

Mesoporous carbon-silica composite from low-cost vinasse for the effective adsorption of methyl orange and methylene blue dyes from aqueous systems

Tippawan Ponnikorn¹⁾, Narong Chanlek²⁾, Duncan J. Macquarrie³⁾, Nontipa Supanchaiyamat⁴⁾, Andrew J. Hunt⁴⁾ and Yuvarat Ngrnyen^{*1)}

¹⁾Biomass & Bioenergy Research Laboratory, Department of Chemical Engineering, Faculty of Engineering, Khon Kaen University, Khon Kaen 40002, Thailand

²⁾Synchrotron Light Research Institute (Public Organization), Nakhon Ratchasima 30000, Thailand

³⁾Green Chemistry Centre of Excellence, Department of Chemistry, University of York, YO10 5DD, UK

⁴⁾Materials Chemistry Research Center, Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

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Abstract

The adsorption behaviour of anionic and cationic dyes, namely methyl orange (MO) and methylene blue (MB), respectively, has been studied on carbon-silica composites. These composites were produced through the valorisation of waste vinasse from industrial sugar production as the carbon feedstock, while the silica production was achieved via a simple sol-gel method using low-cost sodium and potassium silicate solutions (Na_2SiO_3 and K_2SiO_3) or higher-cost tetraethyl orthosilicate (TEOS). Use of Na_2SiO_3 , K_2SiO_3 and TEOS, led to composites with specific surface areas of 375, 343 and 656 m^2/g and % mesoporosity of 79.45, 94.35 and 82.93%, respectively. Adsorption of MO is reduced at higher pH, but MB removal was enhanced under basic pH. Kinetic results demonstrated a strong correlation with the pseudo-second order model, and it was noted that intraparticle diffusion had a key role to play in the mechanism of mass transport. Adsorption data fitted the Sips isotherm model, with excellent adsorption capacity of MO (844.63 mg/g for Na_2SiO_3 , 979.06 mg/g for K_2SiO_3 , 1161.65 mg/g for TEOS) and MB (514.30 mg/g for Na_2SiO_3 , 385.34 mg/g for K_2SiO_3 , 294.88 mg/g for TEOS). Elevated temperatures led to preferential removal of the acidic and basic dyes, suggesting an endothermic adsorption process. Carbon-silica composites derived from vinasse are promising materials for the remediation of MB and MO from aqueous systems, exhibiting comparable or higher surface area and adsorption capacities for both dyes relative to other reported materials, while being synthesized through simple preparation processes from low-cost agricultural by-products.

Keywords: Acidic dyes, Basic dyes, Waste, Silicate, Removal

1. Introduction

Sugarcane is a major crop, produced globally for sugar, bioelectricity and bioethanol production. In 2021, global sugarcane production was estimated at 1.86 billion tons, with around 75% of this production coming from Brazil (38.5%), India (21.8%), China (5.8%), Pakistan (4.8%), and Thailand (3.6%) [1]. Significant low value by-products or waste materials are created in sugar production including, leaves, bagasse, molasses and filter cake. Molasses can be fermented and distilled to produce bioethanol. Vinasse is a dark brown liquid with a strong odour, that is generated in large amounts as a by-product from bio-ethanol distillation, with 10–15 L produced per litre of ethanol. This equates to a global vinasse production of approximately 360 billion litres [1]. Normally, vinasse is used as a fertilizer or animal feed due the presence of organic matter, potassium and calcium in high concentrations, alongwith moderate amounts of nitrogen and phosphorus [2]. However, repeated application leads to soil or groundwater pollution, increased salinity, and can inhibit germination [3]. Moreover, the dark colour of vinasse blocks light and limits photosynthesis and is thus detrimental to aquatic life [3]. To avoid these environmental effects, methods to valorise vinasse wastes are required.

Global annual dye production is over 700,000 tons [4]. MB and MO are some of the most well-known cationic and anionic dyes, utilized in the manufacture of textiles, leather, paper, rubber, plastics, food, cosmetics, pharmaceuticals, and also in printing [5, 6]. Such dyes are non-biodegradable, harmful to the environment and may be carcinogenic, can lead to skin irritation, cyanosis, faster heartbeat, vomiting, quadriplegia, shock, jaundice and tissue necrosis in humans [7, 8]. Thus, treatment of such dyes prior to discharge is essential. Dye remediation from effluent can be achieved through filtration, flotation, coagulation-flocculation, precipitation, chemical oxidation, photocatalysis, biological processes and adsorption [9, 10]. Among these techniques, adsorption has earned attention due to its simplicity, ease of scale up and effectiveness in the adsorption of a broad array of pollutants from aqueous systems [11, 12]. The textural properties of porous adsorbents, including pore structure, pore volume, pore size distribution, and specific surface area, are strongly influenced by the nature of the precursor materials and the applied production routes [13, 14]. Different precursors can lead to significant variations in the development of porous networks due to differences in their inherent chemical composition and

*Corresponding author.

Email address: nyuvarat@kku.ac.th

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structural characteristics. In addition, the processing conditions play a crucial role in tailoring the surface area and porosity of the final adsorbent. Therefore, a proper selection of precursor and production techniques is essential for obtaining the optimal textural properties and enhancing the applicability of the porous adsorbents to various applications.

A significant range of adsorbents has been investigated and used commercially for dye removal including: (1) activated carbon, (2) non-conventional adsorbents including agricultural waste materials, industrial waste materials, natural/synthetic clay and bio-adsorbents [15], (3) hybrid nanomaterials with their sub-categories of non-activated and activated carbon-nanocomposite, carbon nanotube-based material, graphene and graphene oxide composites, fly ash and hybrids of bio-adsorbents, (4) magnetic metal oxide-based hybrid, (5) metal-organic frameworks (MOFs) and (6) polymers and their composites including chitosan-based adsorbents. MOFs have found limited use in adsorption due to their complicated organic ligands and high synthesis cost [16]. Polyaniline-based adsorbents also suffer from high costs and limited adsorption performance due to aggregation, low surface areas and poor mechanical properties [17]. Carbon adsorbents exhibit poor thermal stability, which under certain conditions can cause them to easily ignite and result in combustion. In addition, the abundant number of micropores may lead to irreversible adsorption, thus making desorption challenging. In contrast, silica adsorbents have remarkable thermal stability but also strong hydrophilicity, which can limit applications [18]. Combining the advantages of carbon and silica into composite materials, results in enhanced thermal stability and hydrophobicity.

Recently, carbon-silica composites have found use as adsorbents due to their significant surface area, mesoporosity and stability [19, 20]. Wiśniewska et al. [21] synthesized carbon-silica composite from pyrogenic silica A-300 and phenol-formaldehyde resin. These materials were evaluated for their adsorption properties of Basic Blue 3 and Basic Yellow 2 [21]. Fu et al. [22] prepared nanoporous carbon-silica composite by utilizing tetraethyl orthosilicate (TEOS) and activated carbon. The resulting composites were utilised in the adsorption of n-hexane [22]. In addition, sucrose, polyfurfuryl alcohol and metal-organic frameworks (MOFs)/Pluronic P123/2-methylimidazole (2-MeIM)/triethylamine (TEA) were used as the carbon source, while silica gel and MCM-41/tetramethylammonium hydroxide pentahydrate (TMAOH)/hexadecyltrimethylammonium chloride (CTAC)/tetramethylammonium silicate solution (TMASi) were used as the silica source for adsorption of Congo red, nitrogen, carbon dioxide, methane, ethane, ammonia, sulfur dioxide and nitrogen dioxide [23-26]. Janekarn et al. [20] prepared carbon-silica composites from sugarcane by-products, namely molasses, and used them as adsorbents for Congo red and methylene blue remediation. The resulting composites contain mainly mesopores which led to efficient dye removal. While Duengsuwan et al. [27] synthesised nitrogen doped carbon-silica composites from molasses for the recovery of Au(III) from aqueous solutions. In some cases, the application of carbon-silica composites has been hampered by the use of costly reagents and complex synthetic methods. To overcome such challenges, it is still important to investigate low value waste feedstocks, that can be combined to produce carbon-silica composites through simple but effective synthetic methods.

Vinasse is one such resource that has been used as a carbon source for the manufacture of adsorbents [28]. Limited research has been conducted on this subject, however vinasse was demonstrated to be a suitable feedstock for the manufacture of activated carbons [29, 30]. The activated carbons contained mainly micropore (73–94%) and were able to remove MB. However, these adsorbents require high temperature between 600–1000 °C for their preparation, resulting in high energy cost. Low-cost vinasse was combined with silicates i.e. Na_2SiO_3 and K_2SiO_3 to develop carbon-silica composites [28]. The composites were synthesised by simple method of vinasse with silicon sources such as Na_2SiO_3 , K_2SiO_3 or TEOS to achieve a desired weight ratio, ranging from 1:1 to 20:1, at 85 °C over 6 h. The optimum ratios that gave highest specific surface area were 2:1 and 5:1 for $\text{Na}_2\text{SiO}_3/\text{K}_2\text{SiO}_3$ and TEOS, respectively. These materials demonstrated promise for the adsorption of four commercial silk dyes from aqueous systems with composite prepared from TEOS gave higher adsorption capacities. However, limited characterisation has led to poor understanding of the adsorption mechanism. In addition, the sustainability of their synthesis may be reduced by long mixing times.

Herein, carbon-silica composites have been synthesized from vinasse and silicates, with a focus on optimising the mixing time. Defining the optimum time to produce highest surface area will help to reduce preparation time and energy cost (heating at 85 °C). The sustainability aspect of this work lies in the use of the industrial by-product (vinasse) as an environmentally benign feedstock. In addition, low-cost silicates (Na_2SiO_3 and K_2SiO_3) are economically attractive alternatives to conventional silica sources such as TEOS. Although TEOS is included for comparative purposes, the primary focus of this study is the development of a sustainable synthesis route based on waste valorization and low-cost precursors. Proximate analysis, the point of zero charge (pH_{pzc}), density, hardness, higher heating value (HHV), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX), X-ray photoelectron spectroscopy (XPS), X-ray Diffractometer (XRD), thermogravimetric analysis (TGA) and N_2 adsorption porosimetry have been used to characterise the resulting composites. For the first time, composites from vinasse and silicates have been used for the MO and MB adsorption. Kinetic and isotherm analysis were also evaluated, along with the influence of experimental parameters. Importantly, characterisation analysis and adsorption data has shed vital light on the mechanistic understanding of adsorption on composites from vinasse and silicates.

