KINETICS AND THERMODYNAMIC STUDIES ON SORPTION POTENTIAL OF HYBRID ADSORBENT PRODUCED FROM SNAIL SHELL AND RICE HUSK

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ABSTRACT

The present study deals with the application of Snail Shell and Rice Husk (RH-SS), an agricultural and animal waste, for the adsorptive removal of phenol from pharmaceutical effluent. This paper incorporates the effects of time, dose, temperature, concentration, and pH on the efficient removal of phenol from pharmaceutical Effluent. Batch kinetic and isotherm studies have also been performed to understand the ability of the adsorbents. The adsorption behavior of the Phenol has been studied using Freundlich and Langmuir adsorption isotherm models. The monolayer adsorption capacity determined from the Langmuir adsorption equation has been found as 149.25 mg/g. Kinetic measurements suggest the involvement of pseudo-second-order kinetics in adsorptions. Adsorption of phenol on adsorbents was found to increase on decreasing phenol effluent concentration, increasing pH up to 5 and increasing effluent temperature up to 35°C. Overall, the present findings suggest that the composite of Rice Husk and Snail Shell (RH-SS) is environmentally friendly, efficient and low-cost biosorbent which is useful for the removal of Phenol from waste water.

Keywords: Rice Husk and Snail Shell Composite; Adsorption; Phenol; Kinetics models; Isotherms models.

1.0 INTRODUCTION

In most developing countries, most industries dispose their effluents without treatment. These industrial effluents have a hazard effects on water, habitat quality and complex effects on flowing waters (ethan et al., 2003). There seem to be little or no control over the way pharmaceutical waste are disposed, some are disposed directly into the lagoon or gutters without treatment and this eventually seep into the ground and surface waters. Wastewater with organic pollutants contains large quantities of suspended solids which reduce the light available to photosynthetic organisms and, on settling out, alter the characteristics of the river bed, rendering it an unsuitable habitat for many invertebrates. Organic pollutants include pesticides, fertilizers, hydrocarbons, phenols, plasticizers, biphenyls, detergents, oils, greases, proteins and carbohydrates (Ali et al., 2012).

Phenol is one of the crucial pollutants released from the wastewater originating from the chemical industries like pulp and paper, gas and coke manufacturing, tanning, textile, plastics, rubber, pharmaceutical industries, ferrous industries and petroleum refinery (Polat, etal., 2006). The uncontrollable discharge of phenol into the environment has caused adverse effects on public health and environment. The allowable concentration of phenol in surface water should be less than 1.0μg/L according to The United States Environmental Protection Agency (USEPA) (Chung, etal., 2003). Compounds containing phenols at very low concentrations are very harmful due to their irritating, toxic and carcinogenic properties, thus causing damage to the eyes and the skin tissue, inhalation, or ingestion, can damage the respiratory and gastro intestinal tracts, and in most cases

can lead to gene mutation, (Damjanovi, etal., 2010). According to the statistics from the United States Environmental Protection Agency, Phenol is designated as the 11th of the 126 priority pollutants, (Caturla, etal., 1988). Therefore, it is absolutely necessary to treat the phenol from industrial effluents especially the pharmaceutical wastewater before discharging into the water stream. Efficient techniques for the treatment of pharmaceutical effluents containing phenols have drawn significant interest. A number of methods such as coagulation, filtration with coagulation, precipitation, ozonation, ion exchange, reverse osmosis and advanced oxidation processes have been used for the removal of phenolic compounds as pollutants from wastewater, (Girish etal., 2012). These methods have been found to be limited, since they often involve high capital and operational costs. Among the possible techniques for water treatments, the adsorption process on activated carbon is the most widely used and the most effective adsorbent in treating phenolic wastewaters. It has been demonstrated that activated carbon can be formed from any carbonaceous solid precursor material. The required physical and chemical properties attained in the final activated carbon depends on the choice of the starting material. A wide range of diverse materials have been investigated as potential adsorbents for phenol removal in wastewater treatment. The prominent among them comprises silica gel, activated alumina and zeolites. Basically the disadvantage of the above materials is high cost and being nonrenewable in nature, which is a major economic consideration. This has ignited a growing research interest in the production of activated carbon from locally available agricultural materials, especially for application concerning wastewater treatment, (Girish, etal., 2013). According to Mohd Din, etal. (2009) the biomass obtained from these materials is cheaper, renewable, and abundantly available. A vast number of agricultural materials have been used as adsorbents for the removal of phenolic compounds from wastewater. These included banana peel (Achak, etal., 2009), palm seed coat (Rengaraj, etal., 2002), oil palm empty fruit bunch (Alam, etal., 2009). Black stone cherries, (Arana, etal., 2010) vetiver roots, (Altenor, etal., 2013) sugarcane bagasse, (Karunarathne, etal., 2013) and Luffa cylindrical, (Abdelwahab, etal., 2013). All these materials provide an alternative to conventional sources, which are prospective raw materials for activated carbon production. Also, using these agricultural materials for adsorbent preparation brings the solution to the problem of handling wastes, (Mohd Din, etal., 2009). An attempt have been made to produce adsorbent from rice husk and snail shell by the chemical and thermal treatment process. In this study, the potential of chemically and thermally treated carbon from rice husk and snail shell was studied for the removal of phenol from Pharmaceutical waste water. A detailed study of the adsorption of phenol on chemically treated Rice Husk and Snail Shell material was reported. The research addresses the batch experiments carried out to study the effect of process variables such as pH, adsorbent dosage, initial phenol concentrations, and temperature on adsorption. The optimum experimental conditions were determined and thermodynamic studies were carried out to determine the nature of the adsorption process. From the literature, it is understood that the adsorption of phenol can be by three possible mechanisms: The hydrogen bonding formation, the π-π dispersion interaction, and the electron donor-acceptor complex mechanism (Moreno-Castilla, 2004). Therefore, in order to understand the above mechanisms, different adsorption isotherms (Langmuir,Freundlich,) and kinetic models (pseudo-first, pseudo-second-order kinetics and Elovich kinetic plot)were investigated to find out the most suitable models describing the experimental findings and the adsorbate-adsorbent interactions.

