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*Research Article*

# Dye wastewater treatment with rice husk-derived silica xerogel: An eco-friendly process

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**Abstract**
Removal of dye contamination from wastewater is crucial for protecting human health and the environment, and adsorption is considered an effective removal method. In addition, agricultural residues are attractive for use as adsorbents for the adsorption due to their renewability. Therefore, the present work aimed to develop silica xerogel from rice husk (agricultural residue in rice production) into an adsorbent for dye wastewater treatment. In the xerogel synthesis, a non-toxic organic acid (citric acid) was used instead of a toxic inorganic acid for leaching and precipitation steps to lower the environmental impact of the process. It was found that the obtained silica xerogel has physical properties such as a surface area and pore volume, comparable with silica xerogels in other literature. When applying it in the dye (methylene blue) wastewater treatment, the obtained silica xerogel showed better adsorption capacity than unprocessed silica at all studied conditions, i.e. various times, pH and initial concentration. The maximum adsorption capacity of the xerogel and unprocessed silica were 103.45 and 61.78 mg/g, respectively. This indicates the benefit of silica xerogel with low environmental impact when applied in dye wastewater treatment. The adsorption isotherms and kinetic for both types of silica were also conducted. It was found that the adsorption process of methylene blue on the silica fitted the Langmuir adsorption isotherm and followed the pseudo-second-order kinetic model. This provides valuable information for optimizing the operating parameters for best performance in a given situation.

**Keywords**: Adsorption isotherm, Adsorption kinetic, Dry wastewater, Methylene blue, Silica xerogel

## INTRODUCTION

Synthetic dyes widely used in many industries, such as paper, textile, food, and pharmaceutical industries, generate wastewater (containing up to 10% of used dye), which can cause adverse effects on aquatic life and human health (Bawa *et al.*, 2023; Forgacs *et al.*, 2004; Gregory *et al.*, 1981). The remaining dye in the industrial effluents must be removed before draining to lower those effects. Adsorption is considered one of the most

effective and accepted removal methods because it is cheap, renewable and easily available. A variety of materials have been used as an adsorbent, such as biomass (Aragaw *et al.*, 2021), activated carbon (Husien *et al.*, 2022), inorganic materials (Gupta *et al.*, 2009; Kasbaji *et al.*, 2023), and nanomaterial (Ruan *et al.*, 2019).

Biomass, particularly agricultural residues, is very attractive for use due to its renewability and ability to lower its environmental impact. Silica ($SiO_2$), biomass's most abundant inorganic component, is usually extracted and employed for adsorption (Chen *et al.*, 2022). Silica gel is an amorphous and porous form of silica, consisting of an irregular tridimensional framework of alternating silicon and oxygen atoms with nanometer-scale voids and pores. When the void of silica gel contains gas or vacuum, it is properly called silica xerogel (Henisch, 1988). With many benefits of silica xerogel such as absorbing water readily, high pore volume and surface area, low cost and low energy production, silica xerogel is usually applied as adsorbents (Guzel Kaya *et al.*, 2019).

Synthesis of silica xerogels from agricultural residues have been studied, including rice husk (Kalapathy *et al.*, 2000; Omatolaa *et al.*, 2023), sugarcane bagasse (Affandi *et al.*, 2009), sugarcane leave (Maseko *et al.*, 2023) ] and corn husk (Dahliyanti *et al.*, 2022). Nevertheless, most processes to obtain silica xerogel use toxic acids, e.g. hydrochloric acid (HCl) and sulfuric acid ($H_2SO_4$) during the acid leaching for contaminant removal in the biomass. To reduce the environmental issues of the processes, non-toxic acids should be used instead.

Therefore, the present work aimed to develop silica xerogel from rice husk into an adsorbent for dye wastewater treatment through the eco-friendly process using citric acid $C_6H_8O_7$ (non-toxic acid). The obtained silica xerogel was evaluated for its adsorption capacity and adsorption characteristics from the adsorption process with methylene blue, represented as a dye pollutant in the wastewater.

## MATERIALS AND METHODS

### Material

Rice husk, high-content silica biomass (up to 97%) (Nzereogu *et al.*, 2023), was used as silica precursor in silica production. It was collected from a rice processing factory in Ratchaburi province, Thailand. Analytical grade chemicals, i.e. citric acid, sodium hydroxide and ethanol were obtained from Merck. Methylene blue was supplied by the RFCL Limited Co., Ltd.

