Original Article

Efficacy of Adsorption of Congo Red Dyes from an Aqueous Media using Silicon Nitride (Si_3N_4) Adsorbent Derived from Sand and Coffee Husk Wastes

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ABSTRACT

The current study utilizes Silicon Nitride (Si_3N_4) as a novel adsorbent in evaluating its adsorptive ability for Congo red dyes from an aqueous solution. The adsorbent was prepared using extracted silica from sand and coffee husk biochar in an ammonia environment. The Si_3N_4 adsorbent was characterized using a Field Emission Scanning Electron Microscope (FEI ESEM) which showed rod-like and fiber-like structures for α-Si_3N_4 and β- Si_3N_4, respectively. The SEM results also showed pores on the adsorbent surface before adsorption and a more rigid and restrained surface after adsorption. The adsorbent surface is hydroxylated in water to give important adsorption sites of silanolate ions ($Si\text{-}O^-$) and silazane groups ($Si_2{=}NH_2^+$) responsible for congo red (CR) dye removal. The adsorption process was investigated by batch mode. The maximum adsorption capacity (28.87 mg/g) was obtained at an optimal pH=1.00, agitation time (50 minutes), adsorbent dosage (25 mg), and initial concentration (50 mg/L). The Langmuir isotherm model was best fitted with equilibrium data with $R^2 > 0.9$, showing that the adsorption was chemisorption in nature. The results revealed Si_3N_4 adsorbent as a potential adsorbent in textile dye wastewater treatment.

Introduction

Safe water is essential for domestic use, agriculture, economy's growth and peoples' health [1]. Due to the essential role that water plays, its demand and scarcity has remained a global problem [2]. The available water reserves are contaminated by industrial effluents, and this affect the quality of life [3]. In Kenya alone, 27% of the population obtains drinking water from these sources water and additional burden for water treatment. The global challenge of the twenty-resulting to water-related diseases [4]. Majority are unable to afford the expensive chemicals needed to treat water from these available water reserves and therefore are forced to drink as it is or source water from the nearby water vendors whose quality is not guaranteed [5]. With the issue of housing being one of the agendas of Kenya kwanza government, this will definitely have an effect on demand for clean first century is therefore to overcome the lack of clean water and to provide safe water for a

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healthier ecosystem [2]. Many industries such as textiles, leather, food, plastics, and pharmaceutical play a crucial role in the global economy, but is also a significant contributor to environmental pollution due to the discharge of dye-containing effluents [6]. Globally, it is estimated that more than 100,000 types of commercially accessible dyes exist and an annual worldwide production of 700,000 tons has been reported [7]. These dyes are used to colour products [8]. Due to this, a considerable amount of coloured wastewater is therefore generated due to large consumption of water at different steps of dyeing and finishing processes [9]. In fact, processing one ton of a dyestuff product consumes between 200-270 tons of water with majority of it going to waste [10]. Approximately, 20% of these lost dyes enter in the nearby water bodies as an industrial wastewater without treatment causing potential damage to the environment [7]. The presence of the dye in water even in small amounts (1 mg/L) is highly visible [11]. The dye synthetic origin, complex aromatic structure and non-biodegradability nature make them stable making it difficult to treat such wastewater [12].

Congo red (CR) dye, a benzidine-based anionic diazo dye is one of the most harmful contaminants that is toxic, mutagenic, and carcinogenic [8]. The dye is irritant to the skin, gastrointestinal tract and eyes [13]. Long term ingestion of the wastewater containing the dye has health hazards such as destroying the human body's blood system, liver, and hematopoiesis and various symptoms such as breathing difficulties, diarrhea, vomiting, and nausea [14]. Therefore, an innovative, cost effective and sustainable treatment methods are essential in mitigating the impacts. Conventional methods for the dye removal such as nanotechnology [15] and electrochemical process [16] often involve chemical treatments or physical processes that are energy-intensive, costly, and may produce large volumes of sludge containing harmful by-products [17]. Adsorption technology has however remained the most effective method for dye removal because of its low cost, environmentally friendly and high efficiency [18]. Low-cost adsorbents such as pine bark [8], banana peel [19] and Silica gel [20] among others have been reported in removal of Congo red dye from wastewater. Silicon nitride (Si_3N_4) adsorbent is reported to adsorb pollutants such as fluoride ions [21] and tetracycline [22]. This is due to hydroxylation of Si_3N_4 surface structure in aqueous phase to yield acidic silanol (Si-OH) and basic silazane (Si_2=NH) groups which then make the surface charged [23]. This is as shown in Equation 1 and Figure 1 [24].

