Removal of Rhodamine B from aqueous solution using silica extracted from rice husk

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Abstract

Global annual production of rice husk is approximately 120 million tons. It doesn't easily biodegrade, resulting in disposal problems. This paper therefore, investigated the use of silica obtained from the burning of the raw rice husk in open air (RHSA) and in a Muffle Furnace at 540 °C (RHSO). The efficiency of the two silica samples in removing Rhodamine B (RB) from aqueous solution was tested using different process parameters. 89% silica was obtained from either method. The removal of RB was more possible on RHSA than on RHSO. This was revealed by calculated Langmuir R_L values of 0.152 for RHSA and 0.558 for RHSO. This was also supported by the obtained Temkin isotherm equilibrium constants values of 3.379 and 0.677 L/mg for RHSA and RHSO respectively. Langmuir monolayer capacities of 6.0 and 6.87 mg/g were obtained for RHSA and RHSO respectively. Increased in mass of RHSA or RHSO greatly enhanced RB removal (65% with 0.05 g to 98% with 0.5 g for RHSA). Optimal removal conditions on each sample were; temperature 27 °C, mass adsorbent 0.5 g, pH 7.05, contact time 24 h and 10 mg/L of RB initial concentration. The RB removal was negatively affected by ionic strength, decreasing from 84 to 46% for RHSA and 60–41% for RHSO with increase in ionic strength from 0.00 to 2 M. The two adsorbents are efficient in RB removal and easily regenerated as it is purely a physical process.

Keywords Rice husk · Rice husk ash · Silica · Adsorbent · Rhodamine B · Ionic strength

1 Introduction

The United Nations demographic report of 2019 shows that the world population as of April 2019 is about 7.7 billion. The findings of the same report shows that this population could attain 8.5 billion in 2030, 9.7 billion in 2050, and 10.9 billion in 2100 [1]. The sub-Saharan Africa countries will contribute half of this growth between 2019 and 2050 [1]. This increase will lead to a boom in industrial, agricultural, domestic etc. activities to meet the needs of this population. These activities will have corresponding negative consequences on the environment (like water resources, urban waste dumping etc.) and human health. There will equally be an increase in the need for food to

feed the increasing population. One of such food item is rice which constitutes the food for about half of the world's population [2]. According to the International Rice Research Institute, 800 million tons of rice will be needed by 2025 to feed the world population [2]. Unfortunately, the transformation of this rice for consumption will generate a significant amount of waste called rice husk with global annual production of approximately 120 million tons [3]. Rice husk (RH) is not good for composting or manure, despite its high organic content (30–50%). This is due to its very low nutritional value and the fact that it takes a very long time to decompose [3, 4]. Consequently, disposal of rice husk and resulting rice husk ash (RHA), the product of incineration of rice husk become an imperative

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as every 100 kg of husks burns yields about 25 kg of RHA [4]. An efficient way of limiting environmental pollution resulting from the disposal of this waste is to transform it to other useful goods. This is because rice husk is a cellulose-based fiber and contains approximately 20% silica in amorphous form. It also contains about 40% cellulose and 30% lignin. Meanwhile, RHA contains approximately 90% silica, which is a highly porous structure and is lightweight, with high specific surface area [4–6]. These properties have favoured its use as a pozzolan in the construction industry, as a filler, additive, abrasive agent, oil adsorbent, sweeping component, and as a suspension agent for porcelain enamels, manufacture of insulation, and materials for flame retardants [4–6]. Thus, RH and RHA are very important sources of silica, which can be used for different industrial and environmental applications as opposed to chemical sources, mainly tetraethoxysilane (TEOS) and tetramethoxysilane (TMOS) which are expensive and toxic [7]. The characteristics of the silica produced depend on the burning temperature, burning time and composition of the rice husks [4, 8]. Burning at temperatures greater than 700–800 °C in open air or furnaces produces significant amounts of cristobalite and tridymite which are nonreactive silica minerals. However, burning from 500 to 700 °C for about an hour produces amorphous silica with high reactivity due to its very large surface area resulting from its microporous structure [4, 8]. Consequently, many methods have been developed for the preparation of silica from rice husk such as soil–gel, precipitation, and pyrolysis method [4, 8]. The most used method worldwide involves the treatment of rice husk with acid to remove metal oxides and silica extracted by sodium hydroxide treatment followed by precipitation with acid and calcination at high temperature. Ma et al. [9] have reported a recyclable method of obtaining silica from RHA by dissolving SiO_2 using NH_4F followed by precipitation of SiO_2 with by NH_3 . More simple procedures have been developed by treating RH or RHA with acid (HCl, H_2SO_4 , organic acids) followed by calcination of the acid treated RH or RHA at temperatures ranging from 500 to 800 °C [7, 10].