2. Materials and methods

2.1 Material

The liquid waste vinasse was obtained from Mitr Phol Innovation & Research Center, Chaityaphum, Thailand. The main physicochemical properties of the vinasse were determined at this research center. These physicochemical properties included a pH of 4.33, electrical conductivity 33.9 mS/cm, organic matter (OM) of 18.36%, total organic carbon (TOC) of 0.82%, Brix of 26.88%, while nitrogen and phosphorus contents were determined to be 4.55 g/L and 0.22 g/L, respectively. Methylene blue (MB) supplied by QR&C and methyl orange (MO) by Ajax Finechem. Sodium silicate (Na_2SiO_3) and potassium silicate (K_2SiO_3) were kindly supplied by C.THAI CHEMICALS, Samutsakorn, Thailand. Tetraethyl orthosilicate (TEOS) was purchased from ALDRICH. Other chemicals used were H_2SO_4 (ANAPURE), NaCl (ACI Labscan), HCl (ANAPURE) and NaOH (LOBA CHEMIE).

2.2 Fabrication of carbon-silica composite

The composites were prepared according to the process below. Briefly, the optimum amount of vinasse described from our previous research [28] with a vinasse:silica ratio of 2:1 was used for Na_2SiO_3 and K_2SiO_3 (10 g), while a 5:1 ratio was utilized with TEOS (25 g). The vinasse was added to 5 mL of distilled water, after which 20 mL of 50% H_2SO_4 was added at ambient temperature to obtain carbon precursor. To which, 5 g of the silicon source was immediately added to this precursor and stirred at 500 rpm at 85 °C for 2, 4, 6, 8 and 10 h, respectively. The resulting composite was washed with distilled water until pH neutral, and dried at 130 °C for 6 h. The

composite was ground in a pestle and mortar and passed through 80-mesh sieve (180 μm) to obtain a dark brown carbon-silica composite adsorbent with uniform particle size for further characterisation and adsorption testing.

2.3 Characterisation studies

Surface textural characteristics of the composites were determined by N_2 adsorption-desorption porosimetry (ASAP 2460, Micromeritics). Scanning electron microscopy (SEM) with EDX analysis were taken using a Helios NanoLab G3 CX (FEI). Transmission electron microscopy (TEM) with EDX were recorded using a Tecnai G2. XPS analysis was conducted using a PHI 5000 VersaProbe II, ULVAC with PHI MultiPak software. X-ray diffraction patterns were obtained with a Bruker D8 advance diffractometer. Thermogravimetric analysis (TGA) profile of the composites was carried out by a Shimadzu, DTG-60H thermogravimetric analyser. 10 mg of composite was added to a platinum pan and heated under N_2 or air flow of 40 mL/min from room temperature to 950 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C}/\text{min}$.

Moisture content was determined by weighing 1.0 g of the composites in a clean, dried, and weighed crucible. The crucibles were placed in an oven (UNE 500, Memmert) at 105 $^{\circ}\text{C}$ for 3 h according to ASTM D2867. The moisture content was determined from the initial mass minus the final mass after heating. Ash content determination followed ASTM D2866-11, 1.0 g of the composite was added to a crucible and heated to 800 $^{\circ}\text{C}$ for 2 h in a TM3-550, VULCAN muffle furnace. The sample was cooled in a desiccator and weighed to obtain the ash content. For volatile matter determination (ASTM D5832-98), 1.0 g of the composite was heated for 30 mins at 900 $^{\circ}\text{C}$. The proportion of volatiles was the difference in mass before and after sample heating. Fixed carbon (percent dry basis) was calculated from the total mass minus the ash and volatile contents. Determination of pH of adsorbent was undertaken using the method of Ekpote et al. [31]. The determination of pH at the point of zero charge (pH_{pzc}) was undertaken using the pH drift method.

The bulk density was determined by filling and tapping the sample in a 10 mL graduated cylinder and then calculating mass of sample/volume of cylinder. Composite hardness was determined according to measure 2 g of sample in a standard sieve no 60 (250 micrometre). The sieve was shaken for 1 h by using mechanical shaker (AS200, Retsch) at 160 strokes per minutes. The amount of composite retained in the sieve after 1 h was expressed in percent. Higher heating value (HHV) was determined using a bomb calorimeter apparatus (Gallenkamp). The sample was compressed into pellet form and then combusted in a calorimeter in pure oxygen and at high pressure (3 MPa). The analysis was done in triplicate and the reported data was obtained from average value.

2.4 Adsorption studies

The adsorption of MB and MO by carbon-silica composite was performed in a batch experiment with an orbital shaker (Gallenkamp) at 130 rpm. Exactly 10 mg of composite was poured into 125 mL Erlenmeyer flask that contained 50 mL of MB or MO solutions. Time effect was carried out in the ranges of 5–240 min. The pH effect was performed by adjusted in the ranges of 2, 4, 6, 8, 10 and 12 with 0.1 M HCl or NaOH. The concentration effect was studied at initial concentrations of 3–1,000 mg/L and 20–1,000 mg/L for MB and MO, respectively. Finally, temperature effect was investigated at 30, 40 and 50 $^{\circ}\text{C}$. The residual concentrations of MB and MO after adsorption were measured at a wavelength of 665 and 463 nm, respectively, using an UV/Vis Spectrophotometer (Analytik-Jena AG). The amount of dye adsorption at equilibrium (q_e , mg/g) and the removal efficiency (%) were calculated with the following equation

$$\text{Removal efficiency} = \frac{C_o - C_e}{C_o} \times 100\% \quad (1)$$

$$q_e = \frac{(C_o - C_e)V}{m} \quad (2)$$

where C_o and C_e are initial and equilibrium concentration of dyes in solution (mg/L), respectively, m is the mass of composite (g) and V for volume of dye solution (L).

3. Results and discussion

3.1 Carbon-silica composite characterisation

Figure 1 illustrates the BET surface area of carbon-silica composites formed with various durations of mixing. The specific surface area increased gradually from 224 to 375 m^2/g for Na_2SiO_3 , 214 to 343 m^2/g for K_2SiO_3 and 353 to 656 m^2/g for TEOS with extended reaction time from 2 to 6 h, respectively. The increase in the surface area with time indicates that prolonged mixing is required for the full development of porosity. After 6 h of mixing, a severe decrease in surface area to 160, 147 and 261 m^2/g was observed for Na_2SiO_3 , K_2SiO_3 and TEOS, respectively. This indicates that longer durations of mixing result in collapse of the pores, resulting in larger pores but with lower surface area. This is confirmed by the average pore size of composites prepared at 6, 8 and 10 h, which were 4.74, 5.60 and 5.92 nm for Na_2SiO_3 , 7.15, 7.53 and 7.62 nm for K_2SiO_3 and 4.25, 5.50 and 5.89 nm for TEOS.

Surface areas of the composite materials developed in this study via a simple synthesis routes are frequently higher than carbon-silica composites reported in the literature. For example, carbon-silica nanocomposites fabricated from the pyrolysis of polyacrylonitrile (PAN) (150 m^2/g) [32], composites derived from pyrogenic silica A-300 and phenol-formaldehyde resin (297 m^2/g) [21], and those prepared from rice husk and activated carbon (307 m^2/g) [33]. Systems employing TEOS can achieve comparable surface areas, for example, carbon-silica composites based on SBA-15 silica containing Pluronic P123 (389–476 m^2/g) [34], TEOS-derived composites with activated carbon powder (718–725 m^2/g) [22], and MCM-41/polyfurfuryl alcohol-derived composites (850 m^2/g) [24]. Although, the use of an industrial by-product (vinasse), low-cost silica precursors (Na_2SiO_3 and K_2SiO_3) and simple synthesis routes, could produce competitive advantages in the production of composites for adsorption. These comparisons highlight that the present approach offers a cost-effective and sustainable alternative while still achieving competitive surface area, thereby supporting the novelty and practical relevance of this work.

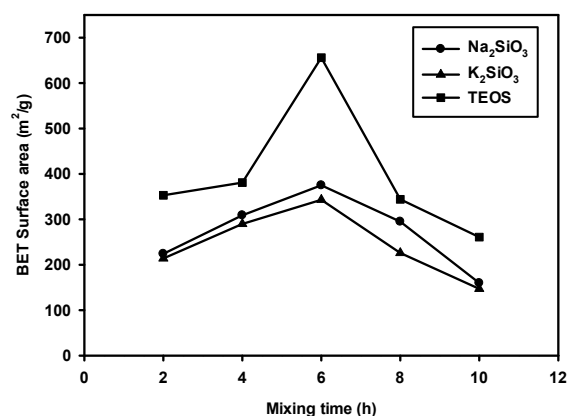


Figure 1 Effect of mixing time on the surface area of carbon-silica composite

Nitrogen adsorption–desorption isotherms of carbon-silica composites prepared at a 6 hour mixing time exhibited Type IV isotherm with capillary condensation at a relative pressure (P/P°) of 0.4, corresponding to the existence of mesopores. These results were consistent with previously published results for these materials [28]. The t-plot micropore volume were 0.060, 0.027 and 0.150 m³/g and the total pore volume at P/P° 0.99 were 0.292, 0.478 and 0.830 cm³/g for Na₂SiO₃, K₂SiO₃ and TEOS, respectively. The mesopore volume for Na₂SiO₃, K₂SiO₃ and TEOS materials after 6 hours of mixing were 0.232, 0.451 and 0.68 cm³/g, respectively. While the % mesoporosity was 79.45, 94.35 and 82.93% for Na₂SiO₃, K₂SiO₃ and TEOS materials, respectively. It can be seen from the results that most pores of the composites are in the mesopore range. Carbon-silica composites derived from vinasse were mesoporous and the pore size distribution also indicated the presence of mesopores for all composites. Due to their high mesoporous content combine with some micropores, these adsorbents have potential in adsorption of dye molecules such as methylene blue (diameter 1.382 nm) [35].

