Asian Journal of Applied Sciences (ISSN: 2321 – 0893)
Volume 03 – Issue 04, August 2015

Liquid-Phase Adsorption of Phenol using Modified Rice Husks: Kinetics, Isotherms and Thermodynamics Studies

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ABSTRACT—***The use of low-cost and ecofriendly adsorbents was investigated as an ideal alternative to the current expensive methods of removing organic compound from aqueous solutions. Modified rice husks MRI, MR2 and MR3 prepared by chemical oxidation with different concentration of $KMnO_4$ (0.05, 0.08 and 0.1M) were used as an adsorbent for the removal of phenol from aqueous solutions. Batch kinetics and isotherm studies were carried out to evaluate the effect of adsorbent dose, pH, contact time, initial phenol concentration. Four simplified adsorption isotherms including Langmuir, Freundlich, D-R and Redlich Peterson were selected to follow the adsorption process. The pseudo-second-order model described the adsorption kinetics well. Intra-particle diffusion process was identified the main mechanism controlling the rate of phenol sorption. Thermodynamics parameters showed that the adsorption of phenol onto modified rice husk was spontaneous and exothermic. The modified rice husks were characterized using TG, DTA, SEM and FT-IR spectroscopy. The study conducted that modified rice husk can be a good adsorbent for removing phenol from aqueous solution.***

Keywords---- Rice husk, phenol, $KMnO_4$, adsorption.

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1. INTRODUCTION

Contamination of ground and surface water by different organic pollutant from various activities include industrial and agricultural, becoming high concern by authorities [1] Phenolic compounds are common contaminants in wastewater, being generated from manufacturing a great variety of chemical products such as petrochemicals, plastics, pesticides, pharmaceuticals and dyes. Besides, they are also used to produce phenolic, epoxy and polyamide resins [2]. Phenolic compounds are harmful to organisms at low concentrations and many of them have been classified as hazardous pollutants because of their potential harm to human health [3]. Phenol constitutes the 11th of 126 chemicals, which has been designated as priority pollutants by U.S. Environmental Protection Agency (USEPA) [1]. The content of phenols in industrial wastewater is usually in the range of 0.1-6800 mgL^{-1} [4]. The allowable discharge limit for phenol is 0.1 mg/L (Standard A) set by the USEPA [5].

The most important technology for eliminating organic pollutant from water and wastewater are chemical oxidation, electrocoagulation, solvent extraction, membrane separation and adsorption [6-10]. Among those methods, adsorption is highly efficiency technique which has gained considerable attention for treating compounds from aqueous streams. The efficiency of the adsorption process is mainly due to the characteristic of the adsorbent such as high surface area, high adsorption capacity, microporous structure and special surface activity. Adsorption by agricultural by-products used recently as an economical and realistic method for removal of different pollutants has proved to be efficient at removing of phenol [11].

In recent years, special attention has been focused on the use of natural adsorbents as an alternative to replace the conventional adsorbents [12]. Natural materials such as rice husk that are available in large quantities or certain waste products from industrial or agricultural operations may have potential as inexpensive sorbents [13]. Rice husk is easily available low cost agriculture waste biomass. Approximately 80 million tons of rice husk are obtained annually in the world [14]. In Egypt, approximately 16 million tons of agricultural residues are currently disposed of every year and the annual amount of rice residues is about 3-6 million tons [15].

Rice husk consists of 32-24% cellulose, 21.44% hemicelluloses and 21.4 lignin [16&17]. The cellulose, hemicelluloses and lignin are associated with each other forming a very stable matrix structure. The inner surface of rice husk is smooth and may contain wax and natural fats that provide good shelter for the grain. On the other hand, the presence of these impurities on the inner surface of rice husk also affects the adsorption properties of rice husk, both chemically and physically [18].

Chemical modification of rice husk surface is thus necessary to upgrade or improve the adsorption properties [18]. Certain modifications could enable rice husk to develop affinity for some contaminants for use in their removal from varying types of water. Strong oxidants such as $KMnO_4$, HNO_3 or O_3 are often used in surface modifications [19&20].

