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Removal of Bisphenol-A from Aqueous Solution Using Rice Husk Nanosilica: Adsorption Kinetics, Equilibrium and Thermodynamic Studies

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Abstract

This study evaluates the adsorption of bisphenol-A (BPA) from aqueous solutions using nanosilica obtained from rice husk. Nanosilica (79 nm) was extracted from acid and thermal treated rice husk waste. The rice husk nanosilica (RHS) was fully characterized through X-Ray Diffraction Spectroscopy (XRD), Scanning Electron Microscopy (SEM), X-Ray Fluorescence Spectroscopy (XRF) and Fourier Transmittance Infrared Spectroscopy (FTIR). The spectroscopic analyses results revealed that the rice husk ash contains large fraction of amorphous silica. Batch adsorption experiments were carried out on BPA as a function of initial concentration, contact time, pH, adsorbent dosage and temperature. The maximum amount of BPA adsorbed was 4.267 mg/g with an optimum contact time of 45 min for 50 mg/L BPA solution at pH 8. The adsorption data were analyzed with adsorption isotherms and fitted best into the Langmuir model with R^2 value of 0.994. The adsorption process followed the pseudo second order kinetics and was exothermic while the negative value of Gibbs free energy obtained revealed that the process is feasible at lower temperature.

Keywords: *Bisphenol-A, adsorption, rice-husk, Isotherm, Silica.*

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Introduction

Pollutants are generally introduced into the environment through various human activities which usually affect both the fauna and Flora ecosystem. Bisphenol A (BPA) with a chemical formula $C_{15}H_{16}O_2$ is one of the most dangerous pollutant among the family of phenolic compounds. it is a non-biodegradable chemical and shows great resistant to chemical decomposition making it more dangerous to both human and aquatic animals [1]. It is a common plasticizer used in making plastic materials. BPA is an endocrine disrupting chemical which is often introduced into the environment through industrial effluents as well as improper discharge of household products. Low dosages of BPA can cause various health problems such as heart disease, diabetes type 2, abnormalities in liver enzymes, proliferation of prostate cancer as well as disorder of blood levels even at low doses [2, 3]. Therefore, there is a great need to remove this pollutant from the environment especially water bodies.

Among numerous methods that have been employed to remove pollutants from water bodies, adsorption stands out due to its simplicity, applicability and cost effectiveness [4-6]. Several researchers have utilized different agricultural waste as adsorbent to remove persistent organic pollutants in the environment such as rice husk [7], melon husk [8], walnut shell [9, 10], groundnut shells [11], sawdust [12], orange peels [13] and coconut husk [14]. Agricultural wastes are usually employed for the removal of BPA instead of the conventional methods that are very expensive, time consuming, do not ensure complete removal and involve the use of toxic reagents.

When rice husk turns to ash, it usually contains 87-97% silica [15, 16] and other constituents includes K_2O, Al_2O_3, CaO, MgO, Na_2O, Fe_2O_3 [17]. The industrial applications of rice husk ash are in the processing of steel, cement, refractory industry and construction industries [16]. Rice husk is an agricultural waste usually dumped on the land or running water, which contributes to environmental problem, therefore, the use of rice husk and its ash is considered an alternative solution to its disposal problem [18]. The objective of this study was to evaluate the adsorption of BPA from aqueous solutions using nanosilica obtained from rice husk and the characterization of the nanosilica by Scanning electron microscopy (SEM), Fourier Transmission InfraRed spectroscopy (FTIR). Thermodynamic and Kinetic studies were also done to evaluate the effectiveness of the adsorbent.

Experimental

The rice husk was obtained from a rice mill at a local market in Ilorin, North-Central Nigeria. Bisphenol A was obtained from Sigma Aldrich and was used without further purification. All other reagents used are of analytical grade which includes hydrochloric acid, sodium hydroxide and distilled water.

Preparation of the adsorbent

The rice husk was washed thoroughly with distilled water to remove dust, particles, sand and other soluble contaminants present. It was then dried in an oven at 110 ˚C for 12 h until the moisture was completely removed. The dried rice husk was then refluxed with hydrochloric acid for 90 min, cooled and kept for 24 h. The rice husk was then decanted and thoroughly washed with warm distilled water to remove all the acid and dried in an oven for 24 h at 110 ˚C. To obtain the rice husk ash, the sample was subjected to thermal treatment at 550 ˚C for 12 h until the sample turned to ash completely. The obtained sample was designated RHA [19].

