



SUGARCANE BAGASSE DERIVED NANO MAGNETIC ADSORBENT COMPOSITE (SCB-NMAC) FOR REMOVAL OF Cu^{2+} FROM AQUEOUS SOLUTION

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ABSTRACT

A novel sugarcane bagasse derived nano magnetic adsorbent composite (SCB-NMAC) was successfully prepared for the removal of Cu^{2+} in aqueous solution. Characterization of the newly prepared material was obtained through SEM, EDX, particle size analyzer and XRD. Results confirmed the presence of iron oxide coating onto the material. The removal of Cu^{2+} by SCB-NMAC obeyed the pseudo second order reaction ($R^2 = 0.982$) as opposed to intra particle diffusion ($R^2 = 0.708$), and pseudo first order ($R^2 = 0.402$) model. Langmuir isotherm was found to be more applicable ($R^2 = 0.996$) rather than Freundlich isotherm ($R^2 = 0.979$), which indicated a monolayer adsorption between Cu^{2+} and SCB-NMAC. The maximum adsorption capacity was calculated as 113.63 mg/g at pH 4. In addition, adsorption-desorption studies indicated that SCB-NMAC displayed high stability for regeneration with good reusability with desorption efficiency up to 60% and reusability efficiency up to 80% for three recurring cycles.

Keywords: adsorption, agro waste, Cu^{2+} removal, nano magnetic particle, sugarcane bagasse.

INTRODUCTION

In recent years, environmental pollution and protection issue have become increasingly important [1-3]. This has caused increased interest in adsorption processes because of its usefulness in water and waste water treatment. Adsorption is a process in which molecules of a liquid or gas, contact and adheres to a solid surface. One of the many types of adsorbent is activated carbon. Activated carbon is a material in the form of granules or powder that is produced from carbon-containing material via physical or chemical activation. However, most traditional activated carbon exists in submicron to micron size and need large porosity to ensure adequate surface area for effective adsorption [4].

Nano materials have been suggested as efficient, cost effective and environmental friendly alternative to existing adsorbent material for environmental remediation [5]. Compared to the micron sized adsorbent, nano sized adsorbent display better performance due to its high specific surface area and effective in both low concentration of pollutants (~ 1 mg/L), and high concentration of pollutants (~ 1000 mg/L) [6-7]. Unfortunately, after the adsorption process, the spent nano adsorbents cannot be separated easily from aqueous solution by filtration or centrifugation [6].

Recently, magnetic separation techniques have received considerable attention to address the separation problem. According to characteristics of the target system, magnetic separation can be employed in two different ways: separation of magnetic target by an external magnetic field and separation of non-magnetic target such as organic molecule through formation of a complex with magnetic particle which shall then be separated by an external magnetic field [8]. If the technology can combine

the advantages of cheap activated carbon and magnetic particles to fabricate new nano composite material with high surface area, appropriate pore size, and magnetic separability, a promising novel adsorbent may be possible to be conceived.

In adsorption technology, application of iron oxide nano materials as magnetic particles have been studied due to their size in nano-range, high surface area, super-paramagnetism, ease of synthesis, and option for coating or modification [5]. In nature, iron oxide exists in many forms. Magnetite (Fe_3O_4), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), and hematite ($\alpha\text{-Fe}_2\text{O}_3$) are the most common forms [4-9]. The limitation of these products is the competitive adsorption due to self-aggregation of iron oxide particles itself. In order to optimize the synthesis of iron oxide nano materials, surface modification and medium modification needs to be studied. This modification is hoped to produce a stable magnetic nanoparticle which can resist oxidation. Generally for medium modification of iron oxide nano material, the mesoporous ($d = 2 - 50$ nm) materials are chosen as the medium or "parent materials" such as inorganic shells, organic molecules, and activated carbon which can afford enough space for particle loading [5, 9].

In this study, a novel sugarcane bagasse derived nano magnetic adsorbent composite (SCB-NMAC) material had been prepared. The new material is a combination of activated carbon generated from sugarcane bagasse as the medium, which was then modified with magnetic iron oxide nano particles. The application of interest was to evaluate its capacity to adsorb copper (Cu^{2+}) from aqueous solution. This SCB-NMAC is expected to be a novel adsorbent with high surface area, super-paramagnetism, and effective adsorption capability, with ease of separation. The new material was



characterized, and Cu^{2+} removal process was followed through by isotherm, kinetic and possible reusability studies. The use of agro waste such as sugarcane bagasse as the sorbent precursor medium in the form of activated carbon to produce SCB-NMAC modified with iron oxide nano materials to adsorb the heavy metals (Cu^{2+}) could decrease overall waste disposal problem. In addition, it is also expected to reduce the effective operating cost of water purification and treatment.