### Silica extraction

Rice husk was washed several times with tap water and dried overnight at 70°C. After that, acid leaching was applied to rice husk to remove metal impurities and decompose organic substances. About 65 g of rice husk was immersed and stirred in 1000 ml of 1 M citric acid at 85°C for 1 hr. The rice husk was separated from acid solution by settling and filtration. Then, acid retained in rice husk was removed by washing with distillation water before drying at 70°C overnight in an Electric oven. The rice husk was then calcined at 700°C using a muffle furnace for 5 hrs. The obtained white powder, designated as rice husk ash (RHA) was milled with mortar and kept in a desiccator before use.

### Silica xerogel synthesis

The silica xerogel synthesis was adapted according to the report by Maseko *et al*. (Maseko *et al.*, 2023). At first, 20 g of RSA was reacted with 2.5 M NaOH at 80° C for 2 hr under reflux condenser and vigorous stirring, and sodium silicate ($Na_2SiO_3$) was then obtained as reaction 1. The obtained sodium silicate was then filtrated and stirred for 1 hr. Citric acid was added to the solution with constant stirring until the solution became turbid around pH 7.5-8.5. The solution was gradually converted into the soft gel and after that was aged for 24 hrs. The gel was washed many times with hot water to ensure that the salt content was sodium citrate salt ($Na_3C_6H_5O_7$) and acid free, as in reaction 2. Ethanol was poured into the gel, kept overnight, and dried at 80°C for 24 hrs. The obtained material designated as rice husk ash xerogel (RHAX) was kept in a desiccator for further use.

$SiO_2 + 2\ NaOH \rightarrow Na_2SiO_3 + H2O$ (1)

$3Na2SiO_3 + 2C_6H_8O_7 \rightarrow SiO_2 + 3H_2O + 2Na_3C_6H_5O_7$ (2)

### Characterization of adsorbent

The surface functional groups of RHA and RHAX were detected by Fourier transform infrared (FTIR) spectroscope (FTIR-2000, PerkinElmer). The spectra were recorded from 4000 to 400 $cm^{-1}$. The crystalline structure of the samples were analyzed by X-ray diffraction, XRD (Aris, PANalytical) with the Cu-Kα radiation, operating at 40 kV and 40 mA with the scanning rate in 2θ range of 10°–80°. The surface morphology of samples was imaged using a scanning electron microscope (MIRA3, Tescan). The samples were coated with tungsten before being imaged. Surface area and pore structure of the samples were measured by nitrogen adsorption at -196 $^{o}$C by the surface area analyzer (Quantachrome, USA) before measurement. The sample was degassed at 150$^{o}$C for 4 hrs.

### Batch adsorption studies

Batch adsorption experiments were conducted by adding 0.1 g of an adsorbent into a 250 mL Erlenmeyer flask containing 50 mL of dye solution and then shaking in an incubator at 120 rpm at 30$^{o}$C for 24 hrs. After shaking, the adsorbent was separated from the solution

by filtration and centrifugation. The concentrations of dye solution were determined by absorbance measurement using a beam UV Vis spectrophotometer at 664 nm. They were then calculated using the standard calibration curves. The percentage of dye removal and the adsorption capacity, q (mg of dye /g of adsorbent) were calculated using Equation 1,

$$q_e = \frac{C_0 - C_e}{m} V \quad \text{Eq.1}$$

where $C_0$ and C represent the concentration of dye (mg/L) in the solution at time, t = 0 and at any time, t, respectively. V is the volume of solution (L) and m is the amount of adsorbent used (g).

The effects of contact time and MB initial concentrations were studied in the range of 0 – 24 h, and 50-400 mg/L. The effect of pH was studied in the range of 2-13 and the pH was adjusted with 0.1 M NaOH and 0.1M HCl solutions. The adsorption isotherms were performed at different initial concentrations of MB between 25-200 mg/L. The adsorption kinetic was studied using MB initial concentrations of 150 mg/L at contact time from 0-2 hrs.