$$\underset{\text{(Tertiary amine)}}{Si_3N_{(s)}} + H_2O_{(l)} \longrightarrow \underset{\text{(basic silazane group)}}{Si_2{=}\ddot{N}H_{(s)}} + \underset{\text{(acidic silanol)}}{Si\ddot{O}H_{(s)}} \quad 1$$

The present work, a continuation of the previous study by [25] sought to synthesize Si_3N_4 adsorbent using extracted silica from sand and coffee husk biochar to assess the efficacy and kinetics of batch adsorption of Congo red dye from an aqueous solution.

Materials and Methods

All the chemicals used were of anal grade. Ammonium solution (NH_4OH), Congo red dye ($C_{32}H_{22}N_6Na_2O_6S_2$), Hydrochloric acid (HCl), Ammonia acetate ($C_2H_7O_2N$), and Sodium hydroxide (NaOH) were all sourced from Sigma Aldrich (Kobian, Nairobi Kenya). Distilled water obtained from Kenyatta University chemistry laboratory was used throughout the study.

Si_3N_4 Adsorbent Preparation

The silicon nitride adsorbent was carried out first by carbothermal reduction followed by nitridation. The biochar powder was mixed with the extracted silica in the ratio of 3 to 2 for

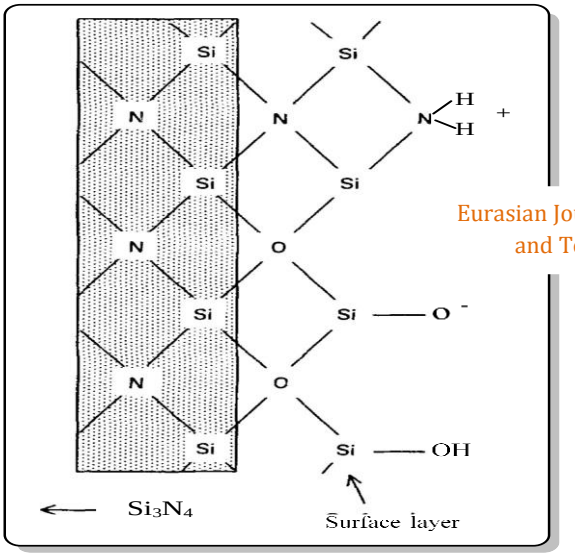

Figure 1 Hydroxylated Si_3N_4 surface structure

two hours and then placed in a digestion bomb. The bomb was tightly closed and placed in a thermostat-controlled muffle furnace and heated at 300 °C for 12 hours and the final product allowed to cool. Approximately 200 mL of NH_4OH solution (28% v/v) was then added, bomb tightly closed and heating continued at 300 °C for another 12 hours. The final product was then allowed to cool, ground and stored in an airtight container.

Dye Solutions

The stock solutions (1000 mg/L) was made by dissolving 1.00 g of the anal grade Congo red azo dye in an ammonium acetate ($C_2H_7O_2N$) buffer media to maintain a constant ionic strength, and then serial dilutions followed to obtain working solutions. 0.1 M NaOH or 0.1 M HCl solutions were used for pH adjustments. The fresh dilutions were used in each adsorption experiment.

Instrumentation

The used instruments and equipment were Field Emission Scanning Electron Microscope (FEI ESEM, Vega3 Tescan LMH), pH meter (PHS-3C), Thermostat-controlled muffle furnace (MC5-12 Biobase), double beam UV-Visible Spectrophotometer (Specord 200, Analytik Jena), Distiller (WSB 14), Lab-line mechanical reciprocating shaker (SSL_2 Harrogate, UK), and Analytical weighing balance (ATX224 Shimadzu).