Extraction of nanosilica from RHA

Nanosilica was obtained by refluxing of the RHA with 6.0 M HCl for 6 h and washed repeatedly using deionized water to neutrality. It was subsequently dissolved in 2.5 M sodium hydroxide by stirring. The pH of the solution was then adjusted to 8 by the addition of sulphuric acid. The precipitate nanosilica was washed repeatedly with warm, deionized water to make it alkali free and then dried at 50 °C for 48 h in the oven. The sample was designated RHS and was used as adsorbent.

Adsorption Studies

Batch adsorption experiments were conducted to study the removal of BPA from an aqueous solution and to determine the optimum condition for its removal. This was done by introducing known concentration (50 mg/L) of BPA solution (pH 7) into a series of 25 ml Pyrex conical flask and known amount of RHS (0.2 g) was added and shaken in the water bath rotary shaker for specific time (45 min) at known temperature (303 K). Specifically, the effect of initial concentration of BPA on the adsorption process was studied using 2 to 100 mg/L BPA solutions. The equilibrium time was determined by performing the experiment within the time range of 5 to 120 minutes while the optimum pH was determined from pH 2–12. The concentrations of the BPA solutions after the adsorption process were determined with UV spectrophotometer at 290 nm wavelength. The amounts of BPA retained in the adsorbent phase were calculated using equation 1 [20].

$$q_e = \frac{(C_o - C_e)V}{M} \qquad (1)$$

Where C_o is the initial BPA concentration (mg/L), C_e is the equilibrium BPA concentration (mg/L), V is the volume of solution (25 ml) and M is the mass of the adsorbent (mg).

The experimental data were subjected to three adsorption isotherm models namely Langmuir, Freundlich and Temkin isotherm. For the Langmuir Adsorption Isotherm which describes a monolayer adsorption, a plot of Ce/qe against Ce was obtained according to equation 2 [21].

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \quad (2)$$

The Langmuir constants q_{max} and K_L are related to the capacity and energy of adsorption, respectively and were obtained from the slope and intercept of the plot respectively.

Freundlich adsorption isotherm plot which is associated with heterogenous behaviour of the adsorbent surface was obtained using the linearized equation shown in equation 3.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

K_f and n are Freundlich isotherm constants which are related to the capacity and intensity of the adsorption respectively. The values of K_f and n were obtained from slope and intercept of the plots of $\ln q_e$ against $\ln C_e$. The model is applicable to the adsorption on heterogeneous surfaces by a uniform energy distribution and reversible adsorption [21].

Temkin adsorption isotherm plot was obtained using equation 4.

$$q_e = B\ln A + B\ln C_e \quad (4)$$

A and B are Temkin isotherm constants related to adsorption efficiency (dm^3/mmol) and energy of adsorption respectively. The quantity adsorbed q_e was plotted against $\ln C_e$ and the constants were determined from the slope and intercept [21].

The kinetic rate of the adsorption process was studied by fitting the adsorption data into Pseudo first-order, pseudo second-order and Elovich kinetic models which are given in linearized form in equations 5, 6 and 7 respectively.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

$$q_t = \frac{1}{\propto} \ln(\propto B) + \frac{1}{\propto} lnt \quad (7)$$

Where k_1 and k_2 are rate constants of adsorption, q_t is adsorption capacity at time t, q_e is the adsorption capacity at equilibrium condition. α and β are Elovich constants related to the initial adsorption rate and the desorption constant during each experiment at time t respectively [22].