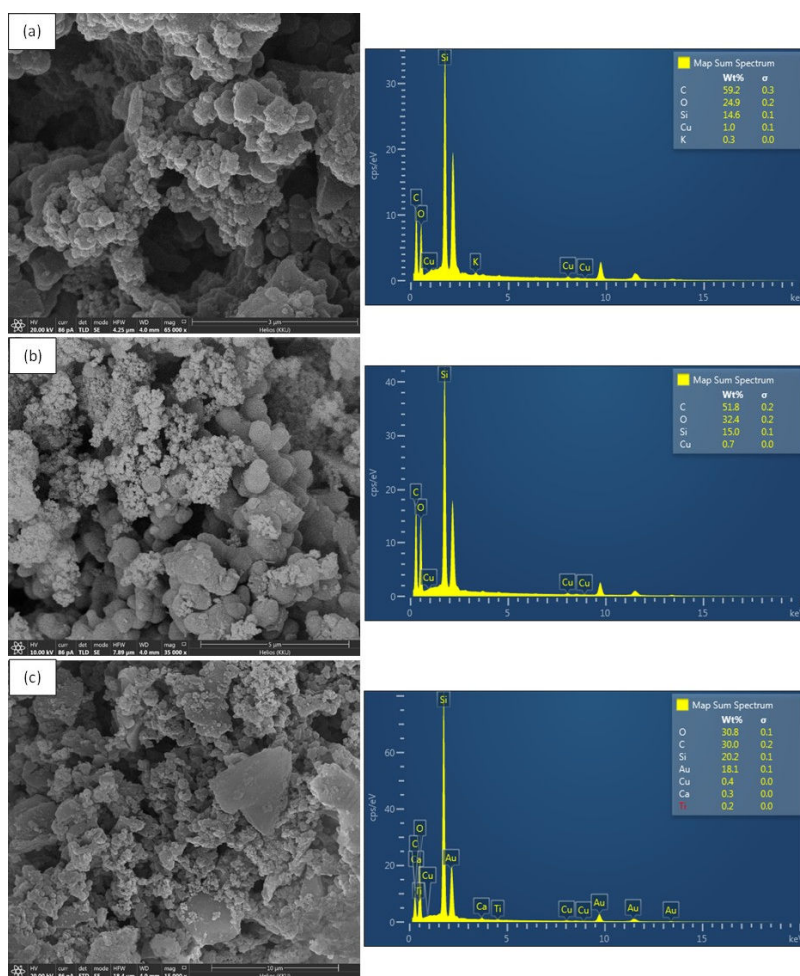


Figure 2 SEM-EDX analysis of the composites prepared from (a) Na₂SiO₃, (b) K₂SiO₃ and (c) TEOS at optimum mixing time of 6 hours

The surface morphology of the composites and elemental composition were determined with scanning electron microscopy coupled with energy dispersive X-ray (SEM-EDX). It is evident in Figure 2 that the structure of the obtained composites is porous with micro and mesopores that seem to be interconnected in between them, which is confirmed by TEM images (Figure 3). EDX spectra of all

composites (Figure 2 and 3) demonstrated a strong intensity of C, O and Si, which confirms the incorporation of silica on the surface of the samples. The results obtained by XPS also suggest that all composites primarily consist of carbon, oxygen and silicon (Table 1). To understand the chemical bonding, the deconvolutions of the XPS spectra was undertaken over the C 1s, O 1s and Si 2p regions to understand the chemical bonding and surface functionalities in all adsorbents. Figure 4 illustrates the optimum curve fitting, while Table 1 shows the calculated percentages of each peak. The C 1s spectrum of composites can be deconvoluted into five peaks at 284.8, 286.1, 287.8, 288.4 and 289.6 eV corresponding to C–O/C–N, Si–O–C, C=O bonds, O–C=O and carbon in carboxyl or ester group, respectively [36-38]. The O 1s analysis indicates the existence of Si–O–C (532.4 eV), SiO₂ (533.5 eV) and C–O (534.7 eV) [36-39]. The Si 2p spectrum involves three bands that can be assigned to Si–O–C (103.7 eV), SiO₄ (104.9 eV) and Si–O (105.1 eV) [36, 40, 41]. These results are also consistent with FTIR results reported in previous publications [28].

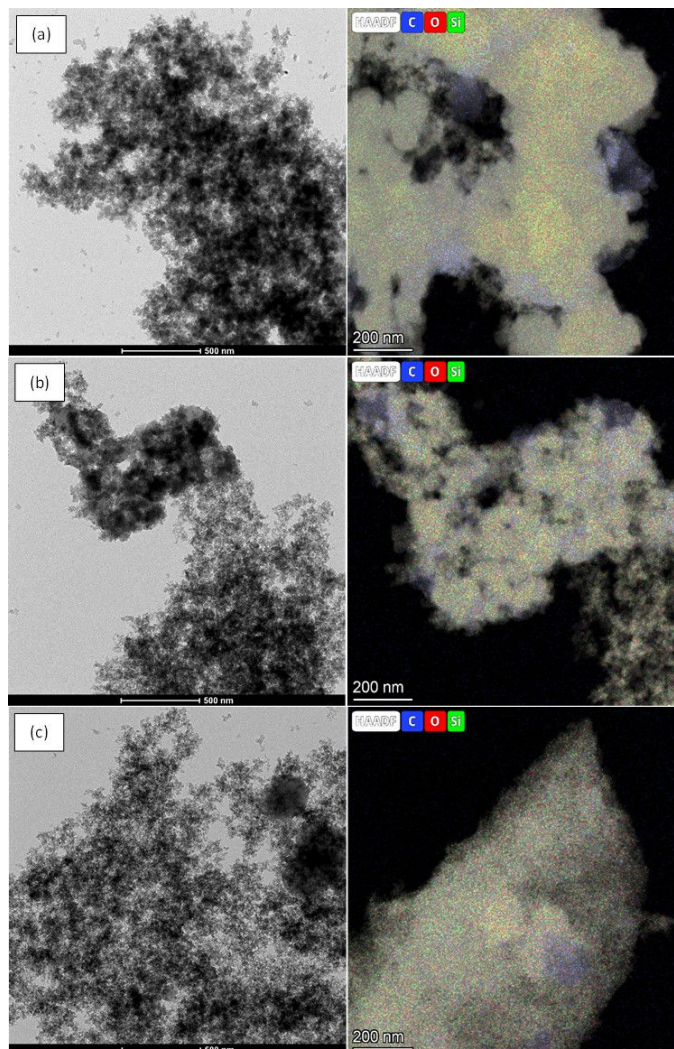


Figure 3 TEM-EDX analysis of the composites prepared from (a) Na₂SiO₃, (b) K₂SiO₃ and (c) TEOS at optimum mixing time of 6 hours

Table 1 Analysis of XPS of carbon-silica composites

Spectra	Binding energy (eV)	Concentration (%)		
		Na ₂ SiO ₃	K ₂ SiO ₃	TEOS
C 1s	-	22.97	16.70	17.06
	284.83, 284.79, 284.81	46.49	63.88	51.29
	286.14, 286.20, 286.12	33.30	28.17	36.46
	287.80, 287.84	13.85	-	12.25
	288.47	-	7.94	-
	289.60	6.36	-	-
O 1s	-	55.45	58.71	59.87
	532.47	20.56	-	-
	533.53, 533.30	53.27	100	74.30
	534.77, 534.52	26.17	-	25.70
Si 2p	-	21.57	24.59	23.07
	103.76, 103.88	52.12	100	70.25
	104.98	47.88	-	-
	105.17	-	-	29.75

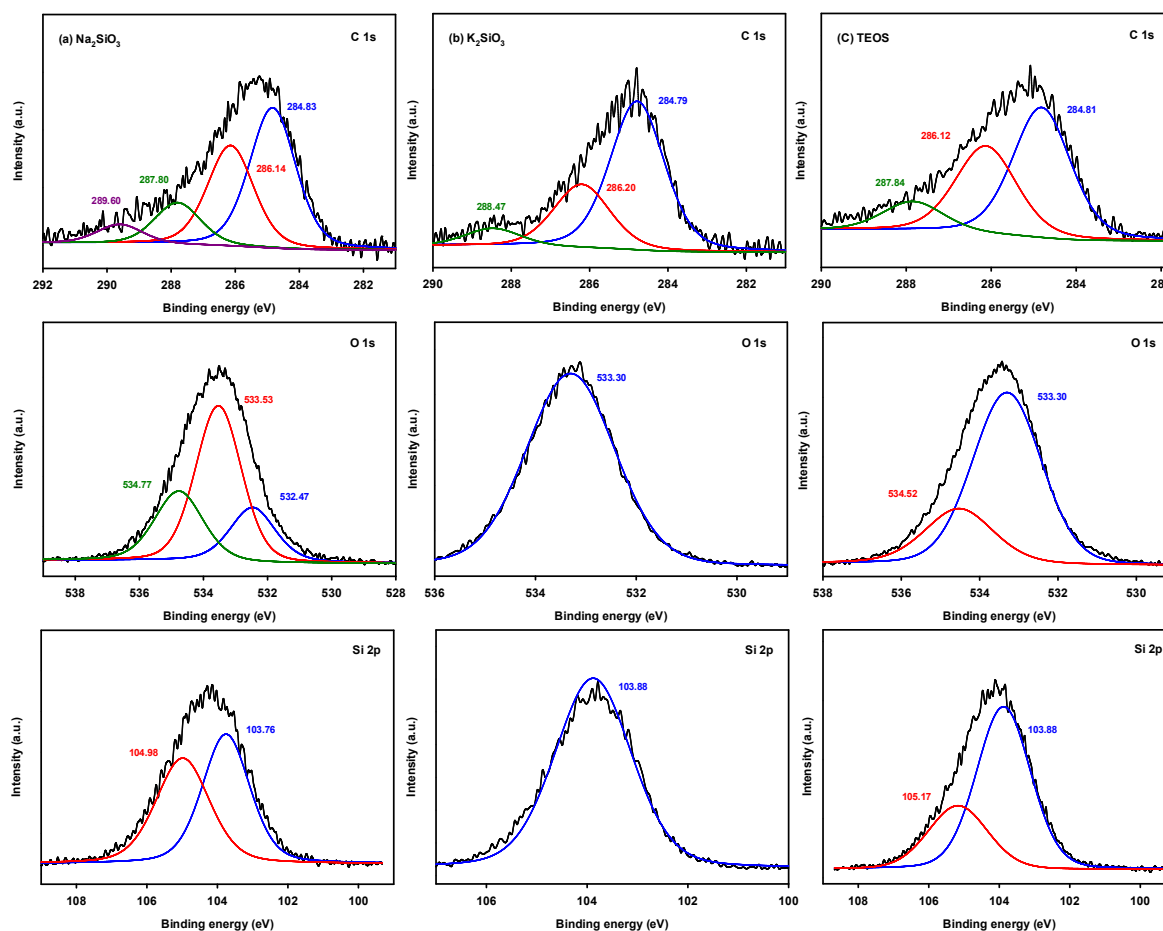


Figure 4 XPS spectra of C 1s, O 1s and Si 2p for composites prepared from (a) Na_2SiO_3 , (b) K_2SiO_3 and (c) TEOS at optimum mixing time of 6 hours

Figure 5 shows XRD of carbon-silica composites with different silica sources. All composites demonstrated a broad diffraction peak at 2θ around 22° attributed to the amorphous carbon-silica composites framework. No significant differences were observed in the XRD of composites prepared with Na_2SiO_3 , K_2SiO_3 or TEOS.