## RESULTS AND DISCUSSION

### Characterization of adsorbent

The XRD patterns of RHA and RHAX are shown in Fig. 1. It was found that both patterns were similar, suggesting that there were no changes in crystal structure inside the silica during the gelation process. They similarly showed strong, broad diffraction peaks at around 2q = 22-24°, which is assigned to the characteristic of amorphous $SiO_2$ structure as reported earlier (Affandi *et al.*, 2009; Kalapathy *et al.*, 2000).

FTIR characterization was carried out to examine the functional group characteristics of RHA and RHAX, as shown in Fig. 2. The FTIR spectra of both samples exhibited the same vibration patterns, indicating that the gelation process does not alter the functional groups of the silica. The peaks at 1055 and 800 $cm^{-1}$ are assigned to the Si-O stretching vibration in Si-O-Si bonds, and the peak appearing at 460 $cm^{-1}$ corresponds to the bending vibration of Si-O-Si (Dahliyanti *et al.*, 2022; Maseko *et al.*, 2023).

The SEM images of RHA and RHAX at various magnifications are presented in Fig. 3. It can be seen that the surface of RHA was compact and smooth and exhibited a non-porous structure. On the contrary, the surface of RHAX was rough with a porous structure. Agglomeration form of nearly spherical particles can be observed in the RHAX structure. This is a general microstructure of silica xerogel, as observed in previous literature (Dorairaj *et al.*, 2022; Vander Auwera *et al.*, 2013).

The surface area, pore volume, and pore diameter of RHA and RHAX are presented in Table 1. All mentioned parameters of RHAX were higher than those of RHA. This is a benefit of xerogel which enhances the properties of typical silica to be suitable for application in various applications, particularly adsorption processes. Compared with silica xerogel from other literature, the surface area of the xerogel produced in this study is still in the range (122-668 $m^2/g$) (Affandi *et al.*, 2009; Arenas *et al.*, 2007; Dahliyanti *et al.*, 2022; Maseko *et al.*, 2023; Omatolaa *et al.*, 2023). The differences in the silica sources and production procedures could lead to different properties of the obtained xerogel.

### Adsorption properties

The adsorption capacities of the samples were evaluated with dye (methylene blue, MB) with an initial concentration of 150 mg/L on 0.1 g of the adsorbent at 30° C for 15-240 min, and are shown in Fig. 4. Methylene blue is a cationic dye widely used in the textile industrial. The process parameters for methylene blue have been studied so far with various adsorbents (Allahkarami *et al.*, 2024; Gherraby *et al.*, 2024). From the experiments, it was found that the adsorption capacity of RHA and RHAX toward MB gradually increased at the beginning of contact time and then remained constant. The equilibrium time observed for RHA and RHAX were 80 and 120 min, respectively. RHAX showed higher adsorption capacities than RHA for all contact times studied. The highest adsorption capacity of RHAX was about 1.4 times greater than that of RHA, which much more than the ratio of surface areas between two materials (1.04 times). This indicates that other factors affected the adsorption capacity of these adsorbents more than the surface area. The larger pore size and pore volume of RHAX may be the mains reason for enhancing the adsorption capacity of the large molecule substance (MB) onto the surface. In addition, more active sites may be available on the xerogel, and they can be easily accessed due to the larger pore size (Ahmad *et al.*, 2014).

The effect of initial pH of the dye solution on the adsorption capacity was studied by varying the initial pH in the ranges of 2–11 under constant process parameters (150 mg/L of MB initial concentration, 0.10 g of the adsorbents and at 30°C). The result of the study is shown in Fig. 5. It can be seen that the adsorption capacity increases with pH until it is constant around pH above 7, indicating a basic solution. This could be reasoned from that at basic condition, the adsorbent surface became negatively charged due to deprotonation and would be more attracted to the positive charges of MB (cationic dyes) and then increased the adsorption capacity (Khan *et al.*, 2016; Kushwaha *et al.*, 2014). Nevertheless, RHAX still had higher adsorption capacities than RHA for all pH ranges. In fact, the pH of MB solution in the study had already been about 6-7. Therefore, the best adsorption condition can be ob-