Adsorption Experiments

Batch Studies

The effect of pH, agitation time, dosage, and initial concentration on Congo red sorption onto Si_3N_4 adsorbent was optimized by batch method using plastic screw cap bottles (100 mL). The process parameters of pH (1.0-13.0), agitation time (10-130 minutes), adsorbent dosage (5.00-40.00 mg) and initial concentration (10-150 mg/L) were varied in 20 mL of the test solution. This was done by adjusting a single parameter while keeping the other parameters constant. The experiments were done thrice at an agitation speed of 150 rpm. The dye concentration was analyzed using a double beam UV-Visible spectrophotometer at an absorbance wavelength (λ_{max}) of 500 nm. The amount of dye ions adsorbed per unit mass of the adsorbent was determined using Equation 2.

$$q_e = \frac{(C_i - C_e)V}{M} \quad (2)$$

Where, q_e is the amount adsorbed (mg/g) at equilibrium, C_i indicates the initial concentration (mg/L), C_e is the final concentration (mg/L), V is the solution volume (mL), and M denotes the adsorbent dosage (g).

Isotherm Studies

The Langmuir, Freundlich and Dubinin-Radushkevich models are employed for fitting of equilibrium data. The Langmuir assumes a monolayer interaction which is chemisorption in nature [26]. Its linearized form is given by Equation 3.

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

Where, q_e (mg/g) is the adsorbed dye ions at equilibrium, q_m (mg/g) is the maximum amount of dye ions, and C_e (mg/L) is the concentration of dye ions adsorbed at equilibrium. K_L (L/g) is a Langmuir constant. The Freundlich isotherm describes a multilayer adsorption on a heterogeneous surface and assumes an exclusively physisorption [27]. Its linearized equation is shown by Equation 4.

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

Where, K_F and n correspond to adsorption capacity (mg/g) and adsorption intensity constants, respectively. The Dubinin-Radushkevich is based on the assumption that the adsorption process is by micropore filling mechanisms onto both homogenous and heterogeneous surfaces [28]. Its linearized expression is given by Equation 5.

$$\ln q_e = \ln q_m - K_{D-R}\varepsilon^2 \quad (5)$$

Where, q_e is the amount of dye molecules adsorbed at equilibrium (mg g^{-1}), q_m is the theoretical isotherm saturation capacity (mg/g), K_{D-R} is the Dubinin-Radushkevich isotherm constant (mol^2/kJ^2), and ε is the Polanyi potential. The model is usually applied to distinguish the physisorption and chemisorption processes [29]. The mean free energy (E) computed by Equation 6.

$$E = \frac{1}{\sqrt{-2K_{D-R}}} \quad (6)$$

The Polanyi potential value (ε) can be calculated by Equation 7.

$$\varepsilon = RT\ln\left(1 + \frac{1}{C_e}\right) \quad (7)$$

Where, R is molar gas constant (8.314 J/mol/K), T is absolute temperature (K) and C_e is the dyes equilibrium concentration (mg/L).

Results and Discussion

Hydroxylation Mechanism

The hydroxylation mechanism of silicon nitride (Si_3N_4) adsorbent surface is displayed in Figure 2.
The presence of charged silazane and silanolate adsorption sites makes the material suitable for Congo red dyes adsorption from water.

Scanning Electron Microscope (SEM) analysis

The SEM micrographs for Si_3N_4 adsorbent before and after adsorption was obtained at an accelerating voltage (20.0 kV) and magnification (Mg = 6.50 K X). The results are presented in Figure 3.
The results in Figure 3 showed the presence of rod-like and fiber-like micrographs. These are attributed to α-Si_3N_4 and β-Si_3N_4 structures [30,31]. Before adsorption (A), the adsorbent surface evidenced pores of different shapes and sizes. The dye-loaded adsorbent surface (B) is more rigid and restrained which is contributed to dyes having occupied the pores.

Optimization

The results on effect of pH on mean uptake of the dye are demonstrated in Figure 4.