Results and discussion

Phase Analysis by X-ray Diffraction Spectroscopy

X-Ray diffractometer (PW 3050/60 Goniometer) was used to examine the phase composition of the adsorbent and the crystallographic nature of the prepared adsorbent. The result is presented in Figure 1. The diffractogram showed a strong broad peak between 18° and 30° (2Θ). This peak is associated to the amorphous nature of silica. The mean particle size was calculated to be 79 nm using the Sherrer's formula (equation 8).

$$D = \frac{0.94\lambda}{\beta Cos\theta} \qquad (8)$$

D represents the average crystallite size, λ is the X-ray wavelength, β is the line broadening in radians and θ is the Bragg angle

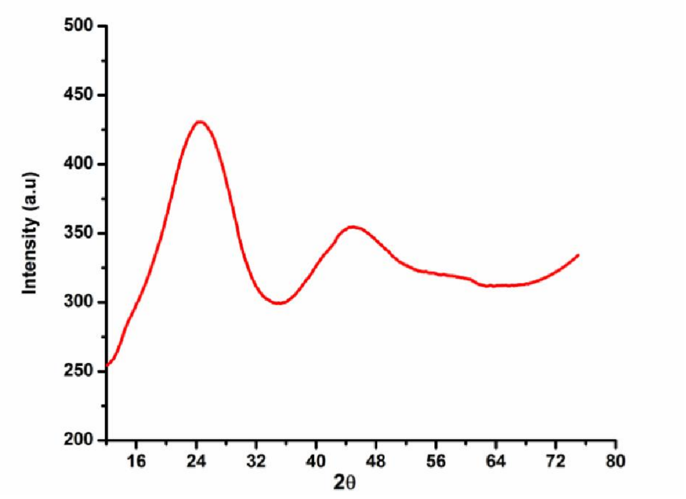

Figure 1. XRD diffractogram of RHS.

X-ray Fluorescence spectroscopy

The elemental composition of the sample was determined by X-ray fluorescence spectroscopy using Kevex Fisons Analyst 771. The XRF analysis showed that the RHS contains silica in high amount (>94%). This high amount is similar to what has been previously documented in the literature [16]. Other metal oxides such as that of Phosphorus (6.67%), Potassium (3.73%)and Calcium (1.04%) are also present but in trace amounts (Figure 2).

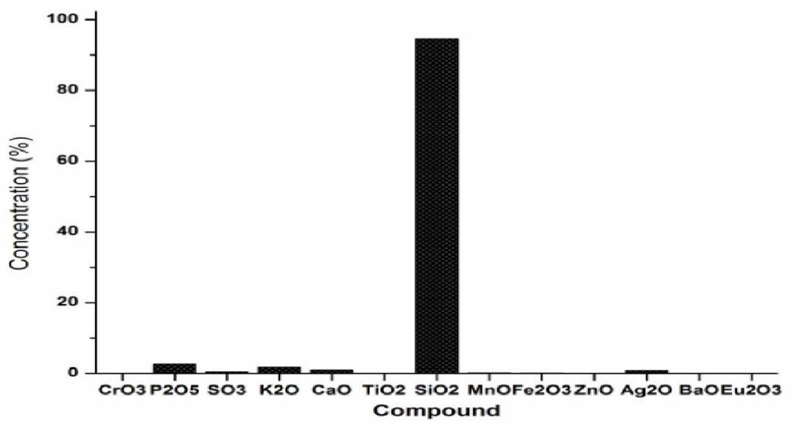

Figure 2. XRF results of the RHS.

SEM Analysis of RHS

The surface morphology of the sample was observed using Carl Zeiss Ultra plus field emission electron microscope. The scanning electron microscopy photograph of the sample is shown in Figure 3. The SEM micrograph revealed an irregular rock-like shape with pores within. This revealed that the material has a good potential as an adsorbent.