Thermogravimetric analysis (TGA) revealed three major mass losses were observed from 25 to 150 $^\circ\text{C}$, 150 and 550 $^\circ\text{C}$, and between 550 to 950 $^\circ\text{C}$ (Figure 6). The initial mass loss resulted from the removal of physisorbed water. This was followed by the loss of organic molecules through the breaking of C–O bonds and the final mass loss was ascribed to additional carbonization [42]. The total mass loss of the composite according to TGA conducted in N_2 was approximately 25 wt% for those prepared from Na_2SiO_3 , whereas those prepared from K_2SiO_3 and TEOS showed slightly higher values (27 wt%). These small differences are likely due to variation in the physisorbed water and carbon content. The mass loss associated with the removal of physisorbed water (between room temperature and 150 $^\circ\text{C}$) varies in all composites reported in this work (Figure 6). Those composites prepared with Na_2SiO_3 , K_2SiO_3 and TEOS demonstrated a mass loss associated with water of 12%, 13% and 11%, respectively. TGA analysis in N_2 recorded a mass loss between 150–950 $^\circ\text{C}$ of 13%, 14%, and 16% for Na_2SiO_3 , K_2SiO_3 and TEOS, respectively. This mass loss is likely to be due to the carbon decomposition and some structural changes associated with additional crosslinking and water loss that can take place in heating the silica supports to higher temperatures. TGA analysis in air revealed a more significant mass loss between 150–950 $^\circ\text{C}$ resulting from the combustion of carbon. TEOS composites demonstrated a 26% mass loss between 150–950 $^\circ\text{C}$ in air, while Na_2SiO_3 and K_2SiO_3 only reported a 19–20% mass loss under identical conditions. This demonstrates that composites produced with TEOS may have a higher proportion of carbon, as compared to those prepared from silicate solutions.

The proximate analysis of the composites is summarized in Table 2. The results revealed the optimum moisture content (11.27–14.37 wt%). The obtained composites also exhibited low volatile matter content (4.45–12.12 wt%), demonstrating a stable structure. Composites exhibit a high content of ash due to the nature of vinasse that contain high amounts of minerals (potassium, sodium, calcium, etc.) [43], along with the addition of silica to produce composites. Therefore, it is suggested that the feasibility study to utilise ash as fertilizer, soil improvement and pozzolanic materials should be performed.

The pH for all adsorbents is shown in Table 2. The pH of all three carbon-silica composites falls in the acidic range. This could be due to the acidic character of original vinasse as shown in section 2.1 and the use of H_2SO_4 to create the carbon layer. Acidity was observed to have a positive effect on adsorption of basic dyes, while for acid dyes the basicity of the composites plays greatly affects adsorption (Figure 7) [44]. The pH_{pzc} are 3.0, 2.5 and 2.3 for Na_2SiO_3 , K_2SiO_3 and TEOS, respectively. These values indicated that all resulting adsorbents have acidic character and consistent with that of the determination of the pH. Moreover, the pH and pH_{pzc} of each adsorbent are very close together (see Table 2) which verifies that pH of the composite is equivalent to the point of zero charge of adsorbent [45]. At pH of adsorbate solution less than pH_{pzc} of each adsorbent, the surface of adsorbent is positively charged, while at higher pH the surface is negative. Therefore, positively charged adsorbates should be adsorbed at a pH greater than pH_{pzc} , in contrast negatively charged adsorbates will preferentially adsorb at a pH lower than pH_{pzc} .

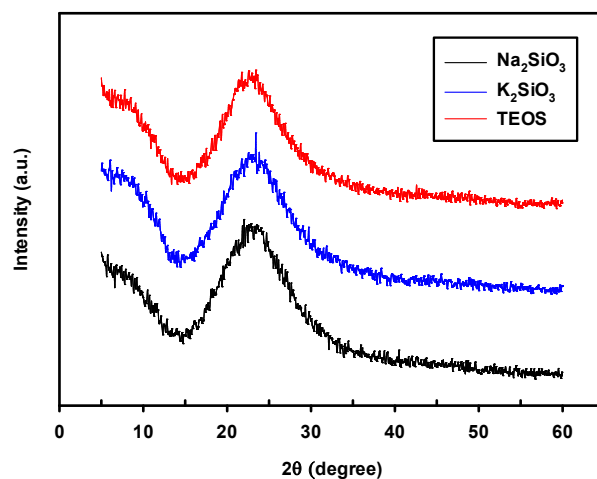


Figure 5 XRD spectra of carbon-silica composites prepared at optimum mixing time of 6 hours

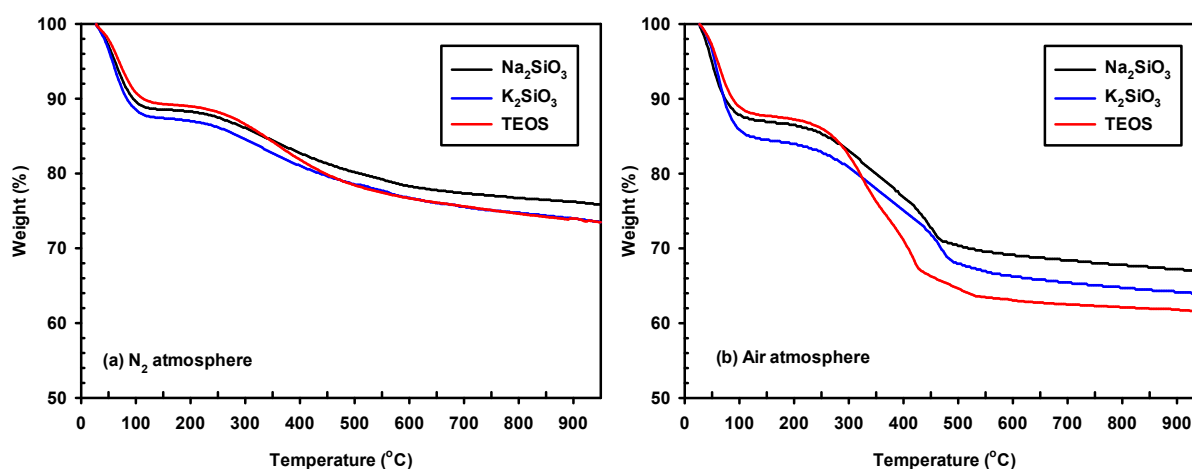


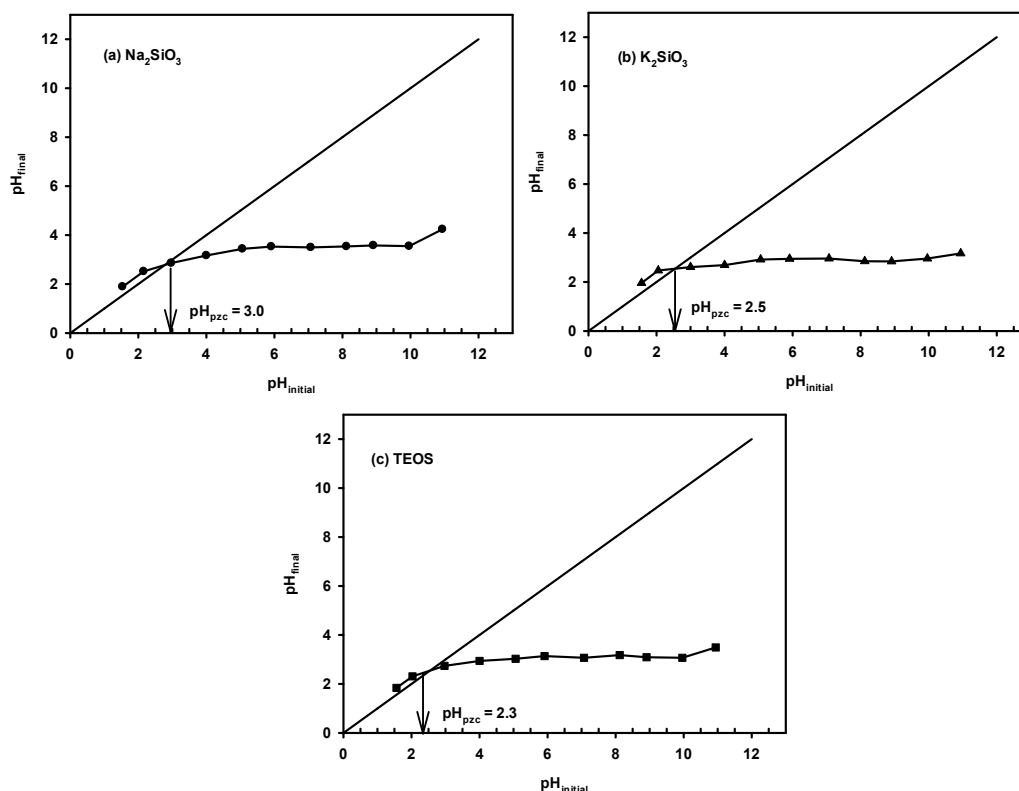
Figure 6 TGA results under (a) N_2 and (b) air atmosphere of composites with different silica sources prepared at optimum mixing time of 6 hours as investigated under nitrogen atmosphere

The bulk density of the obtained carbon-silica composite (Table 2) is comparable to that of other activated carbons prepared from sugarcane bagasse ($0.30\text{--}0.44\text{ g/cm}^3$) [46], maize tassel (0.52 g/cm^3) [47], *ayous* sawdust (0.52 g/cm^3) [41] and *cucurbitaceae* peelings (0.77 g/cm^3) [48]. Moyo et al. [47] suggested that if the bulk density of an activated carbon was less than 1.2 g/cm^3 , this may enhance the removal of adsorbate from an aqueous solution. The hardness of adsorbent is also important property. This mechanical strength of adsorbent informs the resistance to abrasion or attrition during its use, transportation, and regeneration. The hardness was 80.6, 77.5 and 67.8% for Na_2SiO_3 , K_2SiO_3 and TEOS (Table 2), respectively, indicating high abrasion resistance. These results indicated that a low-cost silicon source can create an adsorbent with greater rigidity than high cost silicon. The lowest percentage of hardness observed in TEOS sample may be due to the higher carbon source (5:1) than Na_2SiO_3 and K_2SiO_3 samples (2:1). Ulfah et al. [49] studied the ratio of carbon black and silica filler for rubber compound, it was found that higher ratio of carbon black to silica reduced the impact of the silica, resulting in a reduced hardness. The results of hardness for all adsorbents are in consonance with the hardness of 62.8–88.5% for *Prosopis africana* wood-based activated carbon [50]. However, some activated carbon had very low hardness, for example, banana empty fruit bunch-based carbon (1.5–2.5%) [51], *Delonix regia* fruit pod-based carbon (7.4–10.2%) [51], and *Casuarina equisetifolia* fruit-based carbon (6.55–36.15%) [52]. After use of the adsorbent, various methods of regeneration including thermal or chemical processes were investigated. However, these entail extra costs, therefore the most direct and simple reuse of spent adsorbent is used as a fuel, adding to its value.