Rice husk and rice husk ash as well as their modified forms have been extensively studied as adsorbents for heavy metals and dyes adsorption [11–16]. However, the studies on the use of RH extracted silica are scanty in literature. While the authors [17] have studied the removal of methylene blue from aqueous solution using RH extracted silica, there is no reliable scientific source indicating a similar study with Rhodamine B (RB). Rhodamine B, a basic dye has extensively been used in food, paper printing, textile dyeing and leather industries [18, 19]. But because of its carcinogenic character, its use was prohibited [18]. Unfortunately, despite the risk posed by RB to living organisms and the environment at large, it's currently being used

widely again particularly in the textile industry [18]. Hence, there is the need to reduce or eliminate RB from effluents before discharge. Due to the fact that RB like many other dyes show strong resistance to factors such as temperature, light chemicals, etc., its removal process is very difficult using conventional wastewater treatment methods [18, 19]. Removal by adsorption is attracting researchers because it applies solid adsorbent with several properties. These properties include; reactivity, pollutant selectivity, easy availability and low cost, ability not to generate secondary toxic sludge and high efficiency in removing different types of pollutants at low and high levels [18–20]. The use of silica extracted from rice husk for Rhodamine B removal aqueous solution was investigated in this work because literature review showed no evidence of published work of RB removal using rice husk extracted silica. Firstly, rice husk ash (RHA) was prepared from the raw rice husk by burning in open air and in a Muffle Furnace at 540 °C. Silica extraction from RHA was accomplished by treating each sample of RHA prepared by burning in open air and in a Muffle Furnace at 540 °C with 1 M HCl followed by calcination at 700 °C for 2 h. Each of the samples was tested for the effectiveness in removing Rhodamine B from aqueous solution. The effect of contact time, solution pH, initial RB concentration, dose of silica used, temperature and ionic strength were used to evaluate the adsorption efficiency. Equilibrium adsorption parameters such as adsorption capacity, adsorbent-adsorbate interaction, and adsorption energy/mechanism were evaluated using Freundlich, Langmuir, Temkin and Dubinin-Radushkevich isotherm models while the kinetic parameters of the adsorption process were evaluated using Pseudo-first-order, Pseudo-second-order and Intra-particle diffusion kinetic models. The spontaneous nature and enthalpy of the process was also determined from thermodynamic studies.

2 Experimental

2.1 Materials and equipments

HCl, NaOH, NaCl and Rhodamine B (Fig. 1) used were all of analyte grades from Scharlab S. L. Spain. A Nabertherm GmbH 30–3000 °C Muffle oven model L3/12/C450 with maximum temperature of 1200 °C (Germany) was used for calcination. A UV/visible spectrophotometer, spectro 23RS, labo med.inc (USA) was used for measurement of absorbance. GEMINI-20 Portable milligram scale weighing up to 20 g in 0.001 g increment was used throughout for weighing. The heating and stirring was done on a Thermo Scientific Cimarec stirring hot plate, model: SP 131320-33 while all pH measurements and redox

Fig. 1 Chemical structure of Rhodamine B

potentials were measured using a Mettler Toledo Education line pH meter. All the distilled water used was distilled in the laboratory using Life Basis Water Distiller Stainless Steel 4L 750 W. X-Ray Fluorescence (AXIOS PANalytical, Dy 1680) was used for the determination of the chemical composition. Surface functional groups were determined by Infra-red spectroscopy (FTIR Spectrophotometer (Bruker Make), Model: ALPHA-P).