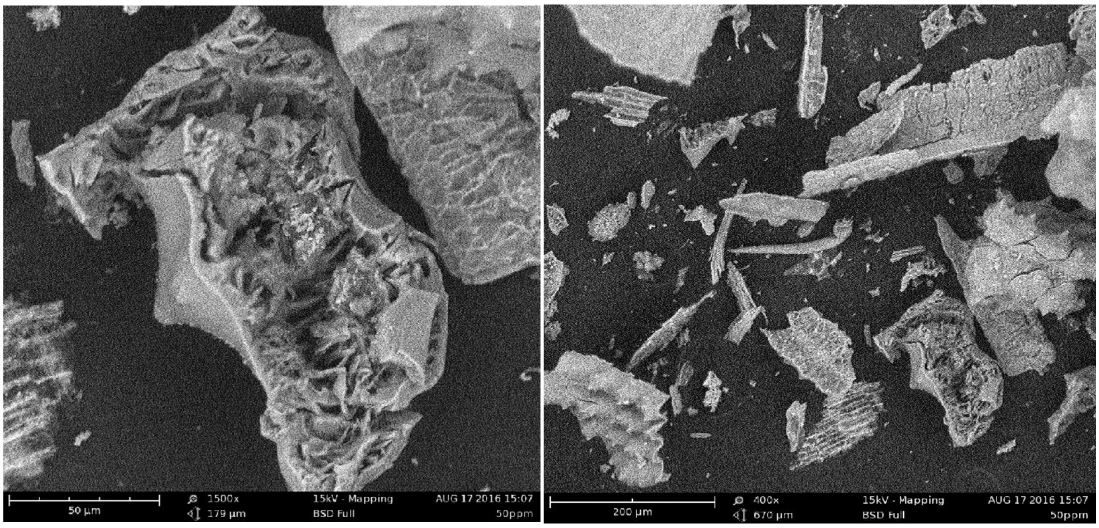

Figure 3. SEM micrograph of RHS with different magnifications.

FTIR Analysis of RHS

The FTIR analysis was done to identify the major functional groups present in the sample and this was carried out using Shimadzu 8400 FTIR spectroscope. The FTIR spectrum is shown in figure 4. The broad band at 3332.2 cm^{-1} has been attributed to silanol OH and adsorbed water while bands at 1051.1 and 663.5 cm^{-1} are related to the typical Si-O-Si bond stretching vibrations. Absence of peaks between 2800 and 3000 cm^{-1} confirmed the absence of original organic compounds in the sample after preparation [7, 19].

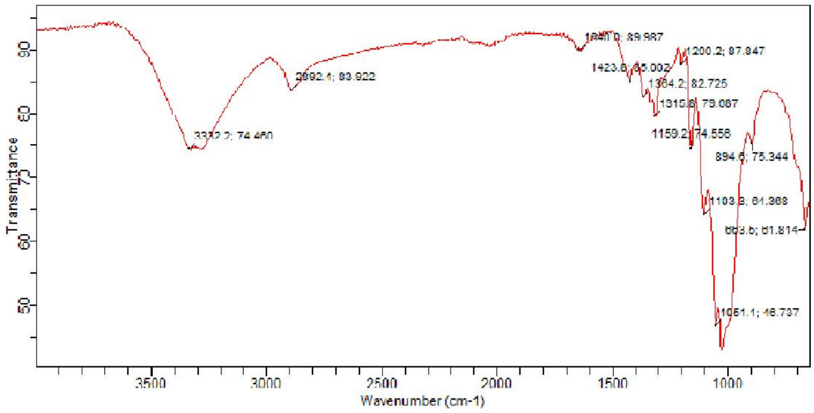

Figure 4. FTIR spectra of RHS.

Adsorption Studies

Effect of Initial concentration and Isotherms Modelling

An important factor that affects the adsorption kinetics is the initial concentration of the adsorbate. It was observed that the quantity of BPA molecules adsorbed increased with increase in initial concentration of BPA up to an initial concetration of 50 mg/L (Figure 5) with quantity adsorbed (qe) of 4.138 mg/g. This is as a result of large driving force provided by the higher BPA concentration, which could defeat the mass transfer resistance between the aqueous and solid phases [23]. At the equilibrium, it can be deduced that the adsorbent have taken as much BPA molecules as it can take and thereby became saturated. Thatchaphong and Gyuhave reported similar trend in the adsorption of Bisphenol-A (BPA) [24]. It is interesting to note that the quantity of BPA adsorbed by the RHS in this study compares well with previously used agricultural wastes that have been reported. For instance Lazim et al reported adsorption capacities of 4.308 mg/g, 4.178 mg/g and 4.159 mg/g for coir pith, durian peel and coconut shell respectively [25]. Similarly, Zhou et al also reported sorption capacity of 1.71 mg/g for modified peat under optimum condition [26].