2.0 MATERIALS AND METHOD

2.1 Collection and Preservation of Pharmaceutical Effluent.

The Pharmaceutical effluent sample used for this study was collected from the discharge unit of pharmaceutical industry in Awka, Anambra State of Nigeria, and preserved using concentrated sulphuric acid

2.2 Adsorbent

The snail shell (SS) and Rice Husk (RH) that was used for this study were obtained as wastes from Eke-Awka market, Awka, Anambra State and Anam in Ayamelum, Local Government area of Anambra State, Nigeria respectively. The snail shell was washed with distilled water properly to remove sand and dirt. The rice husk was sieved to remove dirt and unnecessary materials. Both raw materials were oven dried at 80°C for 4hours to remove excess moisture. The samples of both snail shell and Rice husk collected after drying was stored separately in an air tight container for further use.

2.2.1 Thermal Activation of RH-SS.

According to lekan et al., (2019), a mixture of snail shell and Rice Husk was prepared at equal ratio with the addition of 150ml distilled water in a beaker to form suspension. The mixture was filtered after being homogenized on a hot plate for 2 hours while the residue was placed in an oven to eliminate excess water for 6 hours at a temperature of 105^{0}C. The mixture was calcined at 681.10^{0}C for 3hours in a muffle furnace to obtain the composite adsorbent.

2.2.2 Chemical Activation of RH-SS

According to Mishra et al., (2007), the carbonized RH-SS adsorbent was mixed with 3 molar concentration of othor-phosphoric acid (3M H$_3$PO$_4$), in a 1:1 ratio on volume basis. The adsorbent was thoroughly mixed with the chemical overnight and then the slurry formed was washed with sufficient distilled water until pH comes to 7, and then it was dried at 105$\circ$C for 6h in an oven to remove the excess moisture, and then stored for further studies.

2.3 Batch Adsorption Studies

In order to understand the uptake behavior of phenols from pharmaceutical effluents, a number of batch studies have been conducted to investigate the effect of adsorbent dose and contact time, pH, phenol concentration in the pharmaceutical effluent, and pharmaceutical effluent temperature. For these studies, wastewater of various concentrations of phenol was prepared from the stock solution and kept separately in glass stoppered conical flasks. Then suitable doses of adsorbent were added to the wastewater. The system is placed on top of hot plate and stirred continuously at a constant rate with the help of magnetic stirrer at different temperatures and different contact time. The suspension is filtered through Whatman No. 1 filter paper and the filtrate is analyzed to evaluate the concentration of phenols in the treated wastewater by using UV spectrophotometer. The absorbance of the supernatants was determined by UV-VIS spectrophotometer at 270nm wavelength. The amount of phenol adsorbed at equilibrium (q$_e$) and at time, t (q$_t$) was calculated using Eqs. 1 and 2 respectively. The percentage removal of phenol from the pharmaceutical effluent was calculated using Eq. 3.

$$q_e = \frac{(c_o - c_e)v}{w} \qquad\qquad 1$$

$$q_t = \frac{(c_o - c_t)v}{w} \qquad\qquad 2$$

where q$_e$ are the equilibrium adsorption capacity per gram of dry weight of the adsorbent, (mg/g):   qt is the adsorption capacity at time, t (mg/g): C$_0$ is the initial concentration of phenol in the solution (mg/l); C$_e$ is the final or equilibrium concentration of phenol in the solution (mg/l); C$_t$ is the amount of phenol adsorbed at time, t(mg/l); V is the volume of the solution (1); and W is the dry weight of adsorbent (g). The percentage phenol removal RE (%) was calculated using Eq. 3 (Akpomie et al., 2012).

$$RE\ (\%) = \frac{(c_o - c_t)v}{c_0} \qquad x\ 100$$

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3.0 RESULTS AND DISCUSSION

The results obtained from the above studies have been discussed with plausible explanations as follows:

Table 1: Characterization result of RH-SS

Adsorbents	Moisture content (%)	Surface area (cm^2)
RH-SS	2.9	95.7

3.1 Scanning Electron Microscopy Result

The SEM micrographs for the absorbent is presented in plates 1-2. The surface morphologies of the used and unused adsorbent (RH-SS) is obtained from the scanning electron microscopy (SEM). The SEM image of the unused adsorbent (RH-SS), indicated coarse and loosely packed structures, with some well-formed flakes, irregular and hexagonal edges. Large and well-developed pores were clearly found on the surface of the RH-SS before adsorption. This might be due to the influence of impregnation with othor phosphoric acid during chemical activation of the adsorbents. Pore development in the adsorbent during thermal and chemical activation was also important as this enhanced the surface area and pore volume of the various adsorbent. But the well-developed pores on the prepared chemically activated RH-SS composite adsorbent could be the main factor that led to the high phenol uptake in this study. There were also marked closure in the interstitial spaces in the used RH-SS in plate 2. This could be due to adsorbed phenol that filled some of the void spaces present in unused adsorbents. Chemical activation produced a structural defect in the adsorbents by promoting chemical reaction that opens the pores spaces within the adsorbents thereby increasing the pore volumes and adsorbents surface area which in turn favourably affects the adsorption rates.
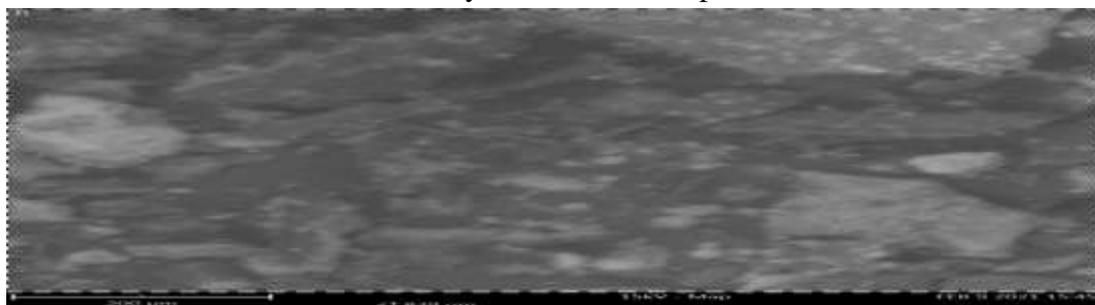
Plate 1. SEM of RH-SS before adsorption
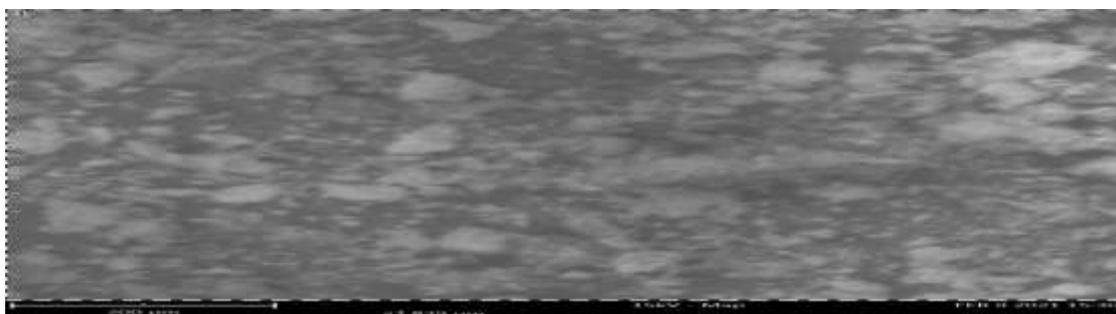
Plate 2. SEM of RH-SS after adsorption

3.2 Fourier Transform Infrared Result

The FTIR spectra of RH-SS before and after phenol sorption were used to determine the vibrational frequency changes in the functional groups of the adsorbents. The infra-red (IR) spectra of the adsorbent sample was recorded over the spectra range of 650-4000cm^{-1}. Plates 3-4. Present the IR Spectra of the used and unused adsorbent. The characteristic peak on RH-SS before adsorption appeared at 2113.4, 3630.4, 3377.0, 1561.8

and 872cm^{-1}. The IR spectra of used RH-SS showed disappearance of some peaks, while there were marked shift in some peaks. This may be as a result of the interaction of the functional groups during adsorption. This shift may be attributed to uptake of phenol by RH-SS (Hajjaji et al., 2001). Some band remained unchanged which indicates that they did not partake in the adsorption process as shown in plates 4.
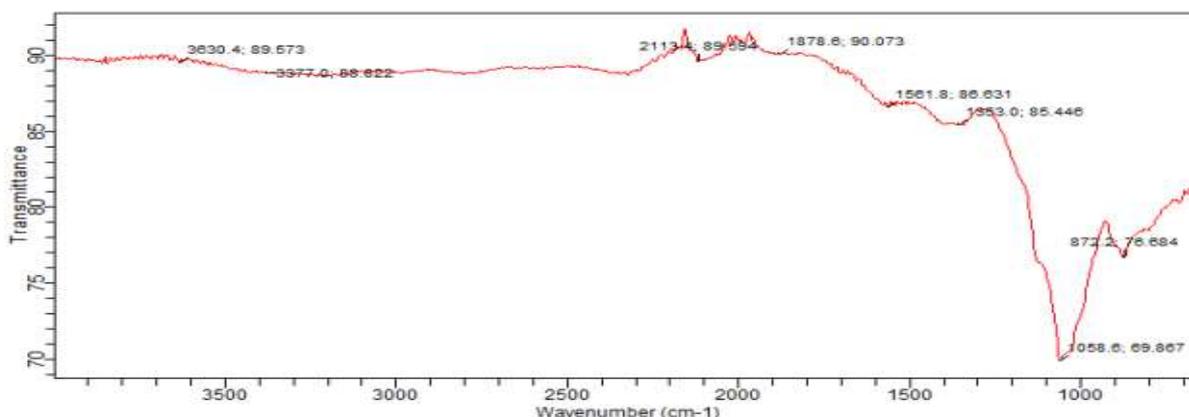
Plate 3. FTIR spectra of RH-SS before adsorption
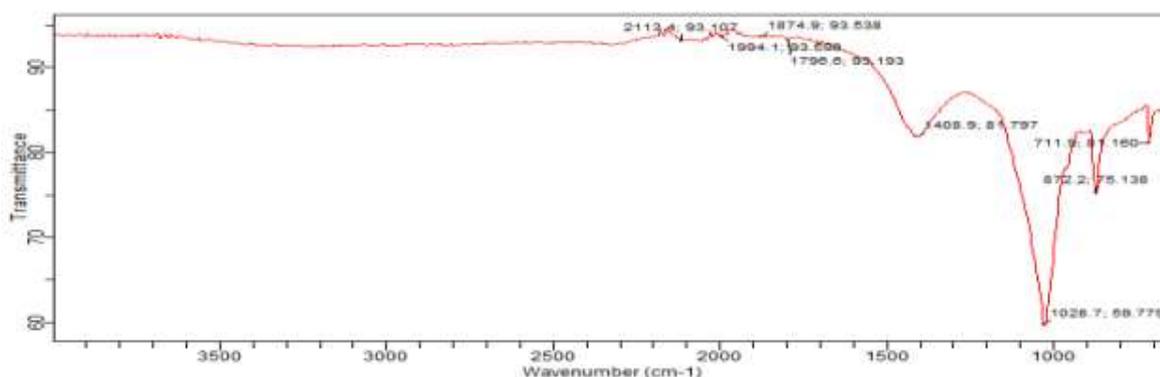
Plate 4. FTIR spectra of RH-SS after adsorption