METHODOLOGY

Chemicals

All the chemicals used were of analytical grade reagent. A stock solution of Cu^{2+} (1000 mg/L) was used and solutions of various concentrations were obtained by diluting the stock solution with deionized water. The following reagents were needed for the synthesis of SCB-NMAC: iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) ACS reagent grade, iron (II) sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) ACS reagent grade, 28% NH_3 in H_2O (ammonium hydroxide solution) ACS reagent grade, and epichlorohydrin ($\text{C}_3\text{H}_5\text{ClO}$) analytical standard grade.

Preparation of sugarcane bagasse derived nano magnetic adsorbent composite (SCB-NMAC)

Activated carbon derived from sugarcane bagasse was prepared by chemical activation using NaOH with ratio 1:4. Pyrolysis was performed at 750-780°C for 90 min before being washed, neutralized, dried and stored for further modification. Synthesis of SCB-NMAC was initiated by modifying the activated carbon using nitric acid (HNO_3) solution for 1 h at 80 °C. This was to remove the impurities and enhance the active surface of the carbon particle. At the same time, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were dissolved with 450 mL of deionized water under mechanical stirring for 30 min at 30 °C. The chemical precipitation was achieved under vigorous stirring by adding 30-60 mL of ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$) solution. The reaction vessel was kept at 70 °C for 1 h. Five grams of modified activated carbon powder was added and mixed completely using mechanical stirring. Afterwards, 6 mL of epichlorohydrin was added and stirred at 85 °C for 1 h. The reaction mixture was then sonicated (Q Sonica) for 1 h. The mixture was continuously stirred for another hour at 85 °C. The mixture was then cooled down to room temperature. The precipitate was washed rapidly with deionized water and ethanol, dried at 50 °C, and collected via an external magnetic field [4, 6, 8-11].

Characterization methods

X-Ray diffraction (XRD; Bruker, D8 Advance XRD) analyses were performed at room temperature using $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) in the range $2\theta = 5^\circ - 80^\circ$ and analyzed using Diffract Plus Eva Software. Particle size was measured in a Zetasizer nano series ver. 7.03 (Malvern Ltd). The morphology and elemental analysis were observed using a JEOL SEM/EDX (JSM 6400)

instrument with a 15 kV accelerating voltage. No coating was necessary as the samples were carbon rich materials.

Adsorption experiments

The adsorption experiments were performed by batch method. Samples of 0.5 g of SCB-NMAC were equilibrated with 200 mL of various concentration of Cu^{2+} (20, 40, 60, 80, 100 mg/L) solution. The Cu^{2+} at equilibrium, q_e (mg/g) was calculated by:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

Where, C_o and C_e (mg/L) are the initial concentration, and equilibrium concentration of Cu^{2+} in the solution, respectively, V (L) is the volume of solution, and W (g) is the weight of adsorbent used [3, 12]. Samples of Cu^{2+} were collected and analyzed using Atomic Absorption Spectrometer (AAS) (PerkinElmer, PinAAcle 900F series). All measurement was conducted in triplicates, and the mean value is reported. The equilibrium data were fitted to the corresponding isotherm models. There are many different types of isotherm models to be used for determining the capacity of adsorbents. However, in this research the following isotherms were used: Langmuir [13] and Freundlich [14] to study the removal of Cu^{2+} .

Determination of optimum pH for adsorption

The optimum pH for adsorption of copper (Cu^{2+}) by SCB-NMAC were determined experimentally. Copper (II) with the concentration of 5 mg/L was prepared from the standard solutions. Samples of 100 mL from these solutions were poured into 7 conical flasks. The initial pH of the samples was adjusted to various values in the range of 3 to 9 by sodium hydroxide (NaOH) and hydrochloric acid (HCl). Subsequently, 0.5 g of SCB-NMAC was added to each flask. Equilibrium condition of the sample was obtained after 60 min of agitation at 50 °C and 150 rpm [6, 10].