Therefore the focus of this research was to evaluate the effectiveness of potassium permanganate modification on rice husk for removing phenol by adsorption from solution. This study includes characterization of the prepared adsorbents and the determination of the factors affecting the sorption, including the contact time, temperature, adsorbent dose, initial concentration of phenol solution and pH. Adsorption data were analyzed using Langmuir, Freundlich, Dubinin-Radushkevich and Redlich-Peterson models. The kinetic characterizations of adsorption were studied also.

2. MATERIALS AND METHODS

2.1 Preparation of adsorbents

The rice husk was collected from local rice field during the milling seasons. Firstly, the rice husk was washed with distilled water to remove all impurities and was dried at 105°C for 24hours. This sample named as R. Then, the rice husks (100gm) were impregnated in three different concentrations of potassium Permanganate 0.05M, 0.08M and 0.1M for 24 hours then washed with distilled water till the filtrate becomes colorless. Finally, the samples dried in an oven at 105°C for 24houres designated as MR1, MR2 and MR3, respectively.

2.2 Preparation of adsorbate

Analytical grade of phenol (C_6H_5OH) was used for the preparation of the synthetic adsorbate solutions of various initial concentrations varying from 10 to 200 mg/L. A phenol stock solution was prepared by dissolving 1gm of phenol (99.99% from Merck, Germany) in distilled water to 1000 mg/L.

2.3 Characterization of adsorbents

The functional groups present on the adsorbent's surface were determined using Fourier Transform Infrared spectroscopy in the range of 4000-400 cm^{-1} using Perkin Elmer Paragon 1000 FTIR spectrometer (USA).

Surface morphologies of the adsorbents were identified using scanning Electron Microscope (SEM-EDX) on a JOEL TSM device.

The thermal property of the modified rice husks was investigated by TG, TDA using Perkin-Elmer DTA thermal analyzer.

The crystal structural of raw (R) and modified (MR3) was studied by X-ray diffractometry (Schimadzu-7000 diffractometry) using CuK-α radiation beam (λ=0.154060 nm), operating at 30 KV and 30 mA with a copper target. Data were collected between 2θ values of 10° and 40° at scan rate of 2 degrees /min.

2.4 Batch studies

Sorption test on the raw and modified rice husk were performed in order to determine the time needed to reach equilibrium and the pattern of the kinetics.

For this purpose batch studies were carried out by mixing 0.25gm portions of each adsorbents with 50 ml of phenol solutions of different initial concentrations (10-100 mg/L) in 250 ml Erlenmeyer flasks. The solutions were agitated at speed of 130 rpm for 2 hours, then filtered and analyzed. The phenol uptake for each concentration of phenol at equilibrium was determined as follows:

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

where C_o and C_e are the initial and equilibrium concentration (mg/L), respectively, V is the volume of adsorption solution (L) and m is the mass of adsorbent (g).

The kinetic studies were performed by the following similar procedure, the initial phenol concentration was set (50, 100 & 200 mg/L) and the samples were separated at predetermined time intervals. The amount adsorbed of phenol at time t was calculated by the following equation:

$$q_t = \frac{(C_o - C_t)V}{m}$$

where C_t is the concentration at time t.