3.3 Influence of Adsorbent Dosage and Contact Time

The optimum adsorbent dosage is a key parameter, which affects the amount of adsorbed adsorbate, (Malihe et al., 2020). The influence of adsorbent dosage on the adsorptive uptake of phenol onto adsorbent RH-SS composite was studied at the optimum condition of 35^{0}C, 35mg/l and pH of 5 for pharmaceutical effluent temperature, concentration and pH respectively. The results are presented in figure 1. The graph showed that the removal of phenol increased with increase in the adsorbent dosage. From figure 1 the maximum percentage removals of phenol was 97.58%

The higher removal efficiency of RH–SS composite could be due to the modification of the binding site by mixing the individual adsorbent at an equal ratio thus improving their adsorptive strength and capacity. Generally, the increase in percentage removal efficiency with increase in dosage was expected, because as the adsorbents dose increased, the number of active sites for binding phenol molecules on the adsorbent increases and thus more phenol was attached to their surface. However, after a certain adsorbent dosage, the adsorption capacity remains constant. This constant is generally due to the presence of a large number of accessible surface–active groups compared to the adsorbate amount. This is in agreement with Malihe et al., (2020) and Siboni et al., (2013).

Also, the results obtained in various batch studies showed that increase in contact time leads to increase in percentage removal of phenol in all cases of adsorbents. Initially there was fast uptake of phenol by RH-SS.

But after the first 35 min, the removal efficiency of phenol was observed to remain almost unchanged up to 55min. The initial rapid phase could be attributed to the availability of more adsorption sites at early stage of the adsorption process. Similar findings were also reported in previous studies by Hameed eta l. (2008).
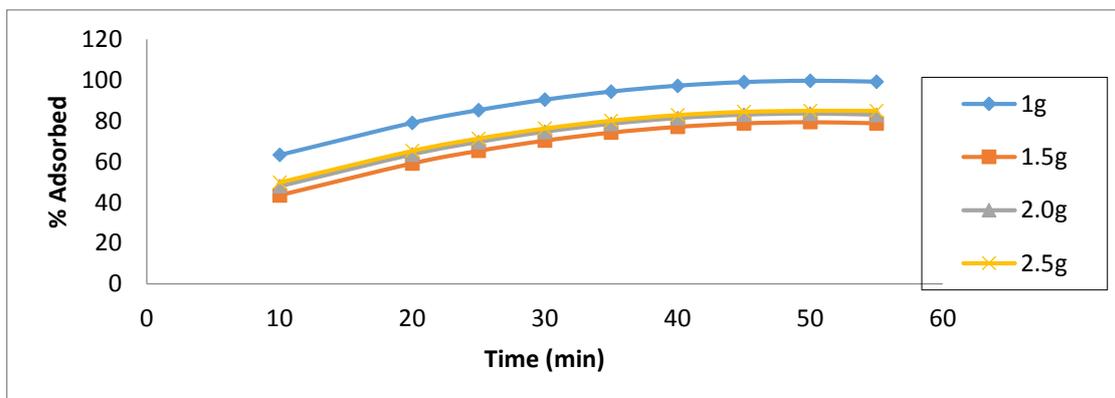
Figure 4.1 Influence of Adsorbent (RH) Dosage and Contact Time

3.4 Influence of Pharmaceutical Effluent Temperature on Phenol Adsorptive Rate

The influence of temperature on the adsorptive uptake of phenol onto RH-SS was investigated while keeping the other influencing parameters constant at pharmaceutical effluent pH of 5, adsorbent dosage of 1g, and pharmaceutical effluent concentration of 35 mg/l. Figure 2. Shows that the percentage phenol adsorbed decreased at higher pharmaceutical effluent temperature. The maximum adsorption rate took place at 35^0C pharmaceutical effluent temperature as shown in figure 2.The decrease in adsorption at higher temperature may be partly due to the weakening of adsorptive forces between the active sites of the adsorbent and phenol, and party due to the enhancement of the thermal energies of the adsorbate, thus making the attractive forces between the adsorbent and phenol insufficient to retain the adsorbed molecules at the binding site. (Mota and Lyubchik, 2008). An increase of adsorption capacity of phenol with decrease in temperature suggest that the process is exothermic, in this case as the temperature increases, the favourable intermolecular forces between adsorbate and adsorbent are much weaker than those between the adsorbate and solvent. In similar studies by lekan et al., (2019), the results also showed that phenol uptake was favoured at lower temperature and therefore was an exothermic process.