2.2 Preparation and characterization of rice husk silica

Rice husk used was collected at the rice processing unit of Semry (rice Cultivation Company) in Yagoua-Cameroun. It was thoroughly washed with distilled water, dried in laboratory conditions for 10 days and used to produce rice husk (RHA). Accordingly, 1 kg of dried rice husk was burnt in open air to ash point (mixture of white ash and black organic material) while the same quantity was burnt in the oven at 540 °C for 24 h. RHA from open air and oven burning were used in the preparation of silica.

Extraction of silica from RHA was accomplished using the procedure of Tuan et al. [7] with modifications. Accordingly, a 100 mL solution containing 5.0 g of RHA and 1 M HCl in a capped Erlenmeyer was stirred at 80 °C for 2 h and left standing overnight to remove metal ions in RHA. After which, the acidified suspension was filtered on Whatman filter paper N° (number) 1 and washed with distilled water to neutral pH [7], then dried at 110 °C in the oven for 24 h. The dried acid treated RHA was then calcinated at 700 °C for 2 h to obtain white silica. The different processes involved used in the preparation of RH silica from rice husk are summarized in Fig. 2. The pH, redox potential, chemical composition and surface groups of these two samples were determined. They were used for adsorption studies without further treatment. Silica obtained from open air burning of RH was designated as RHSA and that from burning rice husk in the oven at 540 °C was designated as RHSO.

2.3 Batch adsorption/desorption studies

A 1000 mg/L stock solution of RB was prepared by dissolving 1 g of RB in 1 L of distilled water and diluted appropriately to obtain RB working solutions. These studies were carried out using 20 mL dye solution of the desired concentration in 20-mL essay tubes and required amount of RHSA or RHSO. All experiments were carried out at solution pH of 7.05, contact time 24 h, temperature 27 °C, 0.1 g each adsorbent type and 10 mg/L RB initial concentration except when these parameters were varied, with all pH adjustments been carried using 0.1 M NaOH or 0.1 M HCl solutions. The essay tubes containing the solutions were kept static without agitation. At the required time interval the dye solution was then separated from the adsorbent by decantation (without filtration) and its concentration in the supernatant determined. The influence of the following parameters was investigated; contact time 5 min, 10 min, 20 min, 40 min, 60 min and 24 h, adsorbent dosages from 0.05 to 0.5 g/L, initial dye concentration from 5 to 20 mg/L, pH 2–10, temperature 27–60 °C and ionic strength 0.05 M–2 M NaCl. Rhodamine B quantity and percentage removed were calculated using the equations:

$$q_e = \frac{(C_i - C_t)V}{m} \quad (1)$$

$$\% \text{Removal} = \frac{(C_i - C_t)}{C_i} \times 100 \quad (2)$$

where q_e is the amount adsorbed (mg/g), C_i is the initial RB concentration (mg/L), C_t is RB residual concentration (mg/L), 'm' is the adsorbent mass (g) and V is the volume of RB solution (L).

Preliminary adsorption studies from 5 to 60 min showed little variation in amount removed. The time of 24 h was thus chosen to verify if the active sites of the materials were saturated or still active for further adsorption. The pH affects the adsorbent surface properties and the adsorbate ionization or dissociation. The process was thus, performed from pH of 2–10 to better understand the influence of the RB solution pH (acidic, neutral and basic) on adsorbent performance. Increasing the temperature is known to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, increasing adsorption. In our preliminary studies, the amount removed increased from 20 to 27 °C and decreased at 35 °C. At 45 °C, the amount removed increased slightly and remained constant 60 °C, thus, the choice of adsorption from 20 to 60 °C.

The RHSA sample was used for desorption study due to its better adsorption potentials. All the solutions used in the study of the effect of contact time were used to carry out

Fig. 2 Processes involved in the preparation of RH silica from rice husk

desorption studies. After contact time required, the dye liquid was decanted and remaining adsorbent in the tube was allowed to dry overnight. Then, 20 mL of distilled water was added to the tube containing the adsorbent and manually shaken for about 2 min. The suspension was allowed to stand for about 2 min to decant. 5 mL of the solution was then decanted and the desorbed concentration determined. Desorption was done in triplicate at each time, t . The percentage desorbed was calculated using Eq. 2. The average desorption efficiency and error factor at each time, t are reported.