Reusability of SCB-NMAC

The reusability of the newly prepared SCB-NMAC was tested by carrying out desorption process by using 0.1 M HNO_3 . Following which, the SCB-NMAC was washed thoroughly with deionized water until the pH of the wash water reached the range of pH 6-7. The washed SCB-NMAC was dried at 60 °C for 24 h and re-used for subsequent adsorption cycle. Three cycles of consecutive adsorption-desorption-regeneration were carried out to validate the reusability of SCB-NMAC for the removal and recovery Cu^{2+} [5, 11].

RESULTS AND DISCUSSIONS

Characterization of sugarcane bagasse derived nano magnetic adsorbent composite (SCB-NMAC)

Figure-1(a) shows the physical appearance of the newly synthesized SCB-NMAC material. The compact form supposed to be formed by the aggregation of



nanoparticles within the size of several nanometers which would be proven by particle size analyzer. The SEM micrograph of SCB-NMAC can be observed from Figure-1(b). The texture was somewhat irregular throughout the surface. Similar observation in terms of magnetic nano

particle aggregation pattern had been reported by Giriet *al.* [11] while using waste iron. Further to this, the agglomeration of nano particles presumably formed during vacuum drying process, leading to a non-uniform size of particles in the sub micrometer range.

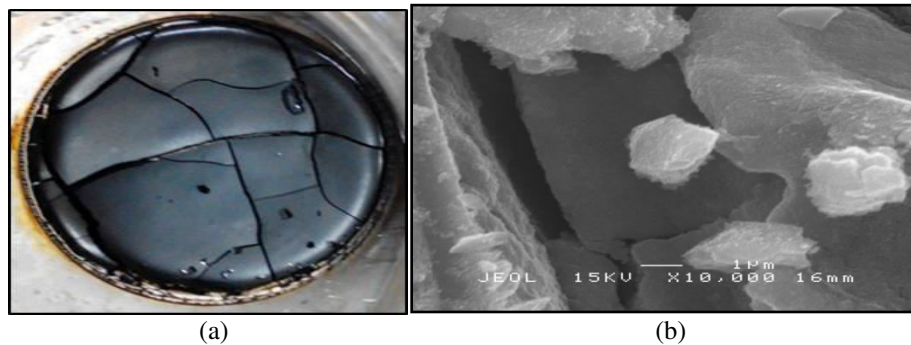


Figure-1. (a) Physical image of the newly prepared SCB-NMAC (scale 1:5); and (b) Image of SCB-NMAC captured through SEM-EDX (10000 x).

Figure-2 shows the EDX spectrum for elemental weight proportion of SCB-NMAC. Peaks corresponding to carbon (C) (67.04%) and iron (Fe) (32.96%) for SCB-NMAC had been accounted through this. These findings confirmed the successful coating and synthesis of SCB-NMAC from the activated carbon produced from

sugarcane bagasse as the medium and iron oxide as the modifying agent. The association were deemed to be stable as no leaching was observed throughout and after the process had been completed. The nano composite adsorbent material was in powder form that will ease further use as adsorbent.

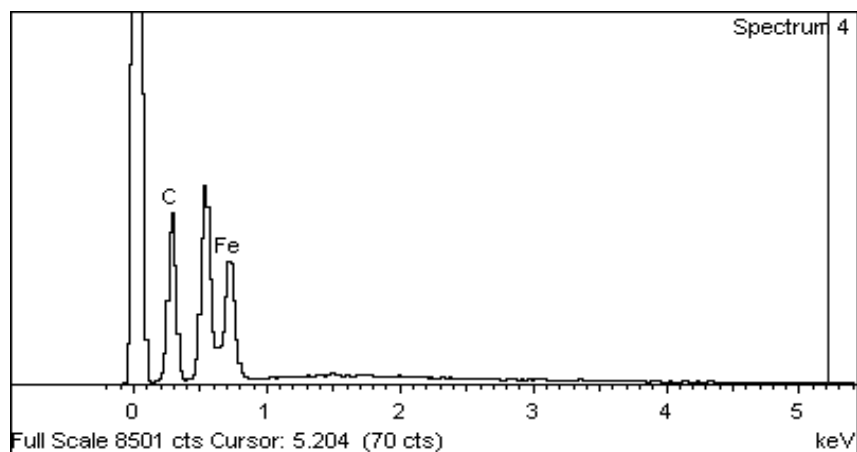


Figure-2. EDX spectrum of the newly prepared SCB-NMAC.