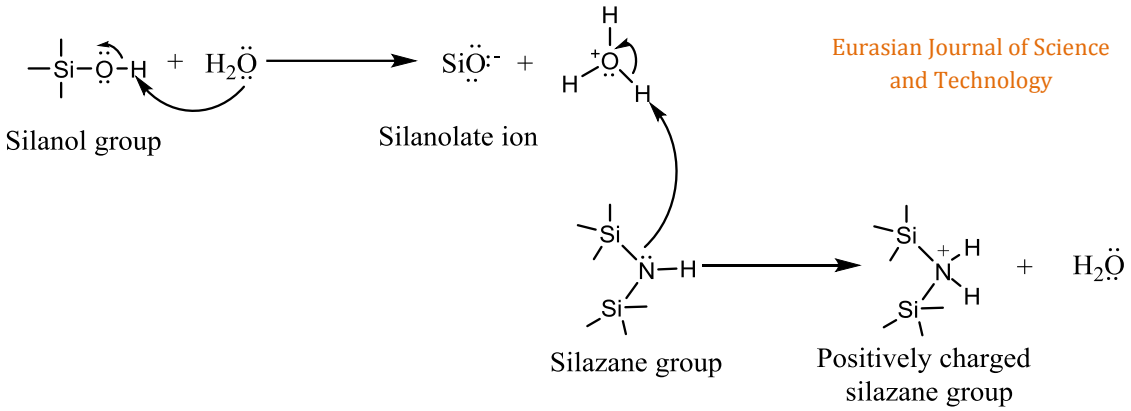

Figure 2 Silicon nitride surface hydroxylation mechanism

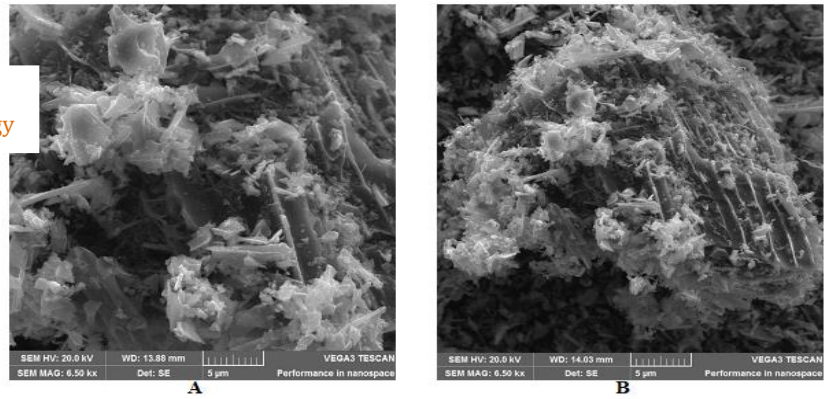

Figure 3 The SEM micrographs before (A) and after (B) adsorption

The mean uptake was maximum (14.37 ± 0.08 mg/g) at optimum pH (1). This was followed by a significant decrease in removal capacity with increased in solution pH. The positively charged silazane groups of Si_3N_4 adsorbent were enhanced in strongly acidic dye solution favoring the adsorption process. At pH 1.00 ≤ pH_{pzc} 5.10, the H^+ ions concentration in the dye solution is increased. This causes electrostatic repulsion between the H^+ ions and the positively charged silazane groups of Si_3N_4 adsorbent. These H^+ ions get attracted by the negatively charged silanolate ions and are neutralized [21]. This leaves more silazane active sites readily available for CR dye adsorption by electrostatic attraction. At pH 1.00 ≥ pH_{pzc} 5.10, the dye solution continues to become more alkaline due to the presence of excess OH^- ions which destabilizes the CR dyes by competing with the $-SO_3^-$ ions for silazane binding sites in a basic dye solution. This consequently weakens its adsorption effect [34]. The adsorption mechanism is shown in Figure 5.