Table 2 shows heating value of all three carbon-silica composites (8,476–8,898 kJ/kg), which are higher or comparable to the other waste materials used as fuel such as pig manure (2,869 kJ/kg), poultry manure (3,423 kJ/kg), cattle manure (4,158 kJ/kg), municipal waste (7,000–10,000 kJ/kg) and wood (7,000–14,000 kJ/kg) [53, 54]. Although the composites exhibit a relatively high ash content (55.52–59.61 wt%), it is important to note that the remaining combustible fraction ($\sim 40\text{--}44\%$) primarily consists of a carbon-rich phase formed during processing. The fixed carbon, which represents the solid combustible residue, provides further insight into the observed HHV values, as higher fixed carbon content is generally associated with higher heating values. All composites showed a relatively high fixed carbon content (18.70–25.66 wt%) and low volatile matter (4.45–12.12 wt%), indicating a more carbon-dense structure. This is typically associated with higher energy density compared to raw biomass and manure, which contain a greater proportion of volatile and oxygen-rich components. Nevertheless, the high ash content acts as a diluent and will limit the efficiency of these materials as primary fuels. Therefore, their utilization is more appropriately considered in the context of low-grade or supplementary fuels. Alternatively, the high mineral (silica-rich) content provides opportunities for value-added applications, including zeolite synthesis, use in the construction industry (e.g., cement and concrete production), and applications in the ceramic industry. Additionally, the presence of nutrient elements such as calcium (Ca) and potassium (K), along with residual organic content from vinasse, suggests potential use as a soil amendment [55].

Table 2 Physical and chemical properties of the obtained adsorbents

Parameter	Na ₂ SiO ₃	K ₂ SiO ₃	TEOS
Proximate analysis, wet basis (wt%)			
Moisture	11.78	11.27	14.37
Volatile matter	8.46	12.12	4.45
Ash	59.61	57.91	55.52
Fixed carbon	20.15	18.70	25.66
pH	3.11	2.97	2.70
pH _{pzc}	3.0	2.5	2.3
Bulk density (g/cm ³)	0.45	0.41	0.63
Hardness (%)	80.6	73.5	67.8
Higher heating value (kJ/kg)	8,476	8,595	8,898

**Figure 7** pH at the point of zero charge (pH_{pzc}) of adsorbents

3.2 Adsorption results

3.2.1 Effect of contact time and adsorption kinetics

The adsorption procedures started with the investigation of effects of contact time. The studies were conducted with a MB concentration of 6 mg/L and 25 mg/L for MO with 10 mg of the adsorbent at room temperature. Figure 8 demonstrates how contact time influences the adsorption capacity of both dyes. As seen in this figure, the initial removal of dye molecules from aqueous solution occurs rapidly but reduces as the equilibrium is established. Initially all adsorption sites are vacant, thus adsorption proceeds at a fast rate. As the active sites get occupied, the rate of adsorption reduces until it reaches equilibrium. Any further adsorption beyond this is through intra-particle diffusion, which is a much slower process [56]. From the obtained results, the time to reach equilibrium for both dyes adsorption onto all three adsorbents was determined to be 100 min.

For MB adsorption, adsorption capacity follows an order of Na₂SiO₃ > K₂SiO₃ > TEOS, although TEOS sample had highest surface area. This indicated that the adsorption capacity was dependent on both surface area and functionality. Wang and Zhu [45] studied the adsorption of MB by using three activated carbons with comparable surface area (972, 987 and 1015 m²/g) but different pH (2.80, 6.58 and 8.75). They found that activated carbon with greater acidity demonstrated the lowest adsorption capacity of MB following the order: AC with pH 8.75 (972 m²/g) > AC with pH 6.58 (1015 m²/g) > AC with pH 2.80 (987 m²/g). This agrees with this current study, where is Na₂SiO₃ with pH 3.11 > K₂SiO₃ with pH 2.97 > TEOS with pH 2.70. Wang and Zhu [45] also proposed that two parallel adsorption mechanisms take place simultaneously, (1) electrostatic interactions between the adsorbate and carbon surface, (2) dispersive interactions between the dye and carbon. For basic dyes, the electrostatic interactions may play a role, but π - π interactions are the dominant interaction between surface and the dye. In fact, the surface basicity arises from oxygen-free Lewis base sites that are related to the delocalized π -electrons in the carbon [57], therefore a carbon with the highest acidity shows a lower adsorption for cationic (basic) dye. In conclusion, cationic dyes are positively charged and form electrostatic bonds with negatively charged surface functional groups on adsorbent such as oxygen-containing groups. On the contrary, the reverse order i.e. TEOS > K₂SiO₃ > Na₂SiO₃ were obtained for MO adsorption. This was due to the different families of dye, including methylene blue (cationic dye) and methyl orange (anionic dye).

In conclusion, the adsorption trends can be explained by the combined effects of surface charge and textural properties. Importantly, the solution pH for both dyes (MB = 5.66; MO = 5.70) is higher than the pH_{pzc} of all samples ($Na_2SiO_3 = 3.0$, $K_2SiO_3 = 2.5$, $TEOS = 2.3$), indicating that all surfaces are negatively charged under the experimental conditions. The Na_2SiO_3 -derived composite has the highest pH_{pzc} and is expected to possess the highest density of negatively charged sites, resulting in the strongest electrostatic attraction toward the cationic dye (MB). This explains the observed trend in MB adsorption. This interpretation is further supported by previously published FTIR results [28], where the higher intensity of Si–O, Si–O–Si, and Si–OH bands ($Na_2SiO_3 \approx K_2SiO_3 > TEOS$) indicates a greater abundance of surface silanol groups, which can deprotonate and contribute to the negative surface charge. In contrast, adsorption of the anionic dye (MO) is electrostatically unfavorable for all samples due to surface charge repulsion. Under such conditions, adsorption becomes more dependent on structural properties. The TEOS-derived composite, which exhibits the highest surface area ($TEOS > Na_2SiO_3 > K_2SiO_3$), provides more accessible adsorption sites and facilitates diffusion, resulting in the highest MO uptake despite weaker electrostatic interactions.

To analyse the adsorption kinetics, pseudo-first order and pseudo-second order models were used. Both models introduced initially by Lagergren are represented by equations (3) and (4), respectively,

$$q_t = q_e(1 - e^{-k_1 t}) \quad (3)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (4)$$

where q_t (mg/g) is the amount of dye adsorbed at any time t and k_1 (min^{-1}) and k_2 ($\text{g/mg} \cdot \text{min}$) are the adsorption rate constants of pseudo-first order and pseudo-second order models, respectively. The experimental kinetic data for MB and MO dyes adsorption on composites are fitted with both models and illustrated in Figure 9 (A and B). The calculated parameters, constants, and corresponding correlation coefficients (R^2) of both models are shown in Table 3. The R^2 values for the pseudo-second order were closer to 1 than that of the pseudo-first order model. In addition, the calculated values of q_e obtained from the pseudo-second order model closely resemble the experimental values (q_{exp}), while the pseudo-first order values of both dyes adsorption demonstrate a worse fit. These indicate that the pseudo-second order kinetic model provides a more accurate description of the system. It indicates that the mode of adsorption on carbon-silica composites is based on the chemical adsorption.