Due to the exothermicity of the adsorption process the forces holding the phenol on the surface of the adsorbents were physical in nature or physicosorption. This arose due to the vander waals forces between the non-reacting molecules. At lower temperatures the molecules were effectively bonded together to the surface of the adsorbent and the stabilization of phenol was maximum. (Hameed etal., 2007).
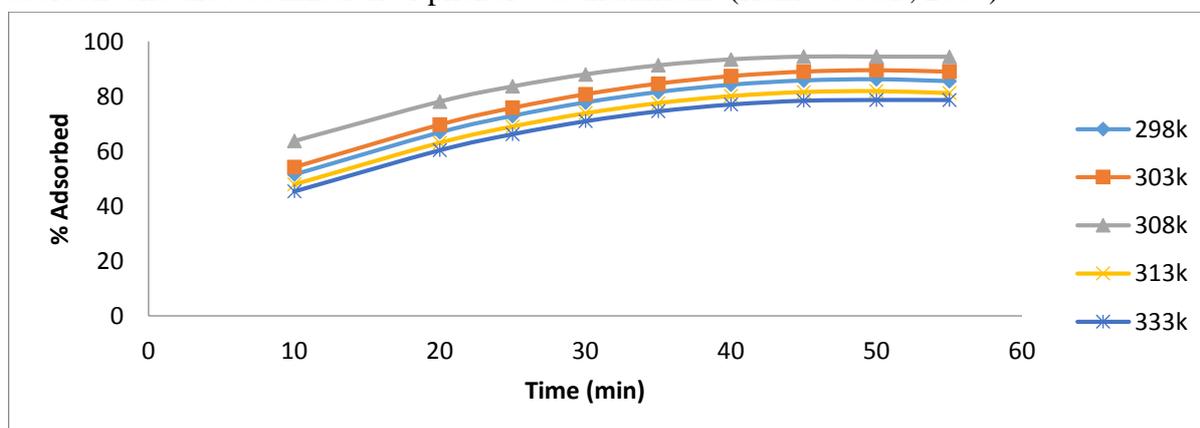
Figure 2. Influence of pharmaceutical effluent temperature on RH-SS

3.5 Influence of Pharmaceutical Effluent pH

The influence of pharmaceutical effluent pH on the adsorptive uptake of phenol onto RH–SS was studied at the optimum conditions: pharmaceutical effluent temperature (35^0C), adsorbent dosage of 1g for all adsorbents, and pharmaceutical effluent concentration of 35mg/l. the results are shown in figure 3. The phenol uptake efficiency at optimum contact time of 35mins was observed to be highest at pH of 5 (87.79%), but decreased to 67.79% and 52.19% at pH of 10 and 12 respectively.

The pH dependence of phenol adsorption can largely be related to the type and ionic state of these functional groups, and on the phenol chemistry in the solution. Therefore the reduction in phenol uptake at higher pH was due to the increased solubility of phenol in the aqueous solution and the abundance of OH^- ions on the adsorbents which limits the diffusion of phenolate ions. Adsorption of phenol at pH above 5 suggests that the positively charged phenol ions binds through electrostatic attraction to negatively charged functional groups on the surface of the adsorbent. This is because at a pH of 5 more functional groups carrying negatively charge would be exposed at the carbon surface (Terzyk, 2003).
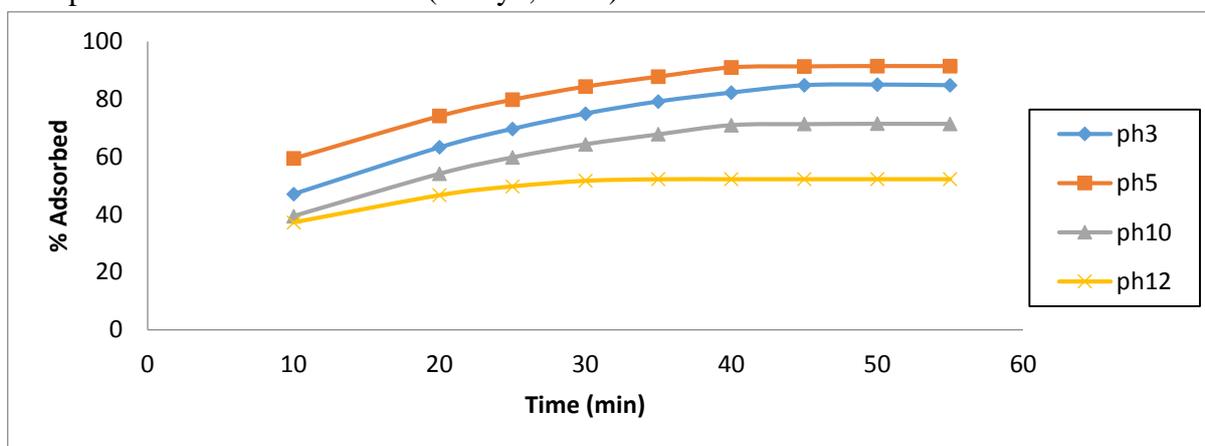
Figure 3 Influence of pharmaceutical effluent pH on phenol uptake by RH-SS