3 Results and discussion

3.1 Characterization

The results of the chemical composition of silica produced under the two conditions studied are presented in Table 5,

where it can be observed that the silica produced by burning in open air and in an oven at 540 °C all have silica content of approximately 89%. These results are similar to those of other studies [7, 15]. However, RHO is seen to contain 1.48% of Al_2O_3 and 1.11% of SO_3 , the other components being in trace. Meanwhile RHSA was purely silica as all other species are present in trace amounts except the loss on ignition which is higher than in RHO. This relatively high content of alumina and SO_3 in RHO is probably responsible for its 89.67% silica content compared to for 89.84% silica content for RHSA (Table 1).

The IR curves of RHO and RHSA are shown in Fig. 3a, b respectively. Three peaks are observed for each sample; 1067.48, 789.61 and 444.24 cm^{-1} for RHO and 1059.64, 797.34 and 443.66 cm^{-1} for RHSA. The bands 1067.48 and 789.61 cm^{-1} for RHO and 1059.64, 797.34 cm^{-1} for RHSA are the asymmetric vibration of Si–O [21] while those at

Table 1 Chemical composition of RHSO and RHSO in % (w/w)

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	P ₂ O ₅	LOI
RHSO	89.67	1.48	0.48	0.68	0.14	1.11	0.19	0.74	0.03	2.78
RHSA	89.84	0.41	0.09	0.31	0.04	0.75	0.2	0.59	0.04	3.94

RHSA = silica extracted from burning of raw rice husk in open air; RHSO = silica extracted from burning of raw rice husk in Muffle Furnace at 540 °C; LOI = loss on ignition

Table 2 Kinetic models and parameters for the removal of RB on rice husk extracted silica

	Pseudo-first-order				Pseudo-second-order				Intra-particle diffusion		
	K ₁	Q _{e,C}	Q _{e,ex}	R ²	K ₂	Q _{e,C}	Q _{e,ex}	R ²	K _{id}	C	R ²
RHSA	0.003	0.548	1.692	0.663	0.053	1.705	1.692	0.9998	0.015	1.111	0.991
RHSO	0.0127	0.389	1.217	0.838	0.119	1.223	1.217	1.000	0.039	0.766	0.527

Units of parameters: k₁ = min; q_{e,C} = q_{e,ex} = C = mg/g; k₂ = g/mg/min

q_{e,C} and q_{e,ex} are respectively, calculated and experimental equilibrium amounts adsorbed

444.24 and 443.66 cm⁻¹ are due to Si–O–Si symmetric bending vibrations [15].

3.2 Batch adsorption/desorption

3.2.1 Influence of contact time and adsorption kinetics

Contact time is used to determine the time it takes for an adsorption process to attain equilibrium and the kinetic mechanism of adsorption. It was studied from 5 to 1440 min and the results are depicted by Fig. 4a. High adsorption is observed at the beginning of the process for the two silica samples, 55% for RHSA and 43% for RHSO. However, there is a gradual increase in adsorption after 5 min attaining 84% for RHSA and 60% for RHSO. The redox potential of RHSA was determined to be –15 mV (pH 7.61) and –26 mV (pH 7.94) for RHSO indicating a reduction of surface charge for open air sample hence creating more space on its surface for the reaction. Also, the relatively high silica content of RHSA indicates that it has a larger surface area, thus, greater porosity. There is equally more purity in the Si–O and Si–O–Si IR bands for RHSA with maximum absorbance of 0.25 absorbance units (Fig. 3b). The maximum absorbance is 0.35 for RHSO (Fig. 3a). These properties contributed in RHSA better adsorption performance than the oven 540 °C sample. High initial adsorption is due to the availability of the many available sites which are reduced progressively in number with further loading. These results are similar to those of Shah et al. [19] who reported the adsorption of RB on walnut shells adsorbents with removal efficiency ranging from 43.34% in 20 min to 81.86% in 120 min. However, Moeinian and Mehdinia [17] obtained methylene blue