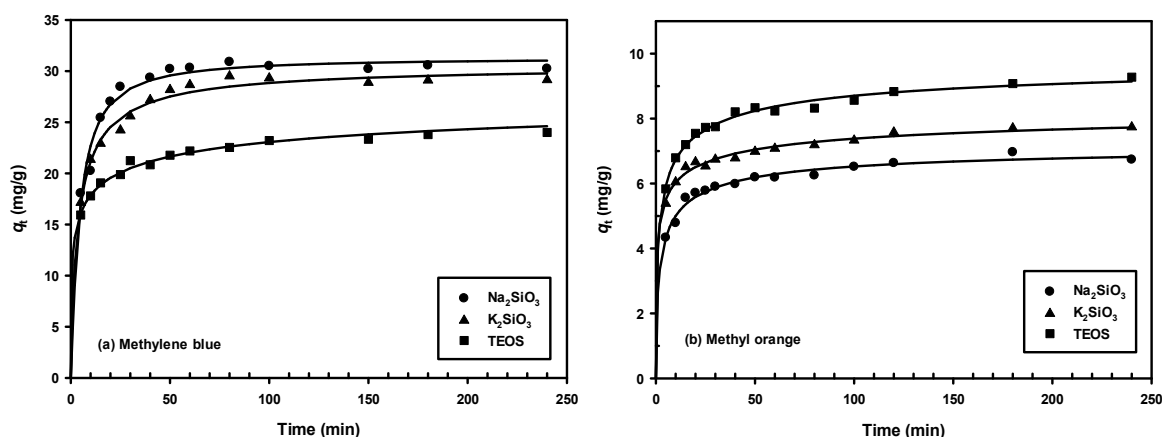


Figure 8 Effect of contact time on (a) MB and (b) MO removal

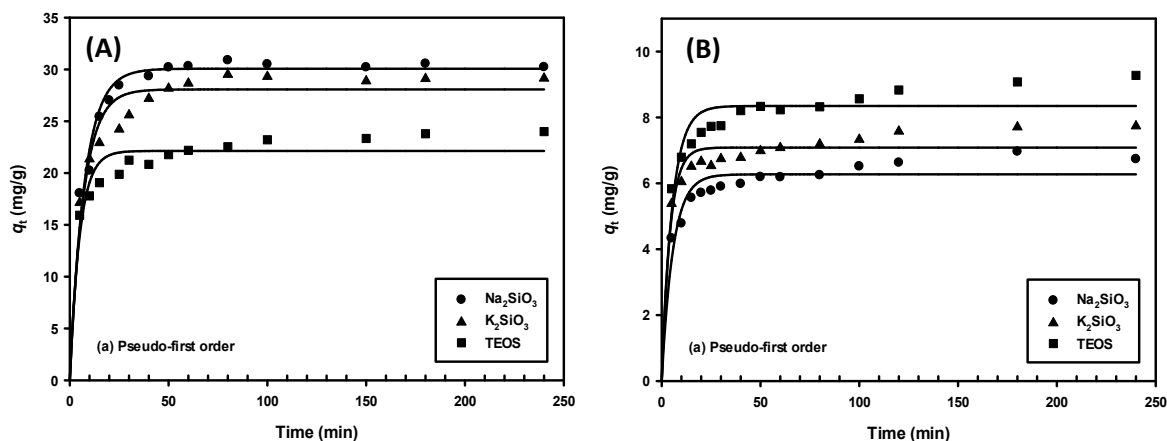


Figure 9 Adsorption kinetic analysis for (A) MB and (B) adsorption onto carbon-silica composite adsorbents. Evaluation of experimental data (symbols) and kinetic model predictions (lines)

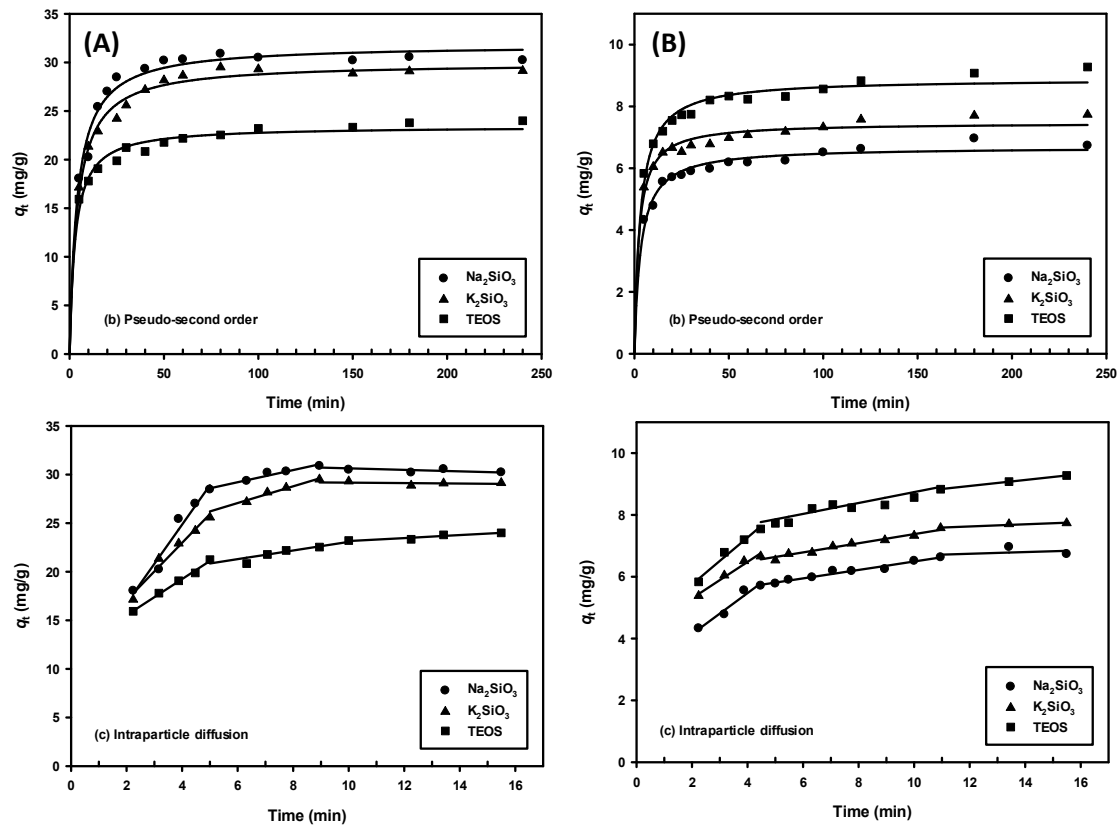


Figure 9 (continued) Adsorption kinetic analysis for (A) MB and (B) adsorption onto carbon-silica composite adsorbents. Evaluation of experimental data (symbols) and kinetic model predictions (lines)

Table 3 Assessment of kinetic models for dyes adsorption on carbon-silica composites

Model	Methylene blue			Methyl orange		
	Na ₂ SiO ₃	K ₂ SiO ₃	TEOS	Na ₂ SiO ₃	K ₂ SiO ₃	TEOS
$q_{e,exp}$ (mg/g)	30.90	29.50	24.00	6.97	7.73	9.28
Pseudo-first order						
q_e (mg/g)	30.07	28.07	22.14	6.27	7.08	8.35
k_1 (min ⁻¹)	0.135	0.144	0.198	0.176	0.242	0.188
R^2	0.978	0.957	0.944	0.944	0.951	0.943
Pseudo-second order						
q_e (mg/g)	31.83	29.96	23.43	6.68	7.47	8.89
k_2 (g/mg•min)	0.008	0.008	0.014	0.045	0.058	0.036
R^2	0.987	0.992	0.988	0.987	0.987	0.988
Intraparticle diffusion						
k_{i1} (mg/g•min ^{0.5})	4.041	2.945	1.860	0.663	0.590	0.759
C_1 (mg/g)	8.696	11.201	11.809	2.820	4.122	4.234
R^2	0.962	0.968	0.994	0.958	0.972	0.975
k_{i2} (mg/g•min ^{0.5})	0.628	0.861	0.445	0.136	0.148	0.176
C_2 (mg/g)	25.442	21.903	18.626	5.128	5.903	6.878
R^2	0.959	0.973	0.953	0.971	0.961	0.902
k_{i3} (mg/g•min ^{0.5})	0.076	0.022	0.153	0.027	0.035	0.098
C_3 (mg/g)	31.398	29.385	21.624	6.420	7.201	7.764
R^2	0.914	0.981	0.996	0.925	0.921	0.999

Adsorption involves four steps [58]: (1) bulk diffusion, (2) film diffusion, (3) pore diffusion, (4) adsorption. The diffusion mechanism cannot be determined by the two kinetic models, therefore the intraparticle diffusion model as expressed in the following equation was utilised:

$$q_t = k_i t^{0.5} + C \quad (5)$$

where k_i (mg/g•min^{0.5}) is the intraparticle diffusion rate constant and C (mg/g) is the diffusion resistance constant. The curves of intraparticle diffusion model (Figure 9 (A) c) displayed three linear segments in the adsorption process, involving 1) the diffusion of dyes onto the external surface of composites, 2) the dye intraparticle diffusion to the internal surface and 3) the equilibrium state. k_i , C_i and the R^2 are provided in Table 3. As shown in table, this model renders straight lines with $R^2 > 0.9$ for all three adsorbents, thus, suggesting the model's suitability in describing the adsorption pattern of both dyes onto the obtained composites. The rate constants for all samples follow the order of $k_{i1} > k_{i2} > k_{i3}$, thus demonstrating that intraparticle diffusion was not the only factor in the rate-

limiting step, and in fact film diffusion and the intraparticle diffusion both play crucial role in this adsorption system [59]. C_i was not zero nor did it pass through the origin, thus confirming the importance of both film diffusion and intraparticle diffusion. Moreover, the constants C_i that provide the information about diffusion resistance were increased from first stage to third stage, indicating the faster process in the first adsorption step. In conclusion, the adsorption of both dyes on carbon-silica composites consists of film diffusion, intraparticle diffusion and surface adsorption.

3.2.2 Effect of pH on adsorption

Many dyes contain ionic groups and therefore adsorption can be influenced by the surface charge of the composite, which itself can be influenced by solution pH [60]. Therefore, the effect of pH on MB and MO adsorption was investigated by varying pH from 2 to 12 with initial concentration of MB 6 mg/L and pH 2 to 10 with MO 25 mg/L (Figure 10). For MB adsorption of Na_2SiO_3 and K_2SiO_3 , as the pH rose from 2 to 8 a significant increase in adsorption capacity was observed. In contrast, the MB uptake was not influenced by pH within the range of 8 to 12. As such, all further experiments were conducted under pH 8. The adsorption capacity of MB by TEOS sample increase from 14.84 to 23.71 mg/g when changing pH from 2 to 8, after which a gradual increase to 24.87 mg/g at pH 12. This can be explained with the pH_{pzc} values of adsorbents, because of the positively charged composite at $\text{pH} < \text{pH}_{\text{pzc}}$ in contrast the composite would be negatively charged at $\text{pH} > \text{pH}_{\text{pzc}}$. The binding of positive-charged MB molecules onto adsorbent surface is facilitated due to electrostatic attraction when the surface of adsorbents is negatively charged at $\text{pH} > \text{pH}_{\text{pzc}}$ ($\text{pH}_{\text{pzc}} = 3.00$, 2.50 and 2.30 for Na_2SiO_3 , K_2SiO_3 and TEOS, respectively). The adsorption of positive charged MB on the composite is prevented by electrostatic repulsion when the adsorbents surface is positively charged at $\text{pH} < \text{pH}_{\text{pzc}}$ [61].

For MO adsorption, the adsorbed amounts are highest at solution $\text{pH} < \text{pH}_{\text{pzc}}$ ($\text{pH} = 2$). This could be a result of electrostatic attraction between the positively charged composites surface and the negative dye anions, resulting in the high dye adsorption at low pH. At pH values above pH_{pzc} , the surface charge of composites is negative, thus leading to a reduction in MO adsorption due to repulsive electrostatic forces.