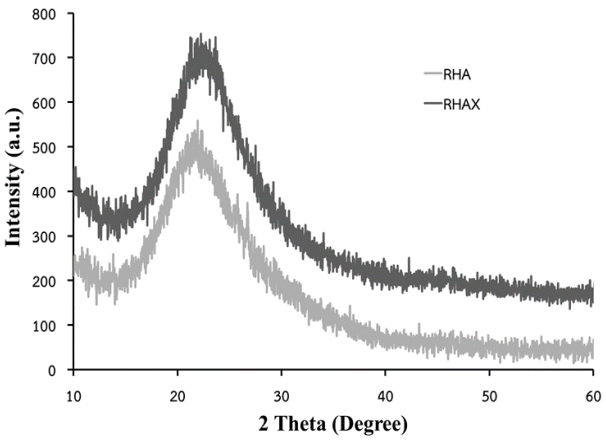


**Fig. 1**. *X-Ray diffraction patterns of the adsorbents*

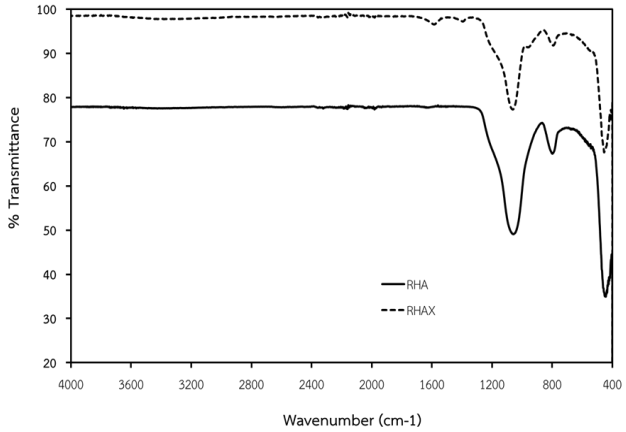


**Fig. 2**. *Fourier transform Infrared spectroscopy spectra of the adsorbents*

tained without adjusting the pH of MB solution. In addition, the actual wastewater generally has a neutral pH around 6-7. Hence, there was no need for pH adjustment for the rest of this study, and the pH was then spontaneously constant at around 6-7.

The effect of MB initial concentration was studied between 25–250 mg/L for 4 h at which the full equilibrium was attained, and the results are presented in Fig. 6. The adsorption capacity increased from 12.37 to 61.78 mg/g for RHA, and from 12.44 to 103.45 mg/g for RHAX. RHA reached the highest adsorption capacity at the lower initial concentration than RHAX. It suggests that RHAX has the higher active sites, and is still available for adsorption, even at the high initial concentration. In addition, for both adsorbents the higher concentration gradient could act as a driving force to overcome all mass transfer resistance for the adsorption process and give the higher adsorption capacity (Foo *et al.*, 2012; Khan *et al.*, 2016).

**Adsorption isotherm**

Adsorption isotherm is a mathematical model of adsorption process, which describes the interaction between adsorbates and adsorbents. In this experiment, three well-known models i.e. Langmuir, Freundlich, and Temkin isotherms were used to describe the adsorption process.

The Langmuir isotherm (Langmuir, 1918) is expressed based on the assumption of monolayer coverage of dyes onto a homogeneous surface of the adsorbent. The linear equation of Langmuir adsorption is represented as Equation 2,

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad \text{Eq.2}$$

where $C_e$ is the equilibrium concentration of the dye (mg/l), $q_e$ is the amount of dye adsorbed per unit mass of adsorbent (mg/g), $q_m$ is the maximum adsorption capacity (mg/g), and $K_L$ is Langmuir constant (L/mg). The $q_m$ and $k_L$ can be calculated from the intercept and slope of a linear plot of $C_e/q_e$ versus $C_e$, as shown in Fig. 7.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant called equilibrium parameter ($R_L$), which can be described for the reversibility of the adsorption process, defined as Equation 3,

$$R_L = \frac{1}{1+K_L C_0} \quad \text{Eq.3}$$

where $K_L$ is the Langmuir constant and $C_0$ is the initial concentration of dye (mg/L). $R_L$ is equilibrium parameter. If the type of isotherm to be irreversible ($R_L$ = 0), favorable (0 < $R_L$ < 1), linear ($R_L$ = 1) or unfavorable ($R_L$ > 1). 12

The Freundlich isotherm (Freundlich, 1906) is derived based on the assumptions of the adsorption characteristics of multilayer and heterogeneous surfaces. The nonlinear equation of Freundlich adsorption is represented as Equation 4,

$$\log q_e = 1/n \log C_e + \log K_F \quad \text{Eq. 4}$$

where $C_e$ and $q_e$ are defined similarly in the Langmuir equation, $K_F$ and 1/n are Freundlich constants related to adsorption capacity and adsorption intensity of the sorbent, respectively, which are calculated from the intercept and slope of a linear plot of log $q_e$ versus log $C_e$ (Fig. 7).