3. RESULTS AND DISCUSSIONS

3.1 Characterization of adsorbents

The FTIR technique is an important tool to identify the characteristic functional groups, which are presented on the surface of tested adsorbents. FTIR spectra of raw rice husk (R) and its modified (MR3) are shown in Fig. (1). As seen in Fig. (1), for the rice husk (R), the adsorption peak at 3431.71 cm^{-1} which indicates the existence of OH groups on the surface [21]. This stretching of OH groups is associated to silanol groups (Si-OH) and to adsorbed water on the rice husk surface. Other OH groups bound to methyl radicals exhibited a band at 2923.56 cm^{-1} [21]. These groups are common in lignin structures. The peaks around 1641.31-1737.74 cm^{-1} correspond to the C=O stretching that may be attributed to the hemicelluloses and lignin aromatic groups [22]. The peak at 1633.41 cm^{-1} is indicative of C=C stretching vibrations of alkenes and aromatic functional groups. The peaks around 1433-82 cm^{-1} indicate the presence of CH_2 and CH_3 groups while those at 1380 cm^{-1} are dinciative of CH_3 [23]. A peak at 1397 cm^{-1} band may be attributed to the aromatic CH and carboxyl-carbonate structures. The peaks around 1238, 1080 and 860-470 cm^{-1} correspond to CHOH stretching, Si-O-Si stretching and Si-H groups, respectively. The peaks around 1153-1300 cm^{-1} corresponds to vibration of CO group in lactones. The bands at 1100 and 710-700 cm^{-1} were attributed to O-Si-O and typical structures of SiO_2, which was an indication of silica [24]. Finally, The presence of a bands at 472.5 and 431.9 cm^{-1} is generally attributable to the bending vibration of O-Si-O [24]. In the modified rice husk (MR3), most of bands have lower intensity after modification with $KMnO_4$. The one significant change from $KMnO_4$ modification of the rice husks occurred on the band at 710 and 1100 cm^{-1} to 540 and 1030 cm^{-1}. The more intense peak for MR3 indicates that it contains more SiO_2 than R. The results from FITR experiments show that this modification in fact occurred having a great number of SiO_2 groups could lead to an increase in the adsorption capacity for the MR3 when compared to the R.

SEM images of both untreated (R) and treated (MR3) rice husks are shown in Fig (2). Fig. (2) shows that SEM images of R and MR3 are different. The ruptured protuberances of MR3 is due to the dissolution of cellulose in $KMNO_4$ solution [25].

EDX for R and MR3 shown in Fig. (3). R shows three characteristic signals for C, O and SiO_2. EDX for MR3 presented two characteristic signals only for O and SiO_2 but atomic percentage for O is increased from 38% in R to 63% in MR3 and SiO_2 increased from 10% in R to 35% in MR3. This provided an evidence for the oxidation of surface groups by $KMnO_4$ and the dissolution of cellulose in $KMnO_4$ solution.

In biomass, wood or agricultural wastes, three major constituents are present; cellulose, hemicelluloses and lignin which exhibit distinct temperature of decomposition. Hemicelluloses are the least resistant to thermal degradation followed by cellulose and then lignin [26]. The thermogravimetric analysis results for raw and modified rice husks are presented in Figure (4).

Fig. (4) displays the TG-DTG curves for both raw rice husk (R) and its modified materials (MR1, MR2& MR3). Although both precursor sample and its treated exhibit three processes for weight loss yet significant variations were observed in the bands intensities and locations. Impregnation with potassium permanganate brought about remarkable modifications to the characteristics. TG curve of the precursor consists of three weight loss processes 10.58%, 19.81% and 40..69% located at 64, 295, 352°C, while three processes present in the treated (MR1)14.75%, 13.46% and 38.79% located at 70, 300 and 357°C, respectively but for MR2 and MR3 only two processes present 17.12% and 41.14% for MR2 and 15.73% and 43.69% for MR3 and located at 300 and 357°C, respectively. The first weight loss in the all samples could be attributed to the elimination of water and other primary volatile substances. The second loss process implies to the decomposition of the hemicelluloses and cellulose. The third weight loss process in the precursor was found around 352°C represent the main decomposition stage and can be attributed to the decomposition of lignin and α-cellulose, while this main decomposition stage delayed in the treated samples to a temperature around ~ 357°C as a consequence to base impregnation.

Figure (5) display XRD for both R and MR3. One peak can be observed for R and MR3 between 17 and $2\theta=17$-28^o, which indicates the presence of amorphous silica [27]. The modification of rice husk by $KMnO_4$ stimulate the formation of amorphous silica of high purity. However, for R, there is four peaks indicate higher quantity of crystalline silica such as quartz, critobalite or tridrimite. This result was also reported by other researchers [28&29].