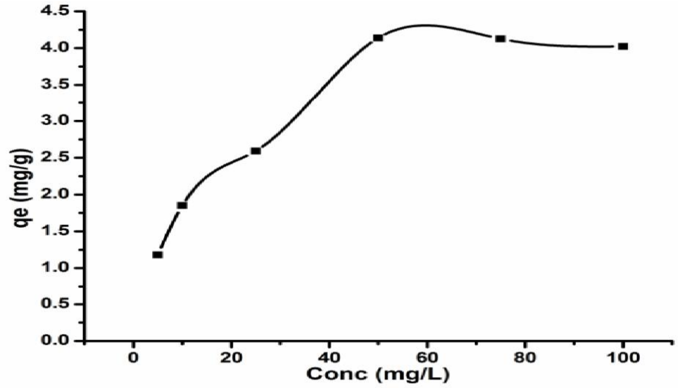

Figure 5. Effect of initial concentration on the sorption of BPA onto RHS (pH 7; 60 min; 0.2 g of RHS; at 303K).

The experimental data were subjected to three adsorption isotherm models namely Langmuir, Freundlich and Temkin isotherm. The plots are presented in Figures 6 (a-c) while the isotherm parameters obtained from the plot are presented in Table 1. The extent of the fitness of data with an isotherm model is determined by the regression value (R^2) of the plot. The experimental data fit best on Langmuir isotherm model with R^2 value of 0.997 (Figure 6a) which suggest a monolayer coverage of the adsorbent surface. The Langmuir constant R_L value of 0.064 which was less than 1 showed that adsorption process is favorable [27]. The Freundlich constant 'n' which lies between 1 and 10 further confirms that the adsorption is favorable. The Temkin isotherm plot has the least regression value of 0.903 (Figure 6c).

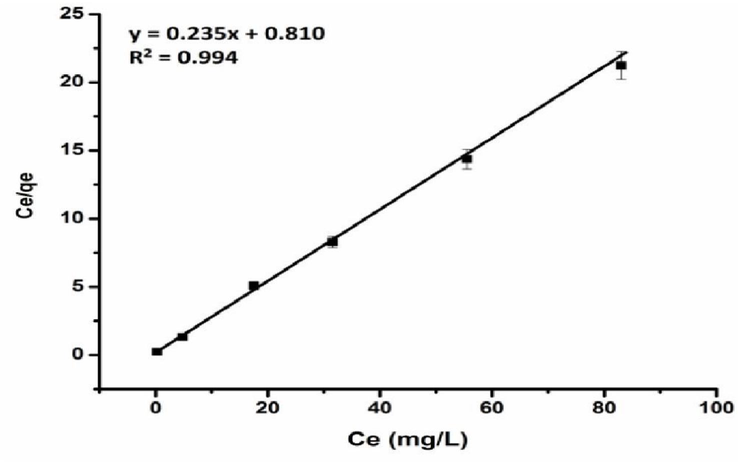

Figure 6a. Langmuir isotherm plot for the sorption of BPA onto RHS.

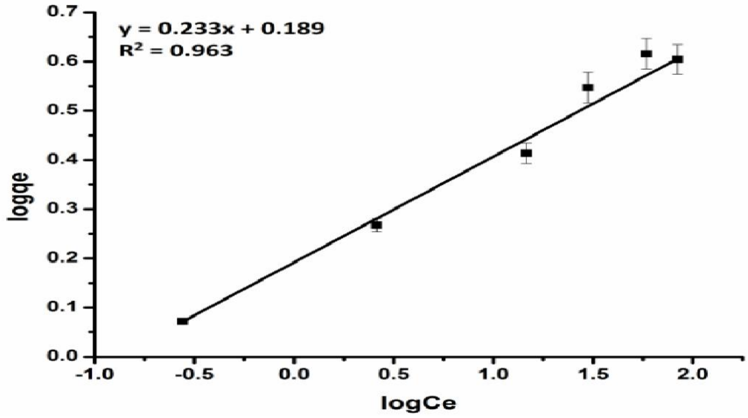

Figure 6b. Freundlich isotherm plot for the sorption of BPA onto RHS.

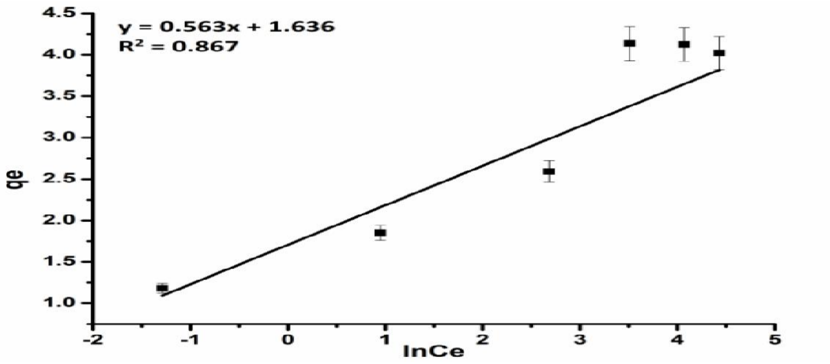

Figure 6c. Temkin isotherm plot for the sorption of BPA onto RHS.