The Temkin isotherm model is based on the change of the adsorption heat in the adsorptive layer. It can be expressed by the linear equation as Equation 5 and 6 (Temkin *et al.*, 1940),

$$q_e = B \ln A_T + B \ln C_e \quad \text{Eq. 5}$$

$$B = RT/b_T \quad \text{Eq.6}$$

where $A_t$ is the Temkin isotherm constant (L/mg), $b_T$ is the Temkin isotherm constant, B is constant related to heat of sorption (J/mol), R is the universal gas constant (8.314 J/mol.K), T is the absolute temperature (K), and B, $A_T$, $b_T$ can be calculated from slope and intercept of a linear plot of $q_e$ versus ln$c_e$ (Fig. 7).

**Table 1**. Surface areas and pore characteristics of the adsorbents

| Sample | Surface area ($m^2/g$) | Total pore volume ($cm^3/g$) | Pore size (nm) |
|---|---|---|---|
| RHA | 189 | 0.240 | 5.31 |
| RHAX | 197 | 0.556 | 11.27 |

RHA: rice husk ash; RHAX: rice husk ash xerogel

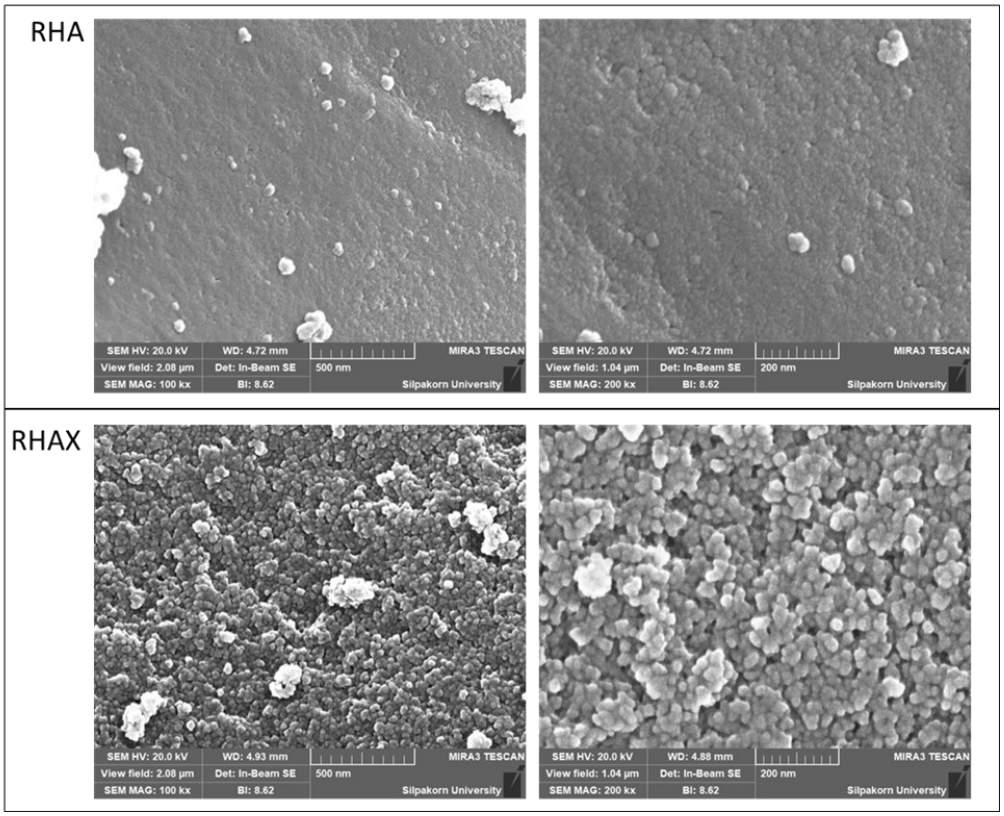


**Fig. 3**. *Scanning electron microscope images of the adsorbents. Showing that RHA surface was compact and smooth with a non-porous structure, while RHAX surface was rough with a porous structure and particle agglomeration*

All experimental data for the adsorption of MB onto RHA and RHAX as presented in Fig. 7 can be extracted for the corresponding parameters of all the three isotherms, shown in Table 2.