3.2 Effect of pH

One of the major factors that affect the adsorption characteristics was observed to be the initial pH of the solution. The effect of initial pH on amount adsorbed was studied in the range of 1-10 at 100 mg/L initial phenol concentration. Raw rice husk (R) is non active along pH value and the effect of initial pH on the removal of phenol by its modified (RM1, RM2 and RM3) is shown in Fig. (6). Figure (6) shown that the amount adsorbed increases with pH from 1.0 to 2.0 and decreases with pH from 2.0 to 6.0, then sharply decreases at pH > 6.0. The maximum adsorption is attained at pH = 2.0. So, the removal of phenol by three adsorbents was found to be in acidic range. Generally, solution pH affects the surface charge of adsorbent and degree of ionization of the adsorbate. Phenol as a weak acid compound with pKa = 9.89 is dissociated at pH > pKa. Therefore, the adsorption decreases at high pH values due to the ioization of adsorbate molecules (phenol) which is to be soluble in water and it is difficult to be adsorbed by tested samples. Also, at high pH, OH^- ions would complete with the phenolate ions could create a negative charge on the surface of modified rice husk resulting repulsion of negatively charged phenoxide ions, and therefore, adsorption is decreased [14]. While at low pH, the surface of the modified rice husk is usually protonated and resulted in a stronger attraction for the negatively charged phenolate ions.

3.3 Effect of Adsorbent Dosage

Dosage study is an important parameter in adsorption studies because it determines the capacity of adsorbent for a given initial concentration of phenol solution. The effect of adsorbent dosage on the removal of phenol at 100 mg/L initial concentration and pH=2 was studied on MR1, MR2 and MR3 and the results are represented in Fig. (7). The removal of phenol was found to increase in adsorbent dosage from (0.25-1g). This can be attributed to the increase of active sites for adsorption of phenol with increasing adsorbent dosage[30]. On the other hand, the amount adsorbed of phenol (q_e) is decreased with the increase of modified rice husks doses. The effect can be mathematically explained by Cardoso *et al*. [31], by the following equation

$$q_e = \frac{\%R \times C_o}{100 \times W}$$

As in equation (1), the amount adsorbed of phenol (q_e) is inversely proportional to the adsorbent dosage. For a fixed % removal of phenol, sorbent doses lead to a decrease in q_e values, since the initial concentration of phenol C_o is always constant.

3.4 Effect of contact time and initial concentration

The effect of contact time on the removal of phenol by MR1, MR2, and MR3 is given in Fig. (8). The contact time curves show rapid adsorption in the initial stages and thereafter the adsorption rate decreases gradually with time and finally, the systems reached equilibrium in about 90 min. for each adsorbents, this due to the increase of $KMnO_4$ concentration. This capability is attributed to the fact that the formation of oxygen groups leads to an increase in active sites on the modified rice husks. The active sites make it easier for phenol to be adsorbed on the surface of treated samples and MR3 has maximum adsorption capacity.

Fig. (9) shows that, the amount of phenol adsorbed increased with increasing phenol concentration by MR3. The initial phenol concentration provides an important driving force to overcome all mass transfer resistance and therefore the rate at which phenol molecules pass from the bulk solution to the particle surface. Hence a higher initial concentration of phenol tends to enhance the adsorption capacity. A similar phenomenom was observed for the adsorption of phenol on to organobentouite [2] and lignite activated carbon [32]. Therefore, phenol solution with higher initial concentration will take relatively longer time to reach equilibrium due to high amount of phenol molecules.

3.5 Adsorption kinetics

Pseudo-first-order, pseudo-second-order and intra-particle diffusion model were used to evaluate the kinetic mechanism that controlled the adsorption process for MR1, MR2 and MR3 and to evaluate the effect of phenol concentration on MR3.

The pseudo-first-order equation [33] is expressed as follows

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t_1$$

where q_e and q_t are amounts adsorbed (mg/g) at equilibrium and at specific time, respectively and k_1 is the first-order rate constant (min^{-1}). The values of k_1 were determined from the plots of log (q_e-q_t) versus t, Figure not shown. The parameters of the pseudo-first order model are listed in Table (1). According to the correlation coefficients (R^2) were relatively poor. Therefore the pseudo-first order could not be used to describe the adsorption behavior of phenol onto modified rice husks.