(molar mass 319.85 g/mol) removal percentage of 93.4% in 90 min using rice husk silica. The difference between these results and those of this work may be due to the size of the molecule involved as RB has a molar mass of 479.02 g/mol. Equally, Bhowmick et al. [13] studied the use of RH and RHA in removing amaranthus gangeticus pigment dye (molecular weight 711 g/mol) from aqueous solution with removal efficiencies of 5.12% in 10 min to 43.91% in 240 min for RH and 2.72% in 10 min to 59.62% in 240 min RHA. While Bhowmick et al. [13] results suggest low adsorption of dye on RH and RHA compared to their extracted silica, it is equally evident from the results of this study that the size of the molecule plays an important role in its removal efficiency.

Adsorption kinetics which helps in the understanding of the rate of adsorption and the rate-limiting step of the transport mechanism was analyzed using pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models. Their linearized model equations are given in [18–22] and the obtained plots are given in Fig. 5 (pseudo-first-order Fig. 5a, pseudo-second-order Fig. 5b and intraparticle diffusion Fig. 5c). The calculated parameters presented in Table 2. These results show that pseudo-second-order kinetic model describes RB adsorption on the two RH silica adsorbents tested with correlation coefficients > 99% and strong correlation between calculated and experimental equilibrium amounts adsorbed, indicating a two-step mechanism of removal. For RHSA, the correlation coefficients for intraparticle diffusion model > 99%, but the intercept is different from zero (Fig. 5c and Table 2). For the process to be completely controlled by the intraparticle diffusion, the plot should yield a straight line passing through the origin [23]. The deviation is due to the difference in the rate of mass transfer in the initial and

Fig. 3 IR spectra of **a** RHSO and **b** RHSA

final stages of the sorption, indicating that some boundary layer effect exists; hence suggesting Intraparticle diffusion was not the only rate-limiting step.

3.2.2 Influence of Rhodamine B initial concentration and equilibrium isotherms

The effect of RB initial concentration on its removal from aqueous solution using silica obtained from open air and oven (540 °C) burning of RH is shown in Fig. 4b for

concentration ranging from 5 to 20 mg/L with all other parameters kept constant. The two adsorbents show the opposite behaviour with RHSA showing highest removal, about 88 for 5 mg/L and reducing to about 80% for 20 mg/L. This trend is similar to that of [17] with a reduction of methylene blue removal efficiency of 96.7% for 10 mg/L to 60.8% for 100 mg/L using rice husk silica as an adsorbent. Conversely, RHSO showed increasing removal with increasing initial concentration (about 60% for 5 mg/L to about 66% for 20 mg/L). This is probably due to the fact

Fig. 4 Effect of process parameters **a** contact time, **b** initial concentration, **c** adsorbent dose, **d** pH, **e** temperature and **f** ionic strength on RB removal

Fig. 5 **a** Pseudo-first order, **b** pseudo-second order and **c** intraparticle diffusion models kinetic plots for RB removal

that the RHSA sample has a stronger affinity for RB, thus a rapid occupation of the sites such that fewer sites are available with high loading. This is probably the reverse with RHSO where there is a low affinity for the surface, hence a gradual occupation with increased loading. Data of influence of concentration was used to model different equilibrium isotherms.

Adsorption isotherm provides information on the distribution of pollutant molecules between the solid and liquid phases and in the determination of adsorption capacity as well as the nature of adsorbate-adsorbent interactions. Langmuir, Freundlich, Dubinin–Radushkevich (D–R) and Temkin isotherm models whose linearized model equations are given in [18–22] were tested and the obtained plots are shown in Fig. 6 (Langmuir Fig. 6a, Freundlich Fig. 6b, Dubinin–Radushkevich (D–R)

Fig. 6c and Temkin Fig. 6d). Their calculated parameters are summarized in Table 3.

The Langmuir isotherm describes adsorption on a monolayer and homogeneous adsorbent surface. Separation factor, R_L , which is considered as a more reliable indicator of the adsorption is defined by:

$$R_L = \frac{1}{1 + bC_0} \quad (3)$$

where the Langmuir constant is b (L/mg) and RB initial concentration is C_0 (mg/L). For favorable adsorption, $0 < R_L < 1$; while $R_L > 1$, $R_L = 1$ and $R_L = 0$, respectively, describe unfavorable, linear and irreversible adsorption [20–23].