Considering $R^2$ and $\Delta q_e$ values of RHA and RHAX, it can be seen that the Langmuir isotherm has a higher value of $R^2$ (0.9892) and a lower value of $\Delta q_e$ (6.549), compared with the Freundlich and Temkin isotherms. This suggests that the Langmuir model could better fit the adsorption processes of both adsorbents than the other models. The $R_L$ values for RHA and RHAX were found to be 0.0036 and 0.0492, greater than 0 but less than 1, indicating that Langmuir isotherm is favourable (Vargas *et al.*, 2011). The maximum monolayer coverage capacity ($q_m$) of RHAX (106.38 mg/g) is much larger than that of RHA (59.52 mg/g), beneficial from a xerogel structure with more surface roughness and higher pore volume. Similar results have been reported with various types of silica (Dahliyanti *et al.*, 2022; Guzel Kaya *et al.*, 2019; Juzsakova *et al.*, 2023). However, silica xerogel from the present study exhibited higher removal capacity than the others.

Nevertheless, it is known that in one adsorption process, many adsorption types could occur simultaneously. Thus, Freundlich and Temkin are still useful for describing the adsorption characteristics of the adsorption process with acceptable $R^2$ values as observed.

The n parameter in the Freundlich model, known as the heterogeneity factor, can be used to describe important information about adsorption systems. If n is in the range of 2-10, indicating good adsorption, 1–2 moderate adsorption and less than one denoted poor adsorption (Shang *et al.*, 2014). From the result, the n values of both adsorbents were higher than 2, indicating effective adsorbents for MB adsorption process.

The Temkin isotherm can be used to identify the two main types of adsorption, i.e. physisorption and chemisorption, by measuring the heat of adsorption "B value". Physisorption occurs if B is less than 1.0 kcal/mol, and chemisorption occurs if B is more than 20 kcal/mol. Both of the adsorption types occur with B between 1 and 20. For RHA and RHAX, their B values (7.97 and

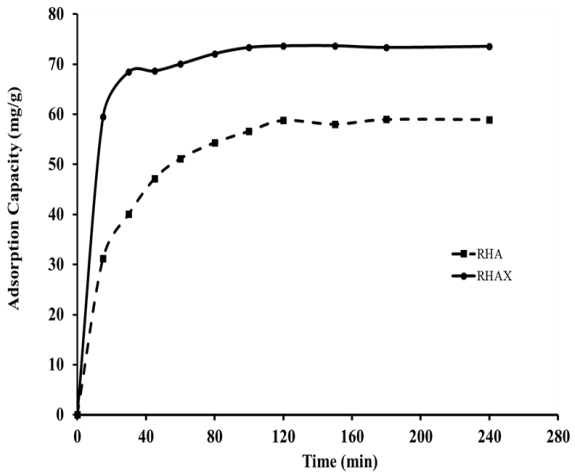


**Fig. 4**. *Adsorption capacity of the adsorbents at various times*

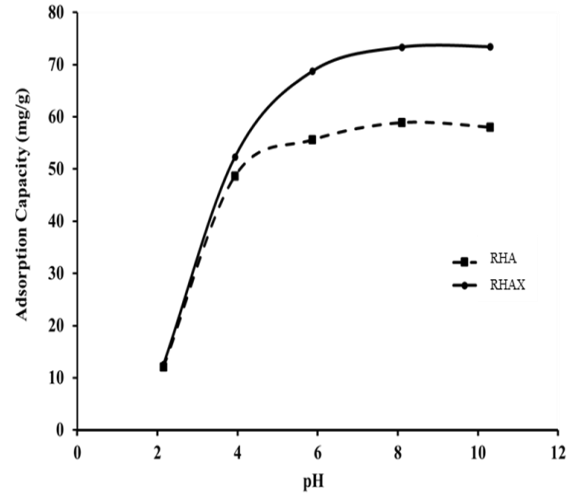


**Fig. 5.** *Adsorption capacity of the adsorbents at various initial pH of the solution*

19.13) are between 1 and 20, pointing out that the adsorption processes involve both physisorption and chemisorption (Mohamed *et al.*, 2022). In addition, the positive values of b also indicate to an exothermic reaction during the adsorption (Hamdaoui, 2006).