Figure-3 shows the XRD analyses output of the newly synthesized SCB-NMAC material. The γ - Fe_2O_3 peak attributes were identified from the XRD patterns by the peak positions at θ : 30.24, 36.63, 43.28, 53.73, 57.27 and 63.07. These matches are marked as observed. This supported the SEM/EDX results and confirmed that the iron magnetic nano particles had been successfully coated

and incorporated onto the newly prepared SCB-NMAC. The study by Balajiet *al.* [15] on the other hand demonstrated the occurrence of nanomagnetic particles in the form of Fe_3O_4 (at θ : 35.5, 43.1, 57, and 62.6) that were synthesized by chemical precipitation of Fe^{2+} and Fe^{3+} salts with alkaline medium for the adsorption of L-phenylalanine.

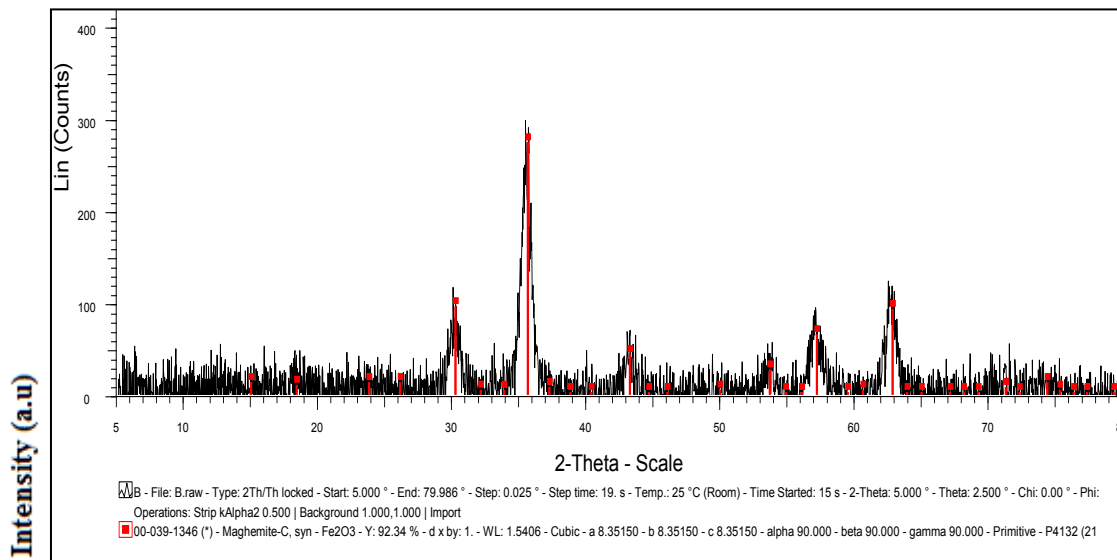


Figure-3. XRD pattern of the newly prepared SCB-NMAC. The γ -Fe₂O₃ peaks are as marked (at θ : 30.24, 36.63, 43.28, 53.73, 57.27 and 63.07).

Figure-4 shows the particle size distribution of the new SCB-NMAC material. Three dominant peaks of diameter were observed. The first peak represented diameter of 219.2 ± 41.56 nm with 5.5% intensity, second

is 1343 ± 394.3 nm with 90.3% intensity, and the last is 5459 ± 257.1 nm with 4.2% intensity. Based on Figure-4, the dominant peak represented the final diameter of SCB-NMAC as 1343 ± 394.3 nm.

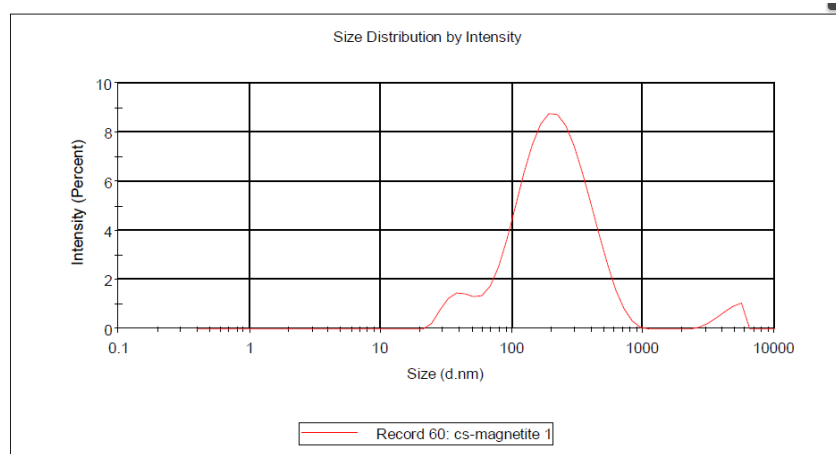


Figure-4. Particles size distribution of SCB-NMAC.