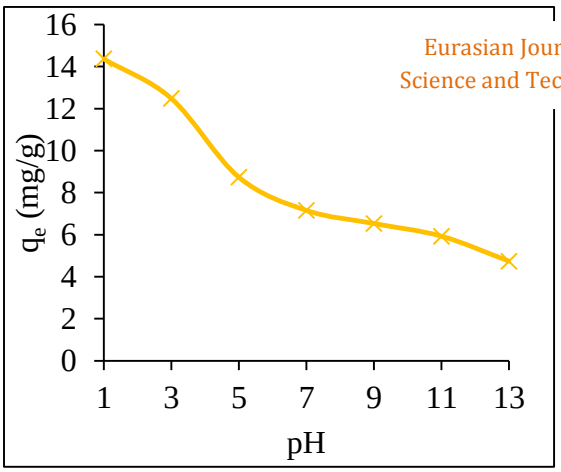

Figure 4 Effect of pH on CR dyes removal onto Si_3N_4 adsorbent

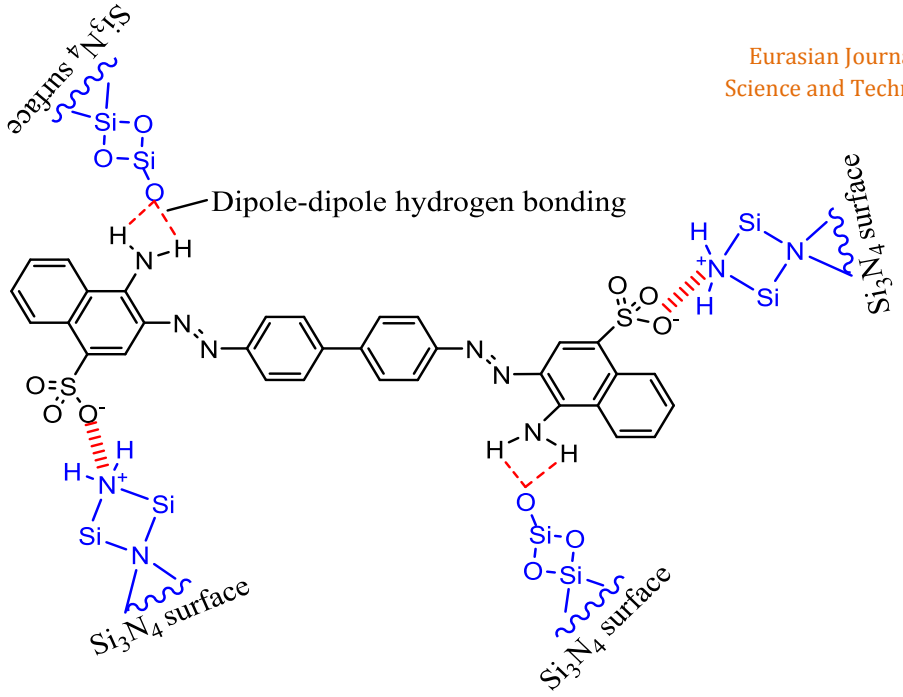

Figure 5 Adsorption mechanism of CR dye onto Si_3N_4 adsorbent

Effect of Agitation Time

The effect of agitation time on sorption of CR dyes was investigated and the results are presented in the Figure 6.

The optimal agitation time 50 minutes with a maximum uptake of 13.06±0.02 mg/g. The uptake increased with increasing agitation time during the initial stages of adsorption to optimal then became constant or lower beyond equilibrium. The rapid adsorption was due to the fact that, at the initial stages of adsorption, vacant adsorption sites are available for maximum uptake [32]. Subsequently, the lower adsorption rate beyond the optimum time is due to a decrease in the number of vacant sites of adsorbent [33].

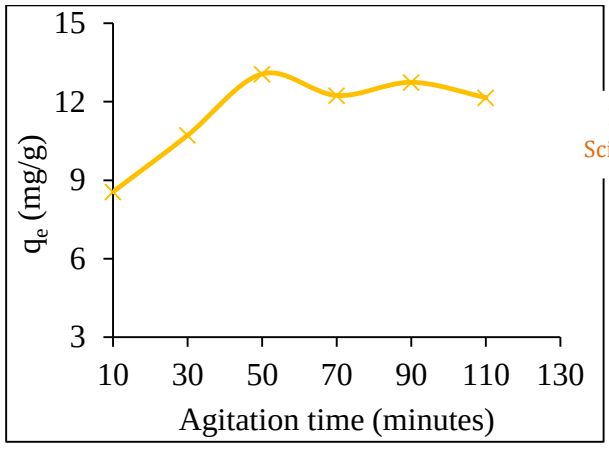

Figure 6 Effect of agitation time on CR dyes removal onto Si_3N_4 adsorbent

Effect of Adsorbent Dosage

The dosage effect on CR adsorption was evaluated by changing the dose from 5 - 40 mg. The results are presented by Figure 7.

From the results in Figure 7, the uptake of CR dyes was maximum at optimal dosage of 25 mg. The uptake was low at low dosages but increased with increase in dosage to optimum then a slight decrease. The number of the active and empty sites for adsorption increased when the adsorption dosage increased in the dye solution [34,35]. A decrease in dye removal capacity beyond optimal dosages could be attributed to the overlapping of the adsorption sites as a result of overcrowding adsorbent particles [36,37].

Effect of Initial Concentration

The influence of initial concentration (10-130 mg/L) was investigated and results are presented in Figure 8.

