7. From the diagram it can be observed that the removal efficiency increased sharply with increase in dosage to slightly more than 98 % at adsorbent dosage of greater than 0.6 g. This increase in removal efficiency is attributed to an increase in available adsorption sites.

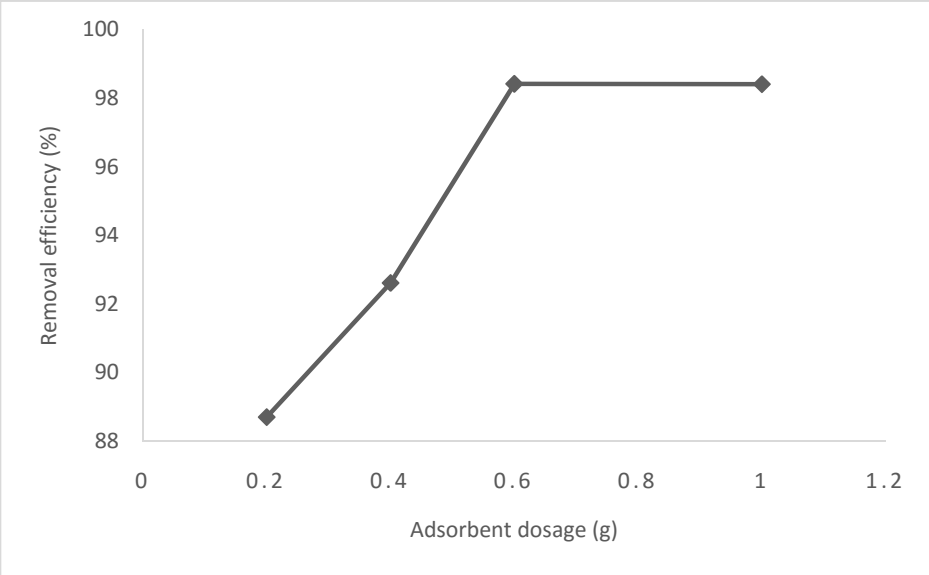

Figure 7: Effect of bio-sorbent dosage on removal efficiency (C_o = 200 mg·L^{-1}, agitation speed = 125 rpm, pH = 6, T = 35 ^oC)

Adsorption isotherms

Adsorption isotherms generally describe the relationship between the quantity of the adsorbed material and the pressure or concentration in the bulk fluid phase at a constant temperature. A number of adsorption isotherms have been developed to describe the adsorption phenomena [23, 24].Experimental data was fitted on to the Langmuir and Freundlich adsorption isotherms. The Langmuir is valid for monolayer adsorption on to a surface containing a finite number of identical sites. The model also assumes uniform energies of adsorption with no transmigration of adsorbate in the plane of the surface. The Freundlich adsorption isotherm on the other hand is commonly used to describe the adsorption characteristics for a heterogeneous surface. Adsorption isotherms, their linearized form and plot are shown in Table 1. Linear plots for Langmuir and Freundlich isotherms are shown in Figures 8 and 9 respectively. A comparison of the results is shown in Table 2. The R^2 values show that experimental data fitted well into the Langmuir adsorption isotherm. The *Pennisetum purpureum* ash-sugarcane bio-sorbent had a high maximum adsorption capacity of 344.83 mg·g^{-1}.

Table 1: Langmuir and Freundlich adsorption isotherms

Isotherm	Equation	Linearized forms	plot
Langmuir	$q_e = \frac{K_L C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} = \frac{1}{q_{max}} C_e + \frac{1}{K_L q_{max}}$	$\frac{C_e}{q_e}$ vs C_e
		$\frac{1}{q_e} = \left(\frac{1}{K_L q_{max}}\right)\frac{1}{q_e} + \frac{1}{q_{max}}$	$\frac{1}{q_e}$ vs $\frac{1}{C_e}$
Freundlich	$q_e = K_F C_e^{\frac{1}{n}}$	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	$\log q_e$ vs $\log C_e$