Effect of initial pH on the adsorption process

pH is an important parameter influencing heavy metal adsorption from aqueous solutions. It affects the solution chemistry of contaminants and the state of functional groups on the surface of the adsorbent [10, 16]. The effect of pH on Cu²⁺ adsorption was investigated at pH 2-6. Higher pH values, i.e. > pH 6 was not studied because due to precipitation of copper hydroxide in the solution [7, 10, 16]. Figure-5 represents the effect of initial pH of the solution towards the adsorption of copper onto SCB-NMAC. The optimum pH was observed to be pH 4 with maximum adsorption efficiency of $77.54 \pm 4.9\%$. Consequently, the working pH value for copper adsorption in this study was chosen as pH 4 and subsequent copper adsorption experiments were performed at this pH value.

The same optimum pH value (pH 4) was reported in study of chitosan coated nano particle to remove copper in aqueous solution [4]. A recent work by Norhaslina *et al.* [17] using rambutan (*N. Lappaceum* L.) wood however showed that optimum removal of Cu²⁺ (88%) occurred at pH 6.

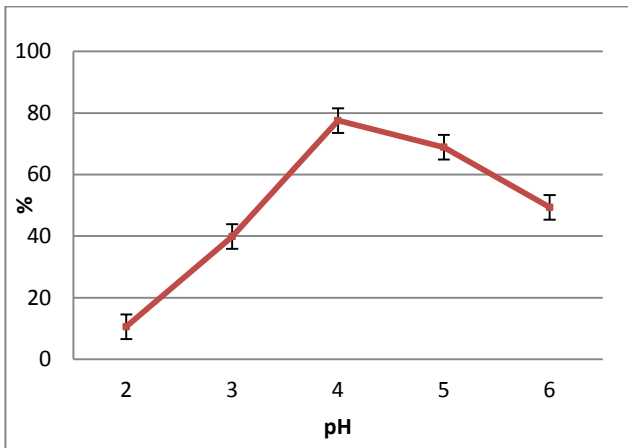


Figure-5. Effect of pH on Cu^{2+} adsorption by SCB-NMAC at temperature of 50°C , initial concentration of 5 mg/L , adsorbent dose of 2.5 g/L , shaking rate of 150 rpm , and contact time of 80 min .

Adsorption isotherm

Adsorption isotherm depicts the pathway of adsorbate interacting with adsorbents [18]. In order to determine the characteristic behavior of adsorption, various isotherm models have been proposed. In this work, isotherms studies were conducted with varying initial Cu^{2+} concentrations ($20, 40, 60, 80, 100\text{ mg/L}$), and analyzed by two isotherm models, namely, Freundlich and Langmuir.

Freundlich isotherm model

The Freundlich isotherm is based on multilayer adsorption on a heterogeneous surface [3, 14]. Linear form of the Freundlich equation is given as:

$$\text{Freundlich isotherm } q_e = K_F C_e^{1/n} \quad (2)$$

Where q_e (mg/g) is the amount adsorbed at equilibrium (mg/g) and C_e (mg/L) is the equilibrium concentration of the heavy metal. K_F (L/mg) is the Freundlich adsorption constant. n describes the empirical parameter relating to the adsorption capacity [1, 3]. From equation 2, by

plotting $\log q_e$ versus $\log C_e$ (Fig 6a), a straight line of slope $1/n$ and intercept of $\log K_F$ [19] was obtained. As seen in Figure-6(a), the Freundlich isotherm model for SCB-NMAC gave a correlation coefficient of $R^2 = 0.979$. The value of R^2 , n , and K_F are presented in Table 1. The n value was found to be high enough for separation, indicating favorable adsorption process using Freundlich isotherm ($n = 1.53$).