The sorption of CR dyes increased to maximum of 28.87±0.07 mg/g at an optimal concentration of 50 mg/L followed by a steady state. The trend can be explained by the fact that at low concentration values, there are available adsorbent sites on the adsorbent surface with less available dye molecules in the solution [38]. Increasing the dye concentration with unchanging amount of adsorbent sites led to increase in their removal capacity to optimal concentration [39]. The decrease in dye removal at concentration values beyond optimal is due to the saturation of active sites at high dye concentration conditions leaving more unadsorbed in the solution [40,41].

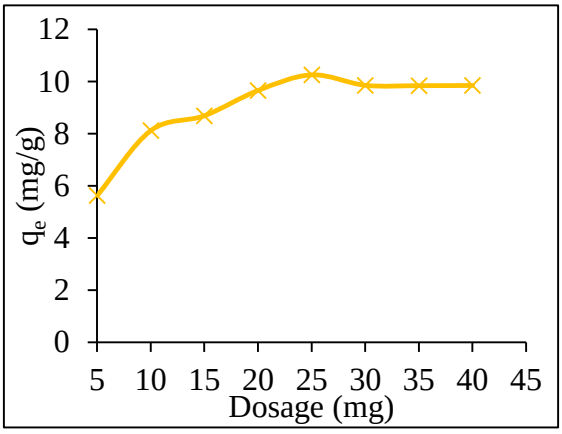

Figure 7 Effect of adsorbent dose on adsorption of CR on Si_3N_4 adsorbent

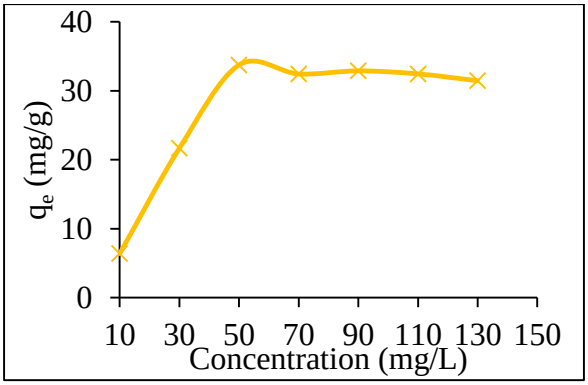

Figure 8 Effect of initial concentration on adsorption of CR on Si_3N_4 adsorbent

Adsorption Isotherm Studies

The Langmuir, Freundlich, and Dubinin-Radushkevich parameters are indicated in Table 1.

The results show that Langmuir gave better regression coefficient ($R^2 > 0.95$) than those of Freundlich and Dubinin-Radushkevich. This suggested a monolayer interaction between the dye molecules and the adsorbent sites which are chemisorption in nature [18]. The comparison of adsorption capacity of Si_3N_4 adsorbent with previously reported adsorbents is presented in Table 2.

Table 1 Langmuir, Freundlich, and Dubinin-Radushkevich parameters for CR dyes adsorption onto Si_3N_4 adsorbent

Langmuir				Freundlich			Dubinin-Radushkevich			
$Q_{m,exp}$ mg/g	$Q_{m,cal}$ mg/g	K_L (L/g)	R^2	$1/n$	K_F mg/g	R^2	$Q_{m,cal}$ mg/g	K_{D-R} (mol^2/kJ^2)	E kJ/mol	R^2
28.87	33.90	9.42×10^{-2}	0.954	4.32×10^{-1}	5.83	0.595	57.22	4.56×10^{-2}	3.31	0.865

Table 2 Adsorption capacity of different adsorbents for the adsorption of CR dyes

Adsorbent	Adsorption capacity (mg/g)	Ref.
Banana peel	1.73	[19]
Jujube seeds (Activated carbon)	19.73	[42]
Commercial zeolite catalyst	21.11	[43]
Pine bark	1.60	[8]
Silica gel (amino-functionalized)	5.37	[20]
Silicon nitride (Si_3N_4)	28.87	This study

Conclusion

In this study, the silicon nitride (Si_3N_4) adsorbent was successfully synthesized and this was confirmed by SEM micrographs. The interactions between CR dyes and the adsorbent surface were also confirmed by the micrographs. The adsorption process was greatly influenced by batch study parameters of pH, agitation time, adsorbent dosage, and initial concentration. The optimum values were pH=1.00, 50 minutes, 25 mg and 50 mg/L. The CR dyes adsorption onto Si_3N_4 adsorbent followed Langmuir isotherm model explaining that the CR dye removal was chemisorption.

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