The pseudo-second order equation is expressed as follows

$$t/q_t = 1/k_2q_e^2 + 1/q_e\ t$$

where q_e and q_t are the amount adsorbed (mg/g) at equilibrium and at time t, respectively and k_2 is the pseudo second-order rate constant (g mg^{-1} min^{-1}). By plotting t/q_t versus t for each adsorbents a straight line was obtained in all cases (Figure not shown). The corresponding calculated parameters and correlation coefficients are given in Table (1).

Inspection to Table (1) reveals that the experimental data fit the pseudo-second-order model with R^2 values ranging between 0.996 and 0.999.

The kinetic result was further analyzed by intra-particle diffusion model. Adsorption is multi-step process involving transport of the solute molecules from the aqueous phase to the surface of the solid particles followed by diffusion into the interior of the pores. The intra-particle diffusion rate equation is expressed by the following equation [34].

$$q_t = k_{ip}t^{1/2} + C$$

where q_t is the amount adsorbed of phenol at time t (mg/g), C is the intercept and k_{ip} is the intra-particle diffusion rate constant (mg/g $min^{-1/2}$). The constants can be obtained from the slope and intercept of a straight line plot of q_t versus $t^{1/2}$ as shown in Fig. (10). If the regression of q_t versus $t^{1/2}$ is linear and passes through the origin, then intra-particle diffusion is the sole rate-limiting step, if not, the boundary layer diffusion controls the adsorption to some degree and this indicated that the intra-particle diffusion is not the only rate controlling step, but also other processes may control the rate of adsorption. As can be seen from Fig. (10), the linear plot did not pass through the origin. The plot has an initial curved portion, followed by an intermediate linear portion and plateau. The first sharper portion is the external surface adsorption on instantaneous adsorption stage. The second portion is the gradual adsorption stage, where the intra-particle diffusion is rate controlled. Intra-particle diffusion rate constants calculated form linear plots and correlation coefficients are shown in Table (1). Similar results were also reported by other workers [34].

3.6 Adsorption isotherms

Equilibrium data are the fundamental requirements for the design of adsorption systems. The adsorption isotherms of phenol from aqueous solutions on the modified rice husks MR1, MR2 and MR3 in the concentration range 10-200 mg/L are shown in Fig. (11).

Sorption equilibrium can be described by a number of models available in the literature. In this work, we selected four models: Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Redlich-Peterson (R-P).

A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous adsorption sites within the adsorbent [35&36] and that intermolecular forces decrease rapidly with the distance from the adsorption surface.

The linear form of the Langmuir isotherm can be written as follows:

$$C_e / q_e = \frac{1}{q_{max} K_L} + \frac{1}{q_{max}} C_e$$

where q_e is the amount adsorbed of phenol at equilibrium (mg/g), C_e is the equilibrium concentration of phenol in the solution (mg/L), q_m is the maximum adsorption capacity surface of adsorbate required to form a complete monolayer on the surface (mg/g) and K_L represents the Langmuir constant related to adsorption heat.

When C_e/q_e is plotted against C_e, q_m and K_L constants can be calculated from the slope and intercept. Their values along with the regression coefficient (R^2) are presented in Table (2).

The essential characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless separation factor (R_L) which describes the type of isotherm and is defined by

$$R_L = \frac{1}{1 + K_L C_\circ}$$

where C_o is the initial concentration of the adsorbate in solution. The R_L value indicates the type of the isotherm as either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The values of R_L are given in Table (2)

Table (2), shows that the correlation coefficients are closer to unity and the maximum adsorption capacity increased with the increase of concentration of $KMnO_4$. The values of R_L for adsorption of phenol onto modified rice husk are between 0 and 1. These values indicated that the adsorption behavior of modified rice husk was favorable for the phenol sorption for all tested samples.

The Freundlich isotherm is an empirical expression that takes into account the heterogeneity of the surface and multilayer adsorption to the binding sites located on the surface of the adsorbent (37&38). The Freundlich model is expressed as follows:

$$ln\ q_e = \ln K_F + \frac{1}{n} \ln C_\circ$$

where q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), K_F is a constant related to the maximum amount adsorbed and 1/n is a measure of the binding energy between the adosrbate molecule and the adsorbent surface.