Table 1. Isotherms Parameters for the sorption of BPA onto RHS.

Isotherm	Parameters	Values
Langmuir	Q_0(mg/g)	4.246
	K_L	0.291
	R_L	0.064
	R^2	0.994
Freundlich	K_f	1.545
	n	4.292
	R^2	0.963
Temkin	b_T	0.563
	A_T	18.281
	R^2	0.867

Adsorption Kinetics

The effect of contact time on the adsorption of BPA onto RHS was studied with 50 mg/L concentration of BPA (pH 7) within the time range of 5 to 120 min using 0.2 g of RHS. The result revealed that the uptake of BPA molecules was rapid and the quantity adsorbed increased with increase in time but reaches an equilibrium at 45 min (Figure 7). The higher removal efficiency at the beginning of the process can be attributed to the availability of an abundance of adsorption sites. As the contact time prolongs, the available adsorption sites diminish as a result of saturation [28].

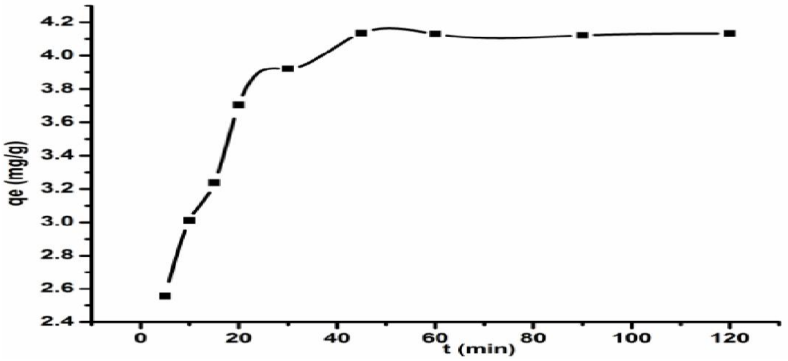

Figure 7. Effect of contact time on the sorption of BPA onto RHS (50 mg/L BPA; pH 7; 0.2 g dose; 303K).

The Pseudo first order, pseudo second order and Elovich kinetics plots are presented in Figures 8a, 8b and 8c respectively while the isotherm constants calculated from the intercept and slope of the plots are shown in Table 2. The experimental data fit the pseudo second order kinetics best with R^2 value of 0.999. Interestingly, the experimental quantity adsorbed (4.138mg/g) was found to be very close to the calculated quantity adsorbed (4.292 mg/g) and this revealed that the process can best be described by pseudo-second order kinetics model. This finding is similar to those reported earlier in the literature [29].

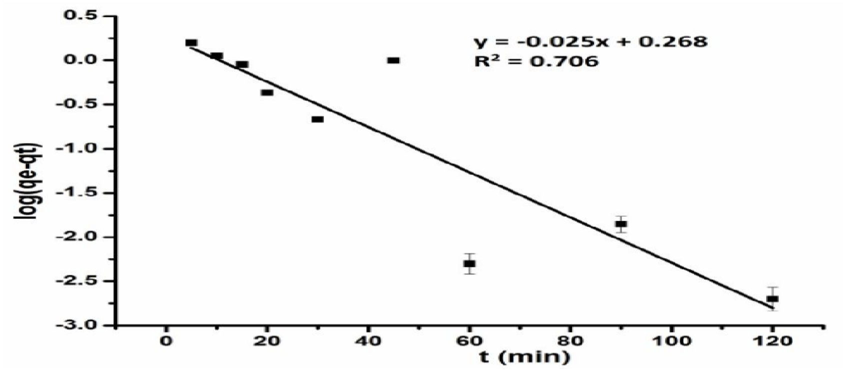

Figure 8a. Pseudo first order kinetics plot for the sorption of BPA onto RHS.