Langmuir isotherm

Langmuir isotherm is based on the assumption that there are a finite number of active sites which are homogeneously distributed over the surface of the adsorbent. These active sites have the same affinity for adsorption of a mono molecular layer and there is no interaction between adsorbent molecules [12-13, 20]. A well-known linear form of the Langmuir equation can be expressed as:

$$\text{Langmuir isotherm } q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

Where q_e (mg/g) and C_e (mg/L) are the equilibrium concentration of the Cu^{2+} ions. q_m (mg/g) is the Langmuir maximum uptake of heavy metal per unit mass of activated carbon, K_L (L/mg) is the Langmuir constant related to rate of adsorption. According to Equation 3, when the adsorption obeys the Langmuir equation, a plot of C_e/q_e versus C_e , Figure-6(b) should be a straight line with a slope of $1/q_m$ and intercept of $1/q_m K_L$ [19, 21]. A higher correlation value was obtained with the Langmuir model ($R^2 = 0.996$). For the Langmuir isotherm, an equilibrium parameter, R_L , is an essential characteristic of the isotherm, expressed as follows:

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

The R_L value indicates the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) [3, 21].

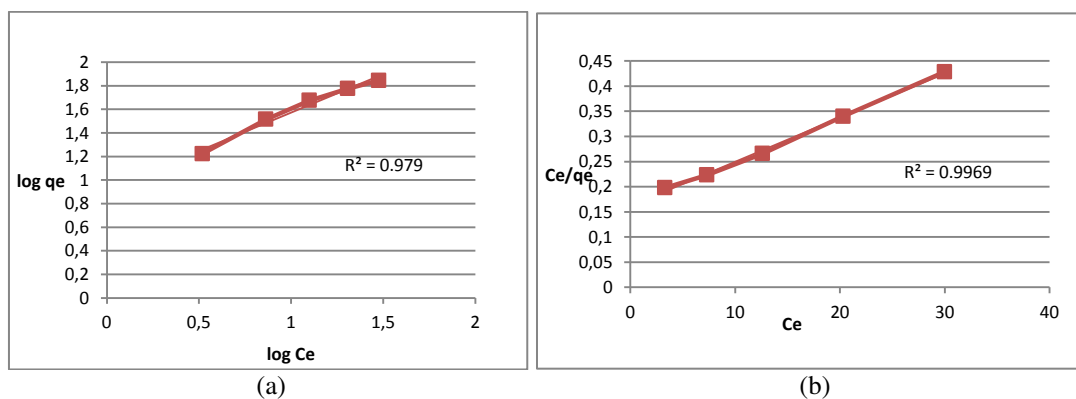


Figure-6. Freundlich isotherm (a) and Langmuir isotherm (b) for removal copper(Cu^{2+}) by SCB-NMAC at temperature of 50°C , initial concentration(C_0) of $20, 40, 60, 80, 100\text{ mg/L}$, adsorbent dose of 2.5 g/L , shaking rate of 150 rpm , and contact time of 80 min .



From Table-1, the value of correlation (R^2), for the Langmuir equation ($R^2 = 0.996$) is higher than that for the Freundlich equation ($R^2 = 0.979$). Thus, adsorption data fitted well with Langmuir isotherm. The adsorption data of Cu^{2+} based on Langmuir isotherm illustrate that the binding energy of the whole surface of SCB-NMAC to be uniform. In other words, the whole surface has identical adsorption activity. These findings also reveal that the adsorbed Cu^{2+} ions do not interact or compete with each other, and they are adsorbed by formation of a monolayer. This phenomenon, at the same time, indicates that chemisorption is the principal removal mechanism during

the adsorption process. The value of q_m and K_L were determined from the slopes and intercepts of the Langmuir plots and given in Table-1. The essential characteristic of Langmuir isotherm model can be explained in terms of dimensionless constant separation factor or equilibrium parameter (R_L) [10]. The R_L values of SCB-NMAC as shown in Table 1 indicate a highly favorable adsorption of copper onto SCB-NMAC which is $0 < R_L < 1$. q_m is the saturation capacity, representing the maximum amount of Cu^{2+} adsorbed per unit weight of nano magnetic adsorbent composite for complete monolayer coverage [7].

Table-1. Isotherm constants and regression coefficients for Cu^{2+} adsorption onto SCB-NMAC.

Freundlich model	1/n	n	K_F	R^2
	0.6511	1.5359	8.3360	0.979
Langmuir model	q_m	K_L	R_L	R^2
	113.636	0.0543	0.1553	0.996

A comparison of the maximum uptake of Cu^{2+} obtained in this study with some other values of maximum adsorbent uptake capacity of Cu^{2+} from previous studies

are summarized in Table-2. This analytical comparison shows that SCB-NMAC can compete with other adsorbent in terms of adsorption and uptake capacity.