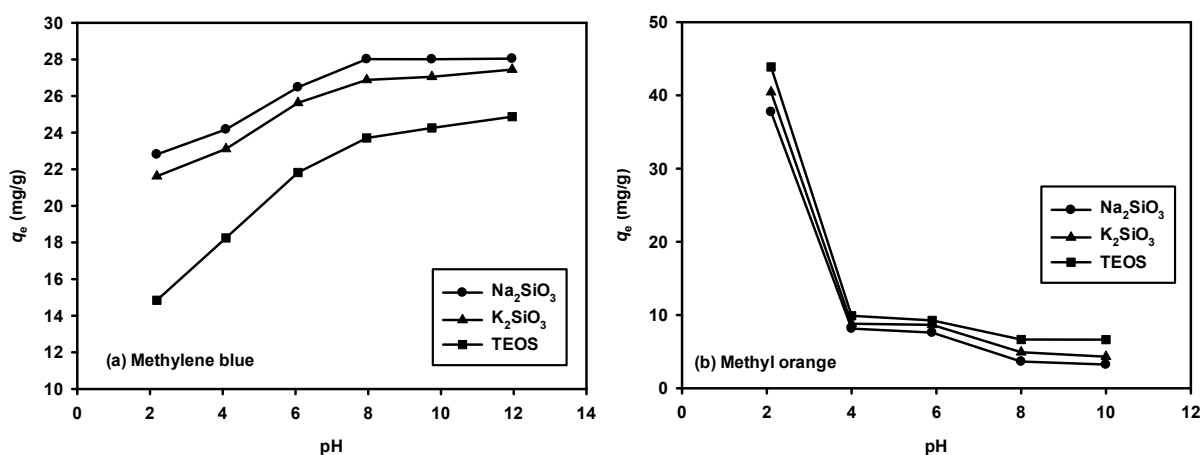


Figure 10 Influence of pH on (a) MB and (b) MO removal

3.2.3 Influence of initial concentration and adsorption isotherms

The influence of initial adsorbate concentration depends on the relationship between concentration and number of active sites on the surface of the adsorbent [62]. The adsorption of MB and MO by carbon-silica composite was studied at different initial dye concentrations of 3–1,000 and 10–1,000 mg/L, respectively. MB and MO adsorption capacities increased with greater initial dye concentration (Figure 11). This is due to the increased probability of collisions and higher diffusion rates [63]. The removal efficiency decreases with a greater initial dye concentration resulting from active site saturation. At lower dye concentrations, the number of available adsorption sites are relatively high, and the dye molecules were easily adsorbed. Conversely, these sites were limited, and dye removal efficiency was reduced at higher initial dye concentrations.

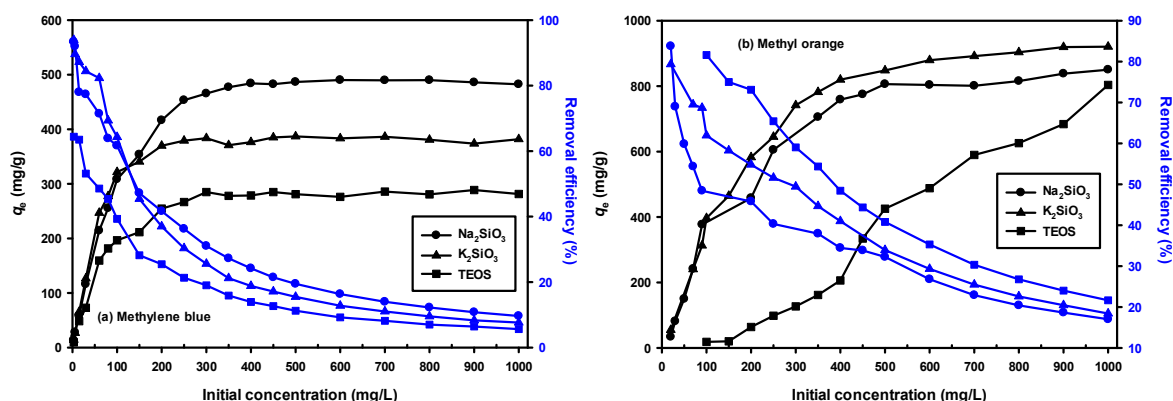


Figure 11 Influence of initial concentration on (a) MB and (b) MO removal

Langmuir, Freundlich and Sips have been used to model the adsorption properties. The Langmuir model is expressed by the following equation:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (6)$$

where q_m (mg/g) and K_L (L/mg) are the maximum amount of adsorption and Langmuir constant, respectively. The Freundlich model is an empirical equation which assume heterogeneous adsorbent surface, where energies of adsorption sites are not the same, thus allowing multilayer adsorption. The Freundlich model is represented as

$$q_e = K_F C_e^{1/n} \quad (7)$$

where K_F and n are Freundlich constants. Typically, if n is large a stronger interaction between the composite and the dye is observed, while $1/n = 1$ is indicative of linear adsorption with all sites having comparable adsorption energies [64]. The Sips isotherm model combines aspects of the Langmuir and Freundlich models, containing three parameters as follows:

$$q_e = \frac{q_{ms} K_S C_e^{1/m}}{1 + K_S C_e^{1/m}} \quad (8)$$

where q_{ms} (mg/g) is the Sips maximum adsorption capacity and K_S (L/mg) and $1/m$ are the isotherm constants. For $1/m = 1$, equation (8) converts to the Langmuir isotherm, while the greater value the more heterogeneous the system.

Figure 12 (A) and 12 (B) demonstrate the amount of MB and MO adsorbed at equilibrium as a function of equilibrium concentration and fitting the experimental data with isotherm models using the nonlinear method. The values of the Sips determination coefficients or R^2 are highest compared to the other models (Table 4) indicating that this model best describes the adsorption process of the MB and MO dyes. This also confirmed that the adsorption mechanism is a mixture of the two models (Langmuir and Freundlich). The highest adsorption capacity of MB was the composites synthesised from low-cost silica source i.e. Na_2SiO_3 ($q_{ms} = 514.30$ mg/g) followed by K_2SiO_3 ($q_{ms} = 385.34$ mg/g), while the carbon-silica composite with the lowest adsorption capacity was synthesised from a high-cost silicon source i.e. TEOS ($q_{ms} = 294.88$ mg/g). For MO adsorption, the reverse trend was found: TEOS ($q_{ms} = 1161.65$ mg/g) > K_2SiO_3 ($q_{ms} = 979.06$ mg/g) > Na_2SiO_3 ($q_{ms} = 844.63$ mg/g). In addition, the values of K_L from Langmuir model and $1/n$ from Freundlich model are lower than 1, so both dyes adsorption is favourable in the composites.

3.2.4 Influence of temperature on adsorption thermodynamics

The effect of temperature was studied in the range 30–50 °C or 303–323 K (Figure 13). It is observed that the composite uptake of dyes is found to gradually increase with elevated temperatures, which indicates the endothermic nature of adsorption system. Rising temperature led to enhanced solubility of the dye and may also improve in the mobility of the dye ion, hence the adsorption rises. Alwi et al. [65] reported that a rise in the adsorption of dyes was observed at elevated temperatures may be partly attributed to chemisorption. This is consistent with the results from kinetics studies.

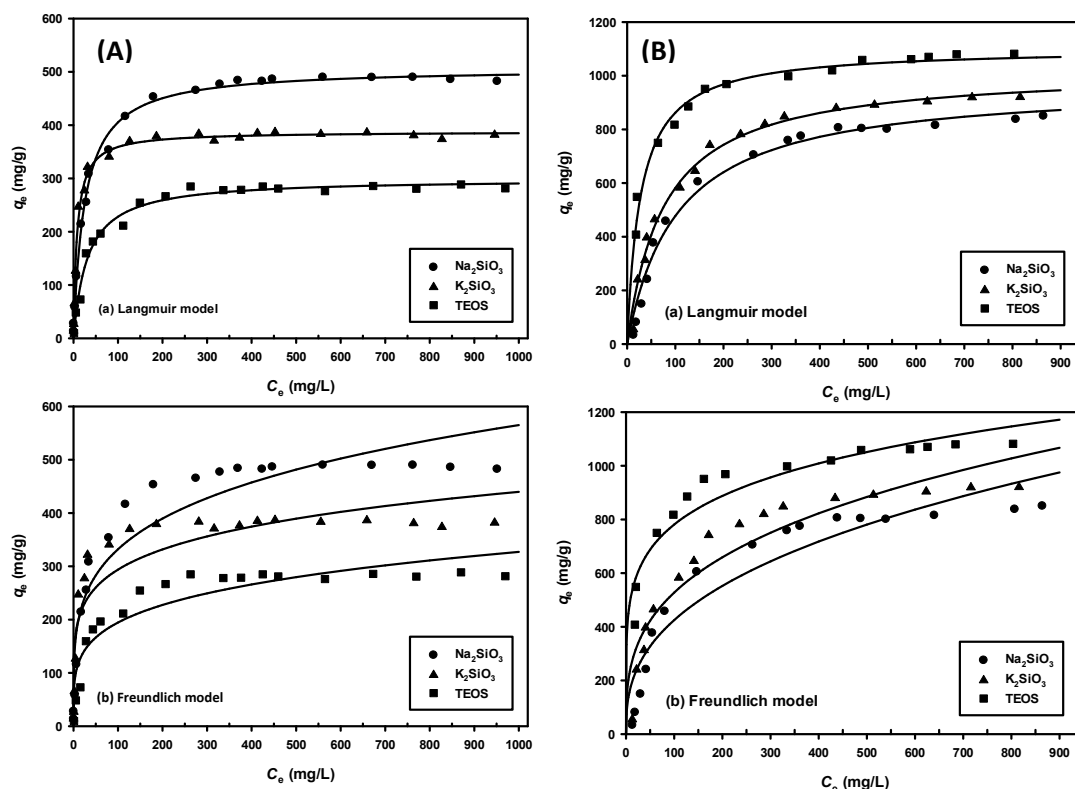


Figure 12 Equilibrium isotherms for (A) MB and (B) MO adsorption onto carbon-silica composite adsorbents. Comparison between experimental data (symbols) and predictions of the isotherm models (lines)