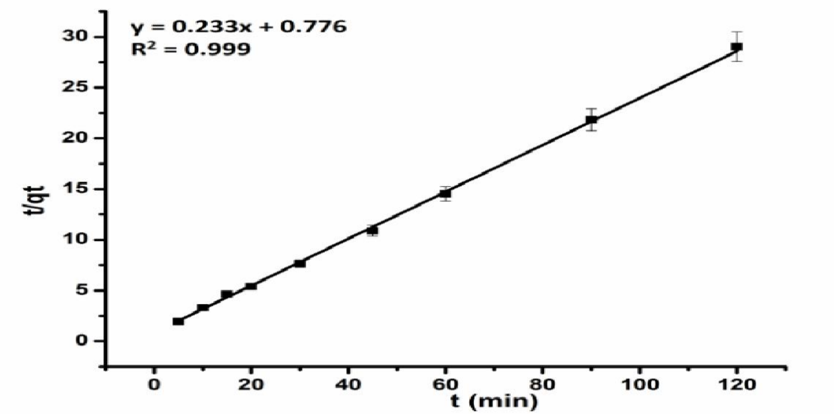

Figure 8b. Pseudo second order kinetics plot for the sorption of BPA onto RHS.

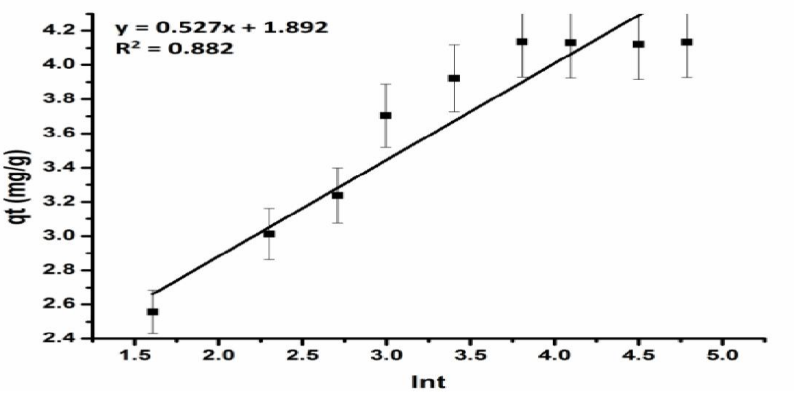

Figure 8c. Elovich kinetics plot for the sorption of BPA onto RHS.

Table 2. Kinetics parametersfor the sorption of BPA onto RHS.

Kinetics model	Parameters	Values
Pseudo-first order	q_e	1.832
	k_1	0.058
	R^2	0.806
Pseudo-second order	q_e	4.292
	k_2	0.070
	R^2	0.999
Elovich	α	1.898
	β	19.093
	R^2	0.883

Thermodynamic studies

The adsorption process was investigated at temperatures of 303, 308, 313 and 318 K. The result revealed a decrease in the quantity of BPA adsorbed onto RHS with increase in temperature as shown in Figure 9. This shows that the process was exothermic and unfavorable with higher temperature [30]. This was further comfirmed by thermodynamics studies of the adsorption process.

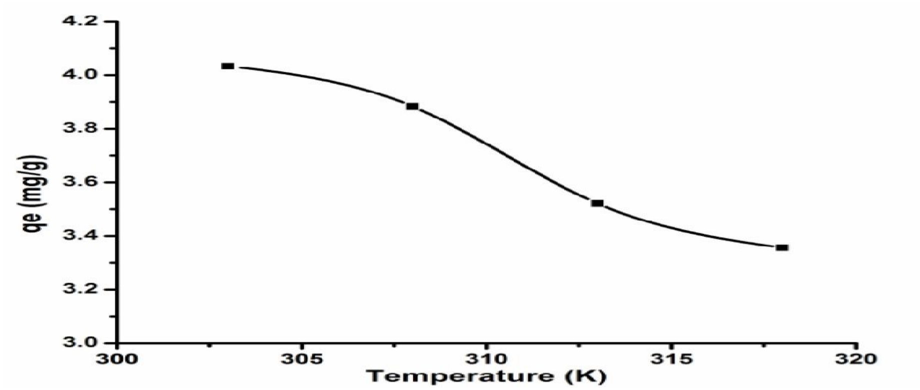

Figure 9. Effect of temperature on the sorption of BPA onto RHS (50 mg/L BPA; pH 7; 0.2 g dose; 45 min).