3.6 Influence of Pharmaceutical Effluent Concentration

The influence of pharmaceutical effluent phenol concentration on a fixed quantity of adsorbent dosage was studied at optimum conditions of pharmaceutical effluent pH of 5, effluent temperature of 35^0C, adsorbent dosage of 1.0g and optimum contact time of 35min. the results are shown in figure 4. The plot in figure 4 showed that an increase in pharmaceutical effluent phenol concentration from 25mg/L to 45 mg/L causes a corresponding decrease in phenol uptake efficiency for the adsorbent. This is due to the insufficient active sites as the concentration of phenol in pharmaceutical effluent is increasing.
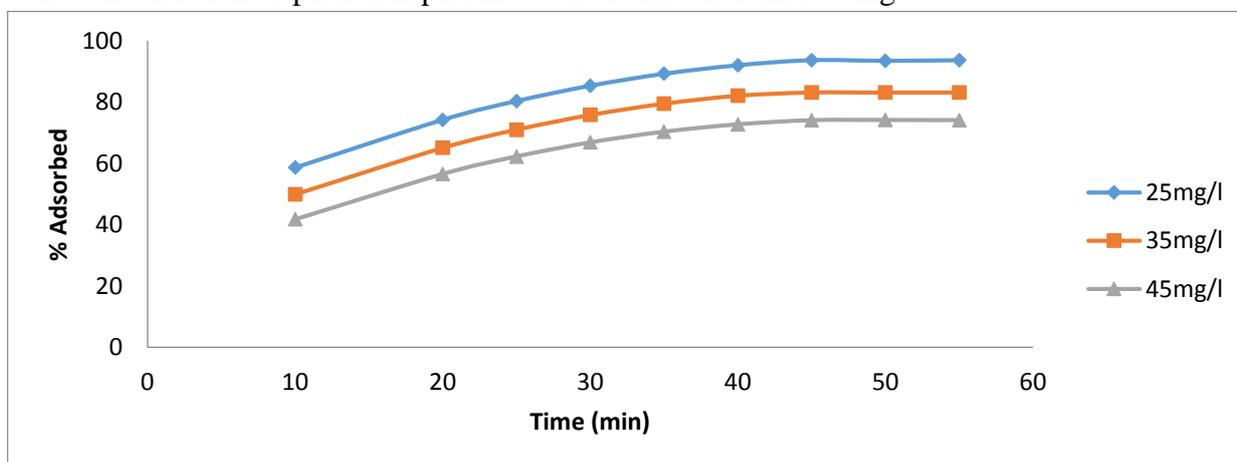
Figure 4. Influence of pharmaceutical effluent concentration on phenol uptake by RH-SS

3.7 Equilibrium Studies.

Langmuir adsorption which was primarily designed to describe gas-solid phase adsorption is also used to quantify and contrast the adsorptive capacity of various adsorbents (Elmorsi, 2011) .Langmuir isotherm accounts for the surface coverage by balancing the relative rates of adsorption and desorption (dynamic equilibrium). The Langmuir equation can be written in the following linear form

$$\frac{C_e}{q_e} = \frac{1}{q_m\,k_L} + \frac{C_e}{q_m} \qquad\qquad 4$$

Where C_e is concentration of adsorbate at equilibrium (mgg^{-1}), K_L is Langmuir constant related to adsorption capacity (mgg^{-1}), which can be correlated with the variation of the suitable area and porosity of the adsorbent which implies that large surface area and pore volume will result in higher adsorption capacity, q_m is the maximum adsorption capacity for a complete monolayer coverage.

Freundlich Isotherm

Freundlich isotherm is applicable to adsorption processes that occur on heterogonous surfaces. This isotherm gives an expression which defines the surface heterogeneity and the exponential distribution of active sites and their energies (Ayawei et al., 2015). The linear form of the Freundlich isotherm is as follows

$$log q_e = log k_f + \frac{1}{n} log c_e \qquad\qquad 5$$

Where K_F is adsorption capacity (L/mg) and $1/n$ is adsorption intensity; it also indicates the relative distribution of the energy and the heterogeneity of the adsorbate sites. The values of n in the range of 2-10 represent good adsorption, 1-2 moderate adsorptions and less than 1 represents poor adsorption characteristics (Hamdaoui et al., 2007). For Langmuir isotherm, the constant K is related to the affinity between the adsorbent and adsorbate (vijayaraphavan et al., 2005). A low value of k_L indicates favourable adsorption. The values of k_L obtained for the adsorbent as presented in table 2 were low, indicating that the adsorption of phenol on to RH-SS were favourable.

The analysis of the result based on the R^2 value showed that the Langmuir isotherm provided a good fit to the experimental data. A dimensionless constant equilibrium parameter R_L can be used to express an essential characteristic of the Langmuir Isotherm. The R_L values indicate the shape of the isotherm. The value of the R_L obtained at different dosage of RH-SS is shown in table 2.The value lie between 0 and 1 which showed that the adsorption process was favourable.

For the Freundlich isotherm, 1/n is a function of the strength of adsorption in the adsorption process. It is a heterogeneity parameter. The smaller the value of 1/n, the greater the expected heterogeneity. Also, the parameter n can be used to indicate whether the adsorption is linear (n = 1), a chemical process (n<l), or a physical process (n>l). The value of 1/n for RH-SS is small and less than 1 as shown in table 2, indicating that the adsorption process was a physical process.