The Freundlich model describes adsorption on adsorption multilayer and heterogeneous surface. Equally, Dubinin–Radushkevich isotherm also assumes a

Fig. 6 Linearized form plots of **a** Langmuir, **b** Freundlich, **c** Dubinin Radushkevich and **d** Temkin isotherms

heterogeneous surface. But its significance is that it can be used to determine adsorption energy (E) calculated from:

$$E = 1 / \sqrt{2K} \quad (4)$$

K is a constant related to the adsorption energy ($\text{mol}^2 \text{kJ}^{-2}$). Adsorption occurs by an ion exchange mechanism if E is between 8 and 16 kJ/mol, physisorption if $E < 8$ kJ/mol and chemisorption if $E > 16$ kJ/mol [24–26]. Meanwhile Temkin

model assumes that the heat of adsorption of the adsorbates in the layer decreases linearly rather than logarithmically with coverage due to adsorbent–adsorbate interactions [20].

From Table 3 and Fig. 6, it can be seen that while all the tested models describe adsorption on RHSA with significant correlation coefficients only Freundlich model describes adsorption on RHSO with a 98% correlation coefficient. However, the fact that Freundlich isotherm

Table 3 Adsorption isotherm models and parameters for the removal of RB on rice husk extracted silica

	Langmuir			Freundlich				Dubinin–Radushkevich				Temkin		
	Q_m	B	R^2	R_L	K_F	N	R^2	X_m	K	E	R^2	A_T	B_T	R^2
RHSA	6.00	0.280	0.933	0.152	1.291	1.500	0.9985	2.818	0.184	1.647	0.902	3.379	2.128	0.951
RHSO	6.87	0.040	0.650	0.558	0.261	0.852	0.9794	2.469	1.413	0.595	0.890	0.677	1.619	0.876

Units of parameters: $q_m = X_m = \text{mg/g}$; $b = A_T = \text{L/mg}$; $K_F = (\text{mg/g})(\text{L/mg})^{1/n}$; $K = \text{mol}^2/\text{kJ}^2$; $E = b_T = \text{kJ/mol}$

model gives the best fit for the two samples (R^2 of 0.999 and 0.978 for RHSA and RHSO adsorbents respectively) suggest heterogeneous adsorption on these silica adsorbents. For Freundlich model, values of n in the range 2–10 represent good, 1–2 moderately difficult, and less than 1 a poor adsorptive potential [20]. Thus, adsorption of RB on RHSA is moderately difficult with n value of 1.500 and very poor on RHSO with n value of 0.852 (Table 3). This is supported by Langmuir values of R_L 0.152 and 0.558 for RHSA and RHSO adsorbents respectively. Maximum adsorption capacity (q_m) was obtained from Langmuir isotherm (6 and 6.87 mg/g) while the highest equilibrium constant was obtained from Temkin isotherm ($A_T = 3.379$ and 0.677 L/mg). The closeness of the q_m values for the two adsorbents shows that they were not significantly different despite being prepared from different precursors. However, the high value of the equilibrium constant (A_T) for RHSA ($A_T = 3.379$ L/mg) shows that it has more affinity for RB than RHSO, in agreement with the magnitude of n values from Freundlich isotherm. Adsorption energies of 1.647 and 0.595 kJ/mol for the two adsorbents calculated from Dubinin–Radushkevich isotherm are all less than 8 kJ/mol (Table 3), an indication that adsorption of Rhodamine B on rice husk extracted silica occurs by physical adsorption. This was further confirmed from Temkin isotherm with low adsorption energy (b_T) values from 1.619 to 2.128 kJ/mol characteristic of physical adsorption.