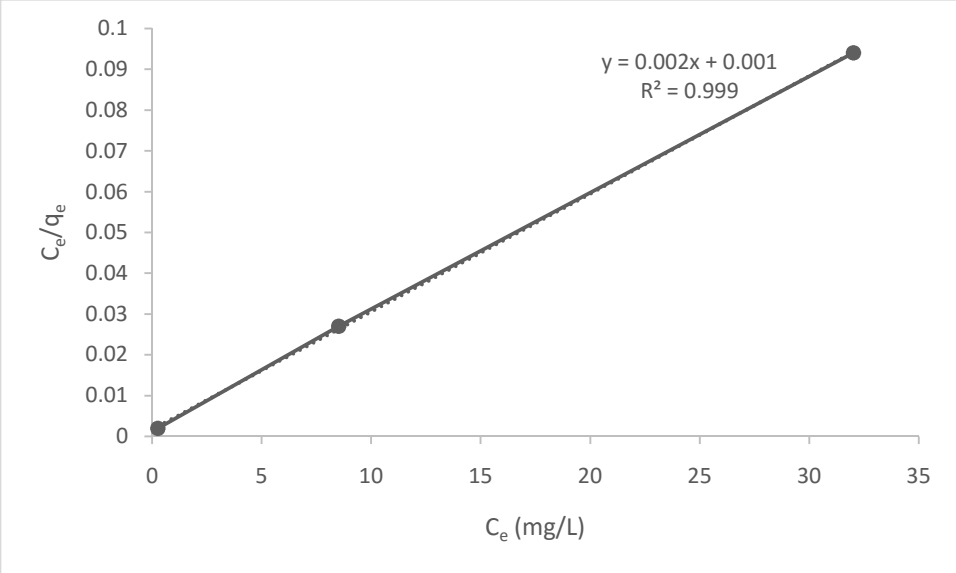

Figure 8: Langmuir adsorption isotherm

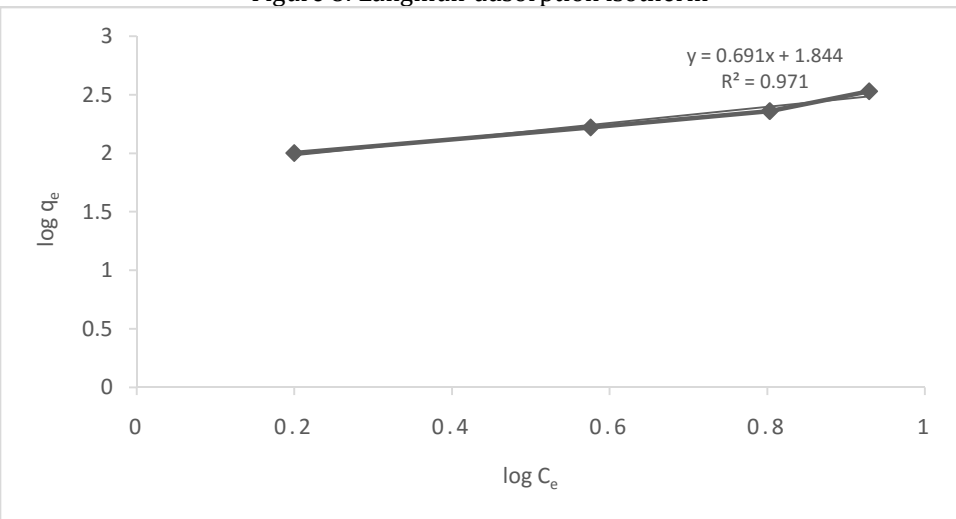

Figure 9: Freundlich adsorption isotherm

Table 2: Langmuir and Freundlich adsorption parameters

Langmuir Adsorption Parameter			Freundlich adsorption parameters		
q_{max}	K_L	R^2	K_F	n	R^2
344.83	0.674	0.9999	164.63	5.208	0.9718

Kinetic studies

In order to understand the nature of adsorption processes, kinetic data was fitted on to pseudo-first and pseudo-second order kinetic models. Equations for the kinetic models, their linearized form and plots are shown in Table 3 below. Plots of the pseudo-first and pseudo-second order rate are shown in figures 10 and 10 respectively and the results are summarized in Table 4 below. It can be observed from R^2 value of more than 0.999 that adsorption processes followed the pseudo second-order kinetic model.This is in agreement with the findings by amany of researchers who reported results that fit into the pseudo-second order kinetic model with different bio-sorbents [25, 19, 26].

Table 3: Pseudo-first and pseudo-second order kinetic models[27, 28].