Table 2: Linear equilibrium isotherm parameters for phenols adsorption onto adsorbent

Adsorption	Isotherm	RH-SS
Langmuir	qm(mg/g)	149.25
	K_L(l/mg)	1.55
	R_L(l/mg)	0.052
	R_2	0.9982
Freundlich	n_F	1.25
	K_f(l/mg)	87.00
	R^2	0.9890

3.8 Kinetic studies

For any adsorption system, the study of chemical kinetics is very important so as to determine the rate constants for the reaction and to know how quickly or slowly the reaction is proceeding. Adsorption mechanisms are explained by applying the kinetic models. In this research work, three kinetic models (pseudo-first order, pseudo-second order, and Elovich model) were applied to the experimental data in order to investigate the kinetics of sorption of phenol on RH-SS. The pseudo first and second order assumed adsorption process to be pseudo-chemical in nature, while Elovich model is applied to explain whether adsorption is physical adsorption or chemisorption (Rengaraj *et al.,*2002b).

The linear form of Lagergren's first order rate equation is as follows (Lagergren , 1898).

$$\log (q_e - q_t) = \log q_e - \frac{K_{p1}}{2.303} t \qquad\qquad 6$$

where q_e is the amount of phenol adsorbed onto the adsorbent at equilibrium (mg/g), q_t is the amount of phenol adsorbed onto the adsorbent at any time t (mg/g), and K_{p1} (min⁻¹) is the rate constant of the pseudo-first-order adsorption which can be calculated from the slope of the linear plot of $\ln(q_e - q_t)$ vs. t

The linearized form of the pseudo-second-order model is given as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_t} t \qquad\qquad 7$$

Where the equilibrium adsorption capacity (q_e), and the second order constants k_2 (g/mg h) can be determined experimentally from the slope and intercept of plot t/q_t versus t. Considering linear kinetic models based on the R^2 analysis, the constants and R^2 values obtained from the linear plots were summarized in Table 3 for pseudo first order, pseudo-second order and Elovich kinetic models, respectively. It was found that for pseudo-second order kinetic model, the R^2 value was relatively high as compared to the pseudo-first order and Elovich, kinetic models. The high R^2 value obtained for the pseudo-second order model suggested the applicability of the kinetic model to describe the adsorption process of phenol uptake on the RH-SS.
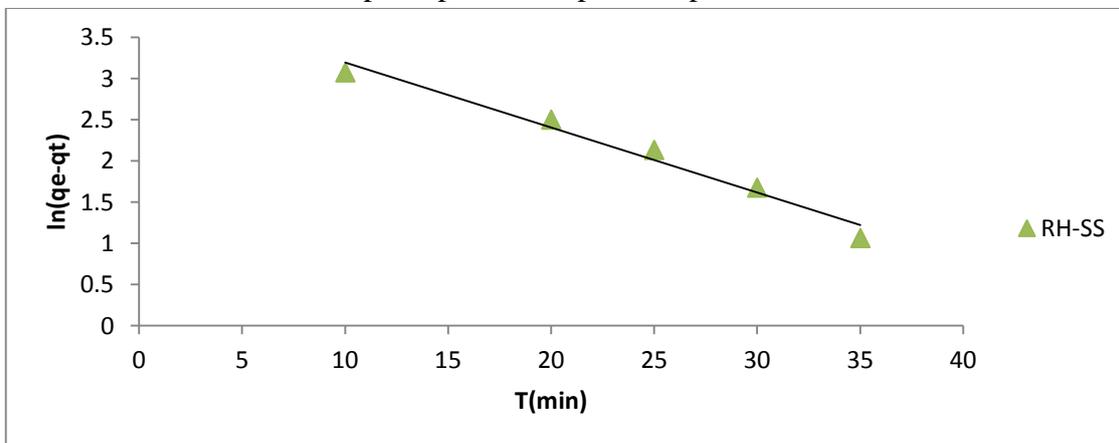
Figure 5. Linear pseudo first order kinetic plot
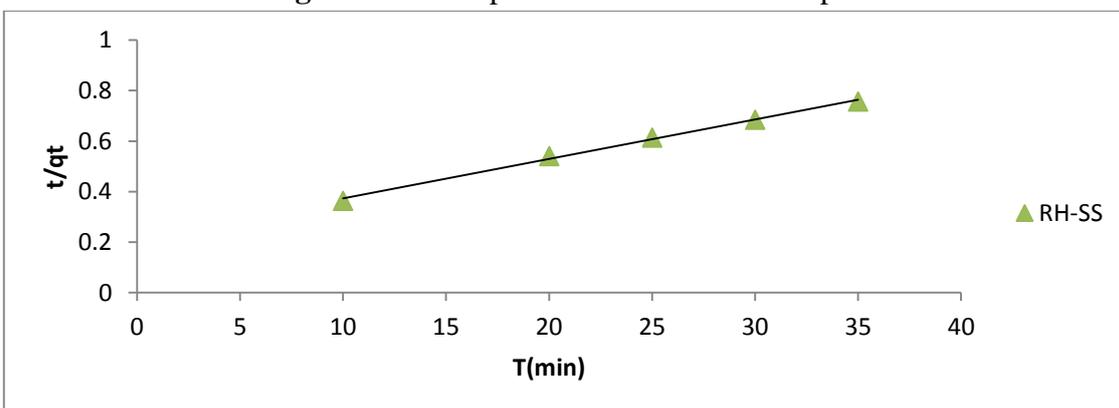
Figure 6. Linear pseudo second order kinetic plot
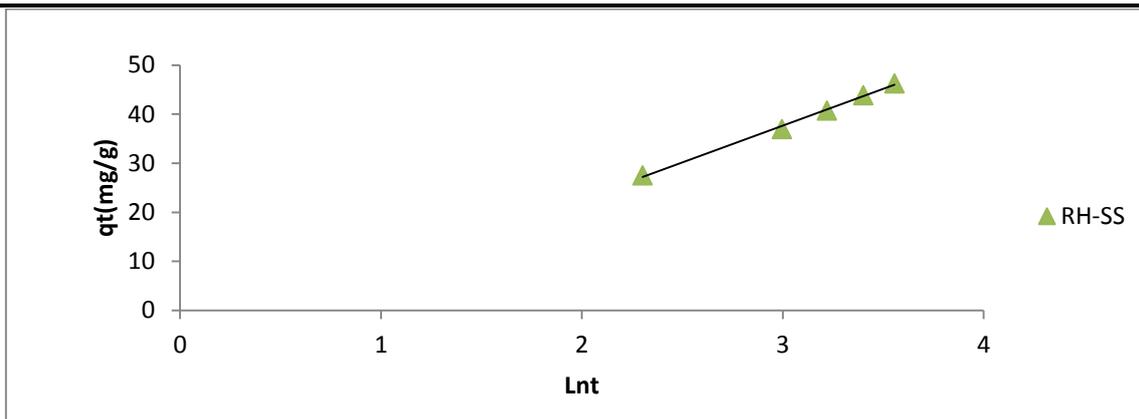
Figure 7. Linear Elovich kinetic plot