Table-2. Comparison of adsorption capacity of various adsorbents for Cu^{2+} .

Adsorbents	Capacity q_m (mg/g)	References
EDTA functionalized Fe_3O_4 magnetic nano particle	46.27	[10]
Chitosan coated magnetic nano particle	92.59	[4]
Mono disperse chitosan bound Fe_3O_4 nano particle	21.5	[22]
Humid Acid coated Fe_3O_4 nano particle	46.5	[23]
Diethylenetriamine functionalized magnetic nano particles	12.43	[24]
Chitosan	174.75	[25]
Resins 252 H	11.74	[26]
Sugarcane bagasse derived nano magnetic adsorbent composite (SCB-NMAC)	113.63	This study

Adsorption kinetics

It is known that adsorption process could be dependent on and controlled by different kinds of mechanisms such as mass transfer, diffusion control chemical reactions, and particle diffusion [4]. In order to clarify the mechanism of adsorption process, the pseudo first order kinetic model, pseudo second kinetic model [27] and intra-particle diffusion model [28] were applied to evaluate the obtained experimental data. These models can be expressed as follows:

$$\text{Pseudo first-order model } \ln(q_t - q_e) = \ln(q_e) - K_1 t \quad (5)$$

$$\text{Pseudo second-order model } \frac{1}{q_t} = \frac{1}{K_2 q_e} + \frac{t}{q_e} \quad (6)$$

$$\text{Intra-particle diffusion model } q_t = K_3 t^{1/2} + C \quad (7)$$

Where, q_e and q_t are the uptakes of heavy metal at equilibrium and at time t (min), respectively. K_1 (1/min) is the adsorption rate constant for pseudo first order, K_2 (g/mg min) is the rate constant of second order equation. K_3 (mg/g. min^{1/2}) is the intra particle diffusion rate constant, and C (mg/g) is a constant that gives an idea about the thickness of the boundary layer. Based on their linear correlation coefficients (R^2), the kinetics models of the adsorption process can thus be determined [1].

The value of rate constants for pseudo-first order (k_1), pseudo second order (k_2) and intra particle diffusion (k_{id}) were determined from the slopes and intercepts of the



linear plots; Figure-7(a), 7(b) and 7(c), respectively. As shown in Table 3, the value of R^2 for pseudo second order kinetic model was higher ($R^2 = 0.9826$) when compared to the other two models. This indicated that the overall rate of Cu^{2+} adsorption process onto SCB-NMAC was

controlled by chemisorption which involved valence forces through sharing or exchange of electrons between the nano magnetic adsorbent composite (sorbent) and Cu^{2+} (sorbate) [27, 29].