Kinetic model	Equation	Linearized form	plot
Pseudo-first order	$\frac{dq_t}{dt} = k_1(q_e \quad q_t)$	$log(q_e \quad q_t) = \log q_e \quad \frac{k_1}{2.303} t$	$log(q_e \quad q_t)\ vs\ t$
Pseudo-second order	$\frac{dq_t}{dt} = k_2(q_e \quad q_t)^2$	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	$\frac{t}{q_t}\ vs\ t$

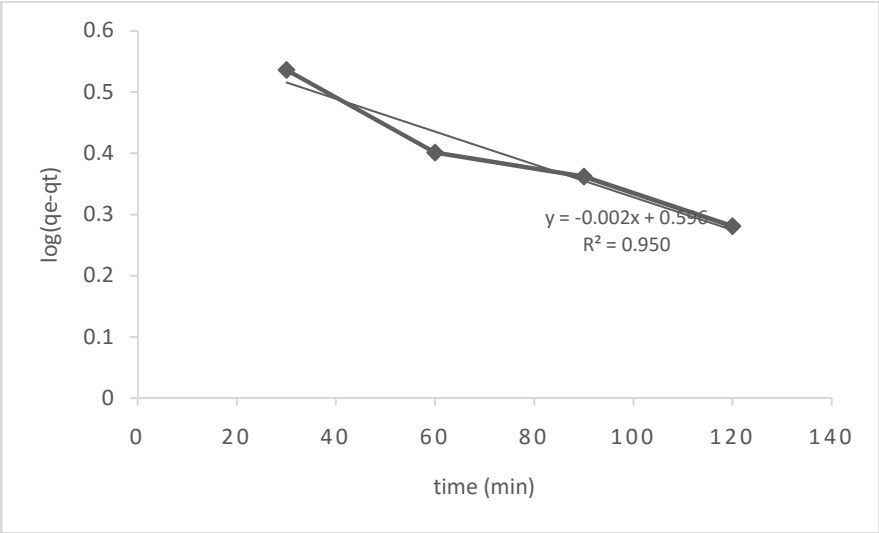

Figure 10: Pseudo-first order kinetics (C_o = 100 mg·L^{-1}, pH=6, dosage=0.8 g, T=25°C, agitation speed=125 rpm).

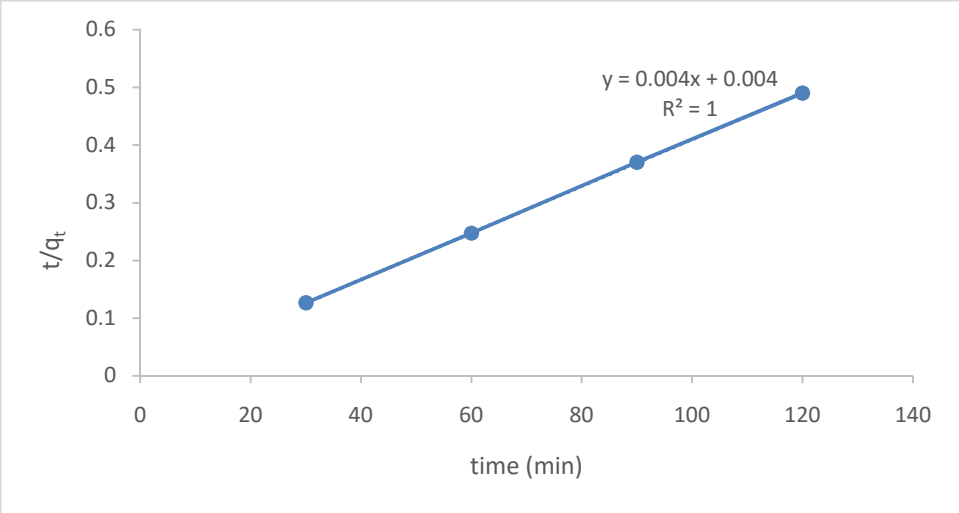

Figure 11: Pseudo-second order kinetics (C_o=200 mg·L^{-1}, pH = 6, dosage = 0.8 g, agitation speed = 125 rpm).

Table 4: Kinetic parameters for pseudo-first and pseudo-second order rates.

	Pseudo-first order parameters			Pseudo-second order parameters		
C_o	q_e	k_1	R^2	q_e	k_2	R^2
25	0.512	0.016	0.6703	30.38	0.098	1.00
50	4.977	0.018	0.7794	62.50	0.010	0.9999
100	4.043	0.007	0.9079	125.00	0.64	1.00
200	8.730	0.028	0.7500	243.9	0.005	1.00

CONCLUSION

The study demonstrated the feasibility of immobilizing sugarcane bagasse into silica gel matrix using *Pennisetum purpureum* ash as a silica source. The bio-sorbent had improved mechanical properties. Removal efficiencies of 99 % at pH 6 were achieved. The bio-sorbent had a maximum adsorption capacity of 344.83 mg·g^{-1}. Experimental data fitted well on to the Langmuir adsorption isotherm. Adsorption processes followed the pseudo-second order rate kinetic model.

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