**Adsorption kinetic**

Two simplified kinetic models, including the pseudo-first order (Lagergren, 1898) and pseudo-second order kinetic models (Ho *et al.*, 1999) were used here to understand the adsorption mechanism influenced by chemical reaction rates and mass transfer.

The pseudo-first-order kinetics is expressed in a linear form as Equation 7.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \text{Eq.7}$$

Where $q_e$ and $q_t$ are the amount of MB adsorbed (mol $g^{-1}$) at equilibrium and at time t (min), respectively, $k_1$ is the rate constant of adsorption ($min^{-1}$), k1 value was calculated from the plots of $\ln(q_e - q_t)$ versus t at different concentrations.

The pseudo-second-order kinetics is expressed in a linear form as Equation 8.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{Eq.8}$$

where $k_2$ is the rate constant of the pseudo-second-order adsorption (g.$mol^{-1}$ $min^{-1}$), $k_2$ value and $q_e$ were

**Table 2**. Isotherm parameters for the adsorption of methylene blue on the adsorbents

| Isotherm | Parameters | RHA | RHAX |
|---|---|---|---|
| Langmuir | $q_m$ (mg/g) | 59.52 | 106.38 |
| | $K_L$ (L/mg) | 1.05 | 1.807 |
| | $R_L$ | 0.0064 | 0.0036 |
| | $R^2$ | 0.9922 | 0.9952 |
| | $\Delta q_e$ (%) | 3.197 | 3.776 |
| Freundlich | $K_F$ (L/g) | 31.62 | 57.16 |
| | n | 5.714 | 2.798 |
| | $R^2$ | 0.8632 | 0.9284 |
| | $\Delta q_e$ (%) | 18.64 | 13.03 |
| Temkin | $A_T$ | 81.13 | 23.38 |
| | b | 7.3761 | 19.13 |
| | $R^2$ | 0.9144 | 0.9813 |
| | $\Delta q_e$ (%) | 8.774 | 6.058 |

$q_m$: maximum adsorption capacity; $K_L$: Langmuir constant, $R_L$: equilibrium parameter;
$R^2$: coefficient of determination, $\Delta q_e$ (%): value of normalized standard deviation;
$K_F$: Freundlich constant, n: adsorption intensity of the adsorbents;
$A_T$: Temkin isotherm equilibrium binding constant, b: Temkin constant related to heat of sorption

**Table 3**. Adsorption kinetics parameters of methylene blue on the adsorbents

| Reaction | Parameters | RHA | RHAX |
|---|---|---|---|
| Pseudo-first order | $q_{e,\,cal}$ | 18.45 | 16.69 |
| | $k_1$ | 0.0104 | 0.0032 |
| | $R^2$ | 0.765 | 0.606 |
| | $\Delta q_e$ (%) | 68.80 | 79.94 |
| Pseudo-second order | $q_{e,\,cal}$ | 59.88 | 74.62 |
| | $k_1$ | 0.0014 | 0.0042 |
| | $R^2$ | 0.9986 | 0.9998 |
| | $\Delta q_e$ (%) | 1.21 | 10.34 |

$q_{e,\,cal}$: the amount of methylene blue adsorbed onto the adsorbents at equilibrium;
$k_1$: rate constant of adsorption, $R^2$: coefficient of determination;
$\Delta q_e$ (%): value of normalized standard deviation