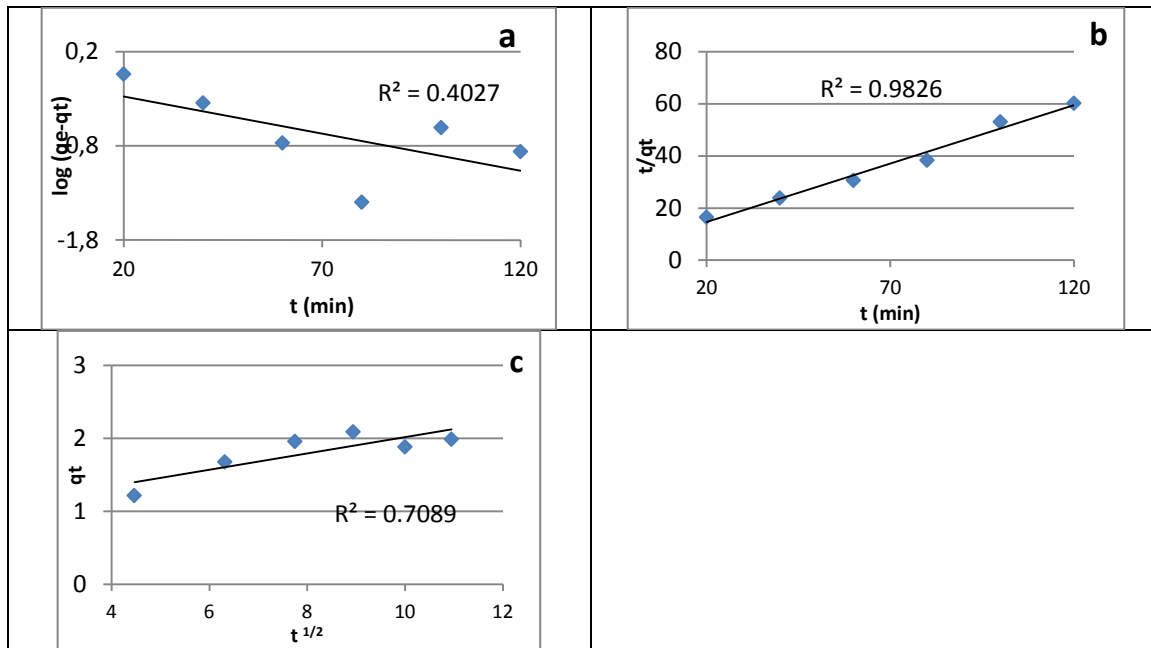


Figure-7. Representation of (a) pseudo first order, (b) pseudo second order, and (c) intra particle diffusion plots for the adsorption of Cu^{2+} onto SCB-NMAC at fixed initial concentration of Cu^{2+} (5 mg/L), adsorbent dose of 2.5 g/L, shaking rate of 150 rpm, and temperature of 50°C.

Table-3. Values of pseudo first order, pseudo second order and intra-particle diffusion constants for the adsorption of Cu^{2+} on SCB-NMAC.

Pseudo first order	k_1	q_e	R^2
	0.007	0.888	0.4027
Pseudo second order	k_2	q_e	R^2
	0.03	2.22	0.9826
Intraparticle diffusion	k_{id}	C	R^2
	0.1116	0.9027	0.7089

Reusability

In order to show the reusability of SCB-NMAC, adsorption-desorption cycles of Cu^{2+} was repeated three times by re-using the test adsorbent. It can be seen from Figure-8 that the adsorbent efficiency mostly maintained at above 80% and no obvious differences was observed during the three adsorptions-desorption cycles. The results supported that the adsorbents were stable with good reusability and could be regenerated for consecutive use in the removal of Cu^{2+} from aqueous solution. Such a property is an economic necessity and advantageous for selection of adsorbent for water and waste water treatment.

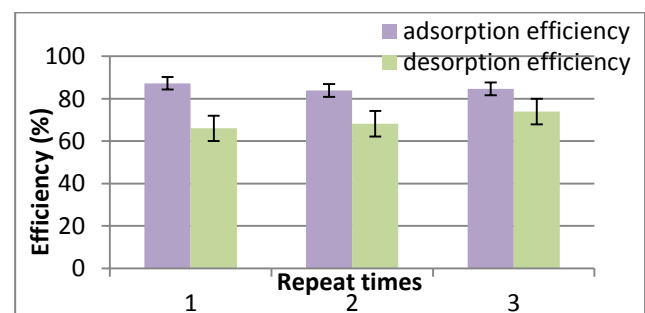


Figure-8. Reusability of SCB-NMAC for adsorption/desorption of Cu^{2+} during three cycles. Adsorption at initial Cu^{2+} concentration of 5 mg/L, adsorbent dose of 2.5 g/L, shaking rate of 150 rpm, contact time of 80 min, and temperature of 50°C. Desorption was performed by addition of 0.1 M HNO_3 .



CONCLUSIONS

In this work, a novel sugarcane bagasse derived nano magnetic adsorbent composite (SCB-NMAC) was successfully prepared and characterized by SEM, EDX, nano particle size analyzer, and XRD analysis. Equilibrium adsorption data fitted well to the Langmuir model ($R^2 = 0.996$) as opposed to the Freundlich model ($R^2 = 0.979$), indicating the occurrence of monolayer adsorption process of Cu^{2+} . Kinetically, the adsorption of Cu^{2+} onto SCB-NMAC obeyed the pseudo second order model ($R^2 = 0.982$). Compared to the other adsorbents, SCB-NMAC nano shows greatly improved uptake properties of Cu^{2+} ($q_m = 113.63 \text{ mg/g}$), probably due to higher concentration of remaining active sites on the surface of SCB-NMAC. Even after three cycles of adsorption - desorption, the adsorption capability was regained completely and the adsorption efficiency of Cu^{2+} was maintained above 80%. Desorption and reusability results indicated that the adsorbent was highly stable with good reusability. In conclusion, SCB-NMAC shows a promising prospect for application in the remediation of heavy metal-containing water and waste water treatment, with great adsorption capacity and favorable stability.

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