The plot of the thermodynamic studies is presented in Figure 10. The thermodynamic parameters give indications about internal energy changes during the adsorption process. From the results, the enthalpy change ΔH was found to be -15348 $Jmol^{-1}$. The negative value of ΔH indicated that the process was exothermic and this was evident in the decrease of adsorption efficiency with increase in temperature. The Gibbs free energy ΔG was found to be negative at lower temperatures (-285 $Jmol^{-1}$ at 303 K and 37 $Jmol^{-1}$ at 308 K) which revealed that at these temperatures the adsorption process is feasible and spontaneous. Similar observations have been reported by Radu et al [27].

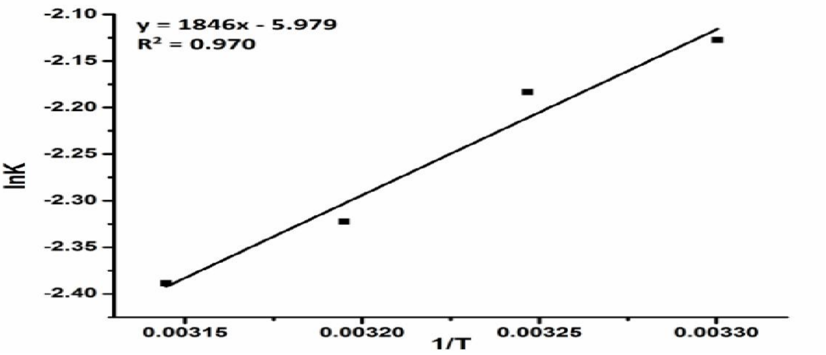

Figure 10. Van't Hoff Equation Plot for the sorption BPA onto RHS.

Effect of pH on the adsorption process

The solution pH plays a pivoted role in the adsorption process as revealed in Figure 11. In the acidic pH range, the adsorption capacity gradually increased while in basic pH range, the adsorption capacity decreased dramatically (pH>8). This severe reduction could be described by the pKa of BPA (9.6–10.2). In aqueous solutions, the adsorbates are in their molecular form at pH lower than pKa and will lose their protons at pH above pKa [24].

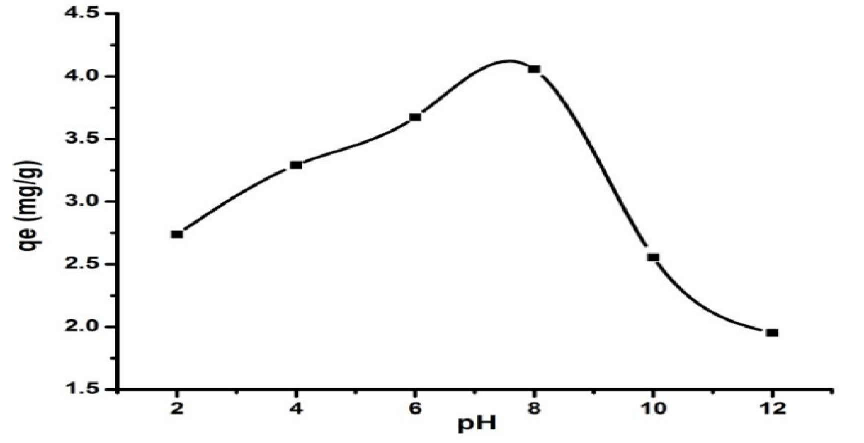

Figure 11. Effect of pH on the sorption of BPA onto RHS (50 mg/ L of BPA; 0.2 g dose; 45 min; 303 K).

Conclusion

This research showed that low cost adsorbent rich in silica content can be obtained from Rice husk. The adsorbent is efficient for the removal of Bisphenol A from aqueous solution. The adsorption process is well described by the Langmuir isotherm which revealed monolayer coverage of the adsorbent surface. The negative values of ΔG obtained from the thermodynamic studies indicated the spontaneity of the adsorption of BPA and the negative value of ΔH showed that the process is exothermic. Therefore, rice husk ash can serve as a good adsorbent for the removal of BPA from waste water.

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