3.2.3 Influence of adsorbent dose on RB removal

This was studied by varying the mass of each sample from 0.05 to 0.5 g using 10 mg/L RB initial concentration, pH of 7.05, temperature of 27 °C and contact time of 24 h. From the results shown in Fig. 4c it is observed that for each sample of adsorbent, removal efficiency increases with increasing quantity of the tested adsorbents. For RHSA, the increase is from 65% with 0.05 g to 98% with 0.5 g and for RHSO, the increase is from about 43% with 0.05 g to 81% with 0.5 g. These results show that for both adsorbents, with an increase in their quantities, there is a corresponding increase in their surface area and the number of active sites available for adsorption. These results are similar to those of [17] who obtained 51.7% removal efficiency of methylene blue using 0.5 g/L of rice husk extracted silica and which increased to 94.8% with 2 g/L of adsorbent.

3.2.4 Influence of pH on RB removal

The pH of the solution has a significant influence on adsorbate uptake because it affects the adsorbent surface properties and the adsorbate ionization or dissociation [19]. The pH of 2, 4, 7, 8 and 10 were used and the results

are shown in Fig. 4d where it is observed that for both samples there is an increase in removal efficiency with increase in pH and attaining a maximum at pH of 7. This is followed by a sharp drop from 71% for RHSA to about 44% at pH of 10 and a reduction from 72% at pH of 7 for RHSO to 38% at pH of 10. These results are similar those of [19] who observed the same trend during the adsorption of RB on walnut shells adsorbents. According to them, RB molecules remain in their monomeric form at lower pH so can go into the pores of the adsorbent, hence high adsorption efficiency. But with increasing pH the reduction in efficiency is likely due to the formation of the zwitterion form of RB which makes it a bigger molecule difficult to enter into the pores on the adsorbent surface. Similar results were obtained by [13] in their study involving the use of RHA in removing amaranthus gangeticus pigments dye from aqueous solution with removal efficiencies of 80.21% at pH 2 and decreasing to 1.51% at pH of 9.

3.2.5 Thermodynamics of RB on removal

Thermodynamic studies were performed to verify if the process is spontaneous, exothermic or endothermic. Hence, enthalpy ΔH° , entropy ΔS° , and Gibbs free energy ΔG° were obtained from the following equations:

$$\Delta G^\circ = -RTK \quad (5)$$

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (6)$$

where R is the ideal gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$) and T is the temperature (K). The enthalpy change (ΔH) and the entropy change (ΔS) were calculated from a plot of $\ln K$ versus $1/T$.

$$K \text{ was calculated from } K = C_{ad}/C_t \quad (5); \quad C_{ad} = C_i - C_t$$

where K is the equilibrium constant, C_t is the residual concentration (mg/L) at temperature T , C_i is the initial concentration (mg/L), C_{ad} is the concentration of RB in the adsorbent at equilibrium (mg/L) at temperature T . The results of the influence of temperature are shown in Fig. 4e where it can be seen that the highest removal efficiency occurred at 27 °C for the two adsorbents (84% at 27 °C for RHSA and reducing to 67% at 60 °C; and 60% at 27 °C reducing to 46% at 60 °C for RHSO). From the calculated thermodynamic parameters summarized in Table 4, RB removal on RHSA is spontaneous (negative ΔG° values) and non-spontaneous (positive ΔG° values) except at 27 °C RHSO. However, the negative values of entropy for the two materials indicate reduced randomness of RB molecules around their surfaces, hence difficult removal. The enthalpy values

Table 4 Thermodynamic parameters for the removal of RB on rice husk extracted silica

	C_0	Temperature (K)	Equilibrium constant	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (KJ/mol K)
RHSA	$C_i = 10$ (mg/L)	293	3.158	− 2.801	− 14.065	− 0.037
		300	5.502	− 4.253		
		308	1.846	− 1.570		
		318	2.063	− 1.914		
		333	2.111	− 2.069		
RHSO	$C_i = 10$ (mg/L)	293	0.782	0.600	− 3.159	− 0.011
		300	1.555	− 1.101		
		308	0.788	0.611		
		318	0.903	0.270		
		333	0.859	0.421		

 C_i = initial concentration

were also negative for the two samples, indicating that RB removal on rice husk silica is exothermic.