Table 3 Linear kinetic parameters for phenol adsorption onto adsorbents

Adsorption kinetics		RH-SS
Pseudo-first order	K_1 (min^{-1})	0.0789
	R^2	0.9678
Pseudo second order	K_2 (L/mg.min)	0.0722
	R^2	0.9989
Elovich	α (mg/g.min)	0.6168
	β (g/mg)	0.0688
	R^2	0.9432

3.9 Thermodynamic studies.

The thermodynamic parameters related to changes in adsorption standard free energy (ΔG), the change in enthalpy of reaction (ΔH), and the standard change in entropy of adsorbate–adsorbent reaction (ΔS), can be calculated by using the Van't Hoff's equatios as stated below (Yao et al., 2010)

$$\Delta G = - RT \ln k_d \qquad\qquad 8$$

$$\ln K_d = - \frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad\qquad 9$$

Where R is the gas constant (8.314J/mol K), K_b is the Langmuir isotherm constant at different temperature (L/mg), and T is absolute temperature in Kelvin. The values of (ΔH) and (ΔS) can be determined from the slopes and the intercepts of the linear graph of $\ln(K_b)$ versus 1/T.

From Table 4, the value of the ΔG became increasingly negative with increase in temperature from 298k to 313k but decreases negatively with further increase in temperature from 323k to 333k. This indicated that the adsorption processes was feasible and spontaneous (Fu et, al., 2009). The ΔG value for the adsorbent at a particular temperature were close indicating that such spontaneity was independent of the temperature of adsorption (Okolo, et al., 2000).
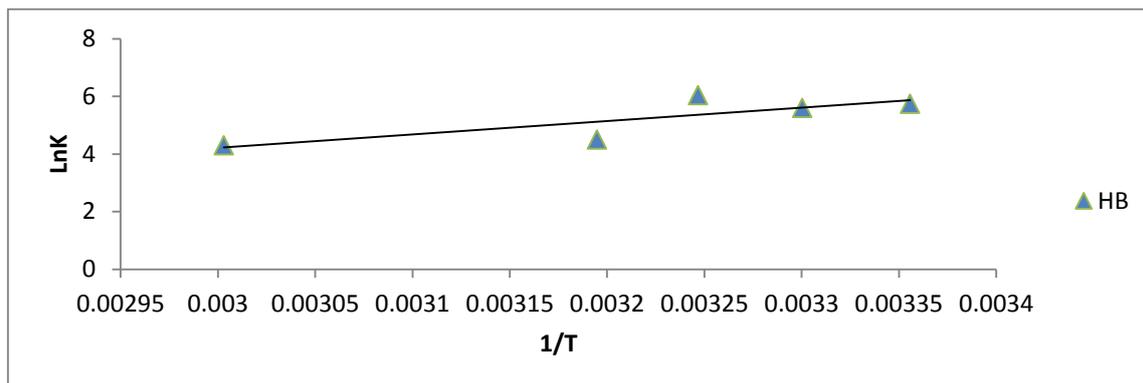
Figure 5. Van't Hoff plot for the adsorption of phenols

The values of ΔS were negative and remained constant with temperature. The negative values of ΔS correspond to a decrease in the degree of freedom of the adsorbed species, suggesting strong interactions between phenol and the adsorbent (RH-SS). The negative value of ΔS also indicated a greater order of reaction during the adsorption of phenol onto the adsorbents. It also reflected the affinity of the adsorbents materials for phenol. The negative values of ΔH showed the exothermic nature of the adsorption process. The values of ΔH were lower than 84 kJ mol^{-1}, suggesting the physical nature of the sorption (Bazrafshan et al.,2015). The overall adsorption process was exothermic. Similar results were reported by Fu et al., (2009), Canizares et al., (2006) and Bhatnagar et al., (2014).

Table 4 Thermodynamic parameter for phenol adsorption

Adsorbent	Temperature	ΔG (kj/mol)	ΔH (kj/mol)	ΔS (j/mol)
RH-SS	298	-14.23		
	308	-14.34		
	313	-15.74	-38.63	-80.82
	323	-12.10		
	333	-11.91		

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