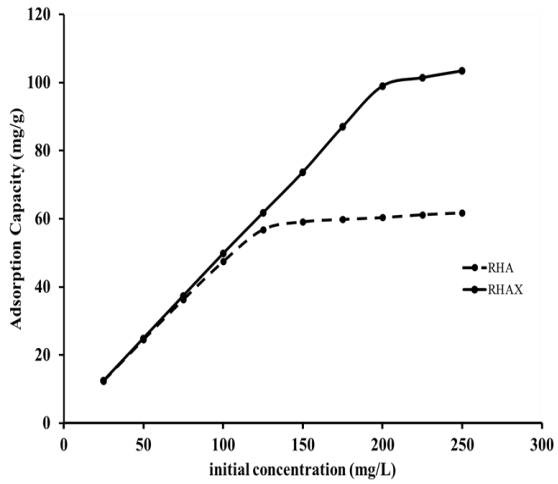


**Fig. 6.** *Adsorption capacity of the adsorbents at various initial concentration of the solution*

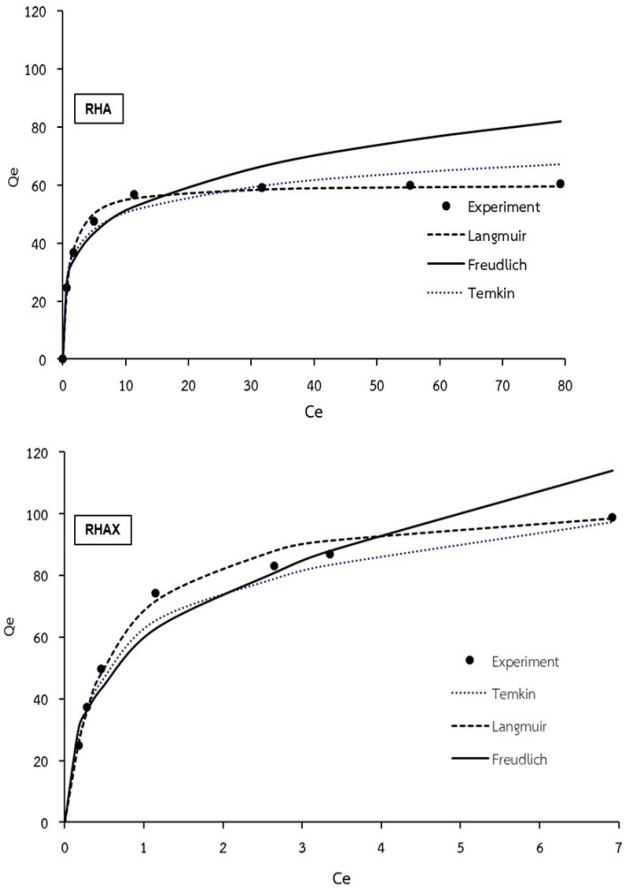


**Fig. 7**. *Various adsorption isotherms of the adsorbents*

calculated from the intercept and slope of the plots of t/$q_t$ versus t at different concentrations.

All kinetic parameters of both reaction types are shown in Table 3. It was seen that the correlation coefficient ($R^2$) of the pseudo-second-order model for both RHA and RHAX (0.9986 and 0.9998) were closer to unity than those for the pseudo-first-order model (0.765 and 0.606). The value of normalized standard deviation Δq (%) of the pseudo-second-order model was also lower than that of the the pseudo-first-order model. It can be concluded that the kinetics of MB adsorption on RHA and RHAX followed a pseudo-second-order model, which could imply that the chemisorption process involved in the adsorption process (Cherifi *et al.*, 2013; Islam *et al.*, 2017). The electrostatic attraction between negative charges on the surface of both silica and the positive charges of cationic dye (MB) may play an important role in adsorption. A similar model was observed for adsorption of methylene blue onto many types of silica (Kushwaha *et al.*, 2014; Li *et al.*, 2020).

## Conclusion

Silica xerogel can be synthesized here using biomass precursor in an eco-friendly process with a nontoxic organic acid (citric acid) presence. The obtained silica xerogel has better physical properties than the normal silica. The methylene blue adsorption capability was also found that the silica xerogel had a higher adsorption capacity than the normal silica at all conditions, i.e. various time, pH, and initial concentrations. This suggests that this low-environmental impact silica xerogel can be a potential cost-effective adsorbent for dye removal in wastewater treatment processes. The adsorption process of MB for both types of silica fitted the Langmuir adsorption isotherm and followed the pseudo-second-order kinetic model. This provides valuable information for optimizing the operating parameters for best performance in a given situation.

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## Conflict of interest

The authors declare that they have no conflict of interest.

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