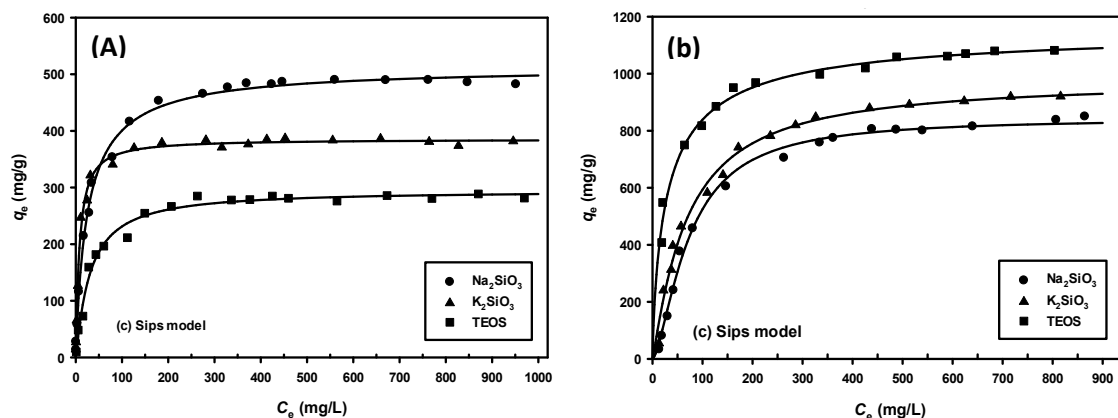


Figure 12 (continued) Equilibrium isotherms for (A) MB and (B) MO adsorption onto carbon-silica composite adsorbents. Comparison between experimental data (symbols) and predictions of the isotherm models (lines)

Table 4 Parameters of the isotherm models for dyes adsorption

Model	Methylene blue			Methyl orange		
	Na ₂ SiO ₃	K ₂ SiO ₃	TEOS	Na ₂ SiO ₃	K ₂ SiO ₃	TEOS
Langmuir						
q_m (mg/g)	507.26	387.91	299.65	972.67	1025.89	1103.00
K_L (L/mg)	0.040	0.124	0.032	0.010	0.013	0.036
R^2	0.995	0.994	0.984	0.979	0.986	0.975
Freundlich						
K_F (mg/g) (L/mg) ^{1/n}	114.61	131.17	68.85	74.47	120.47	333.81
$1/n$	0.231	0.175	0.226	0.378	0.321	0.185
R^2	0.903	0.821	0.849	0.885	0.888	0.896
Sips						
q_{ms} (mg/g)	514.30	385.34	294.88	844.63	979.06	1161.65
K_S (L/mg)	0.048	0.109	0.024	0.001	0.008	0.064
$1/m$	0.933	1.069	1.089	1.533	1.138	0.803
R^2	0.996	0.995	0.988	0.995	0.991	0.992

To completely understand the adsorption nature of carbon-silica composites, the thermodynamics functions include free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were described. ΔG° , ΔH° and ΔS° are listed in Table 5 and were determined using the following equations:

$$\Delta G^\circ = -RT \ln K_o \quad (9)$$

$$\ln K_o = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (10)$$

where K_o is the thermodynamic equilibrium constant and equal to q_e/C_e , T is the solution temperature (K), and R is the ideal gas constant (8.314 J/mol·K). The values of ΔH° and ΔS° were obtained from the slope and intercept of a linear plot between $\ln K_o$ and $1/T$ of equation (10) called Van't Hoff equation, respectively.

For all composites, the ΔG° values are negative indicating spontaneous adsorption with an increase in the degree of spontaneity of the adsorption with increasing temperature. This could be due to reduction in the boundary layer of the composite at elevated temperatures, improving the mass transfer of the dye to the adsorbent surface [66]. ΔH° values are positive for all adsorbents and all dyes confirming the endothermic behaviour of adsorption, corresponding to the increasing adsorption capacities related to the increasing temperature. ΔS° is positive indicating an increase of the randomness at the solid-solution interface during adsorption onto composites.

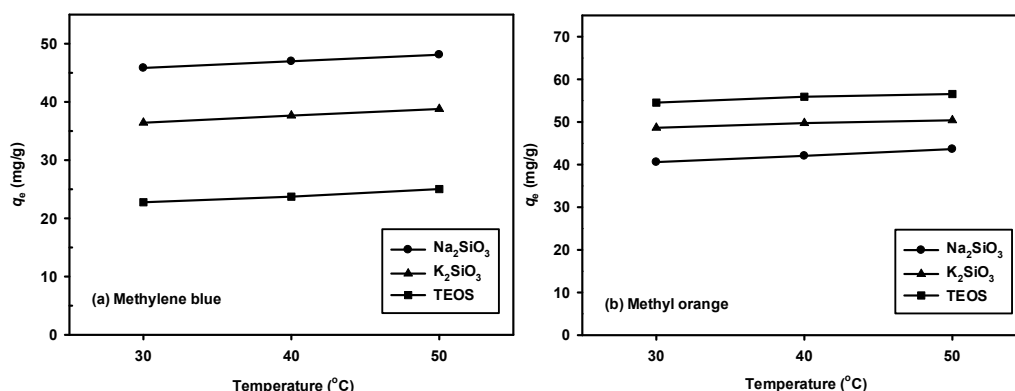


Figure 13 Effect of solution temperature on (a) MB and (b) MO removal

Table 5 Thermodynamic parameters of MB and MO adsorption onto carbon-silica composites at different temperatures

Temperature (K)	Methylene blue			Methyl orange		
	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol·K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol·K)
Na₂SiO₃						
303	-11.50			-2.21		
313	-12.13	6.96	60.95	-2.39	3.94	20.29
323	-12.72			-2.62		
K₂SiO₃						
303	-11.65			-2.62		
313	-12.47	11.58	76.75	-2.75	1.61	13.91
323	-13.18			-2.88		
TEOS						
303	-4.87			-2.78		
313	-5.30	7.10	39.54	-2.98	2.39	17.10
323	-5.66			-3.12		

3.2.5 Composite performance compared to adsorbents in the literature

The obtained maximum theoretical adsorption capacities of the carbon-silica composites for the investigated cationic and anionic dyes have been compared to reported literature values (Table 6). The obtained composites demonstrate excellent performance compared to most of the other reported adsorbents presented in Table 6. This implies that vinasse and silica composites could produce excellent adsorbents for the remediation of dyes. The process eliminates the need for high temperature treatments (like carbonisation of activated carbon and calcination process), which leads to lower production costs and great potential for deployment as adsorbents for decontamination of water. Table 6 presents the BET specific surface area (S_{BET}), micropore volume (V_{mic}), mesopore volume (V_{meso}), total pore volume (V_{T}), and average pore size (D_{p}) of the obtained composites and other adsorbents. It can be observed that a high surface area does not necessarily correspond with a high dye adsorption capacity. In fact, some materials with lower porosity may still exhibit high adsorption performance. This suggests that not only the porous structure of the adsorbent affects adsorption, but also surface chemistry plays an important role. Previously published FTIR results confirm the presence of Si-OH, Si-O, and Si-O-Si functional groups on the composites surface, [28]. These functionalities are known to contribute to dye adsorption [67, 68].

Table 6 Comparison of adsorption capacities of MB and MO dyes with other adsorbents used in literature

Adsorbent	S_{BET} (m ² /g)	V_{mic} (cm ³ /g)	V_{meso} (cm ³ /g)	V_{T} (cm ³ /g)	D_{p} (nm)	Maximum adsorption capacity (mg/g)	
						Methylene blue	Methyl orange
Carbon-silica composite from vinasse and Na ₂ SiO ₃ (this current work)	375	0.16 (55%)	0.13 (45%)	0.29	3.12	514.30	844.63
Carbon-silica composite from vinasse and K ₂ SiO ₃ (this current work)	343	0.14 (29%)	0.34 (71%)	0.48	5.58	385.34	979.06
Carbon-silica composite from vinasse and TEOS (this current work)	656	0.19 (23%)	0.64 (77%)	0.83	5.06	294.88	1161.65
Metal-organic framework (MOF) UiO-66-NO ₂ [69]	970	–	–	–	–	41.7	142.9
Mesoporous carbon prepared by the soft-templating method [70]	710	0.22 (31%)	0.49 (69%)	0.71	6.24	135–187	117–154
Mesoporous carbon prepared by the soft-templating method and activation with CO ₂ [70]	950	0.31 (36%)	0.54 (64%)	0.85	6.10	192–222	323–330
Tamarind seed activated carbon [71]	1.366	–	–	–	53.67	142.12	71.8
Composite of tamarind seed activated carbon with chitosan [71]	0.919	–	–	–	53.19	140.62	94.45
Triptycene-based hyper-crosslinked porous polymer [72]	698	–	–	–	–	159.80	220.82
Coconut shell activated carbon [73]	542	–	–	0.23	1.71	217.35	73.3
Composite of coconut shell activated carbon with chitosan [73]	498	–	–	0.21	1.70	209.37	105.2
Magnetic watermelon shell-based activated carbon [74]	155	–	–	0.32	2.28	303.30	345.70
Activated carbon derived from finger citron residue [75]	2887	1.19 (74%)	0.41 (26%)	1.60	2.48	581.40	934.58
Carbazole-based hyper-crosslinked porous polymer [76]	486	0.18 (56%)	0.14 (44%)	0.32	–	751.88	274.73
Porous carbon material prepared from potassium citrate by calcination [77]	1436	–	–	0.95	–	1853.6	927

4. Conclusions

A facile method was applied to the fabrication of carbon-silica composites from vinasse and silicates or TEOS. The effect of mixing time was investigated and the physical and chemical characteristics of the resulting composites was assessed. The synthesised mesoporous carbon-silica composites demonstrated specific surface areas of 375, 343 and 656 m²/g using Na₂SiO₃, K₂SiO₃ and TEOS, respectively. The adsorption processes of MB and MO are affected by contact time, solution pH, initial dye concentration and solution temperature. Adsorption was via a pseudo-second order kinetic model with the involvement of intraparticle diffusion. Langmuir, Freundlich and Sips isotherm models were investigated and the Sips isotherm equation was found to be the best fit. Thermodynamic

analysis demonstrated that adsorption of dyes onto the composites was spontaneous, feasible and endothermic. Dye adsorption involves surface area and surface functional groups, where surface area provides more physical sites for dye molecules via weak electrostatic forces, while specific functional groups on the composite surface form chemical bonds with the dye molecules. Results from this study indicated that the carbon-silica composites were efficient adsorbents for the remediation of MB and MO, exhibiting surface area and adsorption capacity comparable to or exceeding those of previously reported adsorbents. It is concluded that such adsorption technologies from wastes are highly useful and potentially applicable to dye remediation at scale. Such activities will be the focus of future studies.

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