3.2.6 Influence of ionic strength on RB removal

The influence of ionic strength on RB removal using silica from open air and oven burning of RH was investigated for NaCl concentration of 0.05–2 mol/L and the results are given in Fig. 4f. The quantity of RB removed decreases with increasing ionic strength on the two tested adsorbents (decreasing from 84 to 46% with ionic strength of 0.00 to 2 M for RHSA and 60 to 41% for RHSO). The authors [27] also had similar results when methylene blue removed decreased from 81.5 to 14 mg/g when the ionic strength increased from 0.00 to 0.1 M using orange peel as an adsorbent. The presence of salts in solution blocks the active sites of the adsorbents thereby preventing the RB molecules from attaching to the surface, hence reducing the removal efficiency [27, 28] (Table 5).

3.2.7 Desorption of adsorbed RB

Desorption was performed by manually stirring with distilled water for about two minutes. The results are presented in Table 5. It is observed that there is strong correlation between contact time and the amount desorbed (91% of RB is desorbed from RHSA where adsorption was performed for 24 h against 65% when adsorption was performed for 5 min). This is due to the fact that with increase in contact time, more and more RB accumulates on adsorbent surface in a physical process. With shaking or stirring, most of the accumulated RB goes back into solution. The error factor at each time was equal to or less than 5% confirming the reproducibility of the desorption results. These results show that silica from rice husk can easily be regenerated thus serving as good adsorbent.

Table 5 Error analysis of desorption study

Time (min)	P1 (%)	P2 (%)	P3 (%)	P (%)	Delta (σ) (%)
5	65.83	65.63	64.89	65.45	0.50
10	80.62	80.72	80.74	80.69	0.06
20	84.79	84.68	83.98	84.48	0.44
40	88.78	88.26	87.88	88.30	0.45
60	88.94	88.38	88.04	88.45	0.45
1440	91.98	91.68	91.27	91.65	0.36

P1, P2 and P3 = desorption efficiencies for first, second and third desorption trials at time, t

P = average desorption efficiency at time t; Delta (σ) = error factor from the three desorption trials at time, t

4 Conclusion

Silica was extracted by HCl treatment followed by calcination at 700 °C of rice husk ash obtained by burning of the raw rice husk in open air and in a Muffle Furnace at 540 °C. The two silica samples abilities to remove Rhodamine B from aqueous solution were tested in this study. The silica produced using the two procedures yielded basically the same amount of silica; 89.84% for RHSA and 89.67% for RHSO. However, silica from the burning of the raw rice husk in the open air had a better Rhodamine removal efficiency (84% for RHSA and 60% for RHSO in 24 h of contact time). The silica from open air burning of RH removal efficiency decreases with increase RB initial concentration, but increases with silica obtained from oven (540 °C) burning of RH. Both adsorbents show significant RB removal efficiency with increase in their quantities (for RHSA, the increase was from 65% with 0.05 g to 98% with 0.5 g and for RHSO, the increase was from about 43% with 0.05 g to 81% with 0.5 g in 24 h). Removal efficiency also increases with increasing pH attaining maximum at pH of 7 for both adsorbents (71%

at pH 7 for RHSA and reducing to about 44% at pH of 10; 72% at pH of 7 for RHSA reducing to 38% at pH of 10). The removal efficiency was more favourable at 27 °C for the two adsorbents. The Freundlich isotherm best described the process for the two adsorbents indicating involvement of heterogeneous sites in the removal process. The removal process was exothermic for the two samples ($\Delta H^\circ < 0$), spontaneous for silica from open air burning ($\Delta G^\circ < 0$ at all the tested temperatures) and only spontaneous at 27 °C for silica obtained from oven (540 °C) burning ($\Delta G^\circ < 0$ at 27 °C and $\Delta G^\circ > 0$ at 20, 35, 45 and 60 °C). Pseudo-second order kinetic model also describes the removal process. The removal on the two adsorbents occurs by physical adsorption mechanism as revealed from calculated Dubinin–Radushkevich adsorption energies of 1.647 and 0.595 kJ/mol for the two adsorbents. Silica can easily be obtained from worldwide abundant biomass, rice husk and can effectively be used to treat effluents containing heavy molecular dyes such as Rhodamine B.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Human and animal rights Humans or animals were not involved in this research.

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