The values of the constants were obtained from linear plot of ln q_e versus ln C_e (Fig. not shown) and represented in Table (2).

Another model used in the present study, the Dubinin-Raduskevich (D-R) isotherm. The linear form of D-R equation is given as:

$$\ln q_e = \ln q_m - \beta\varepsilon^2$$

where β is a constant related to the adsorption energy (mol^2/KJ^2), q_m is a constant that indicates the sorption degree characterizing the sorbent (mg/g) and ε is the polany potential shown in the following equation

$$\varepsilon = RT \ln (1 + 1/C_e)$$

where T is the absolute temperature (K) and R is the ideal gas constant (R = 8.314 J/mol K). It is possible to determine the value of β as shown in Table (2) by plotting $\ln q_e$ versus ε^2 Figure not shown. The mean free energy E (KJ/mol) of adsorption in Table (2) can be estimated by using β values as in the following equation [39].

$$E = 1/(2\,\beta)^{1/2}$$

The magnitude of E may characterize the type of the adsorption as chemical ion exchange (E = 8 – 16 kJ/mol) or physical adsorption (E < 8 kJ/mol). From Table (2), the mean free energy of adsorption for all modified rice husks was

< 8 kJ/mol. This means that, the adsorption of phenol on modified rice husk may be considered as physical adsorption process.

The Redlich-Peterson isotherm was proposed by considering the limitations of the Langmuir and the Freundlich isotherms [40&41]. The Redlich-Peterson equation combines elements from both the Langmuir and Frendlich equations and the mechanism of adsorption is a hybrid one which does not follow ideal monolayer adsorption. The isotherm equation is described by:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}}$$

The linear from of Redlich-Peterson equation is:

$$\ln K_R \,.\, C_e/q_e = \beta \ln C_e + \ln a_R$$

where q_e is the amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate in the solution at equilibrium (mg/L), K_R (L/g) and a_R (L/mg) are the Redlich-Peterson isotherm constants and β is the exponent which lies between 0 and 1. When $\beta = 1$, it becomes a Langmuir equation but when $\beta = 0$, it becomes Henry's law. The Redlich-Peterson isotherm constant, K_R, a_R and β are calculated by plotting $\ln K_{rp}.C_e/q_e$ versus $\ln C_e$ as in Fig. (12) and listed in Table (2). A comparison of the isotherms constants along with regression coefficients (R^2) is presented in Table (2).

Comparing the regression coefficient values for all isotherms, it was demonstrated that the Langmuir and Redlich- Peterson isotherms were the most appropriate isotherms to describe the equilibrium data for phenol sorption at different concentration of potassium permanganate onto rice husk.

3.7 Adsorption thermodynamics

Temperature effect on amount adsorbed of phenol by MR3 was studied at 303, 313 and 333 K. Fig. (13) shows that the amount adsorbed increased with decreasing temperature from 330 to 303 K. This indicated that the adsorption process was exothermic. The sorption capacity of MR3 was determined as 13, 7 and 5.5 mg/g at 303, 313 and 333 K respectively. This can be attributed to the physical bonding between the organic compounds (phenol) and the active sites of the adsorbent weakened [42].

In order to fully understand the nature of adsorption the thermodynamics parameters such as free energy change ΔG^o (J mol^{-1}), enthalpy change ΔH^o (Jmol^{-1}) and entropy ΔS^o (Jmol^{-1} K^{-1}) could be calculated using the following equations [43&44].

$$\Delta G^\circ = RT \ln K_L$$

$$\ln K_L = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R}$$

where R (8.314 J/mol K) is the gas constant. T (K) is the absolute temperature and K_L is the adsorption coefficient obtained from Langmuir equation. The values of ΔH° and ΔS° were determined from the slope and intercept of the linear plot of $\ln K_L$ versus (1/T), Figure not shown. The calculated thermodynamics parameters for the adsorption of phenol by modified rice husks are given in Table (3).

The negative values of ΔG^o indicate the feasibility and the spontaneous nature of the adsorption. ΔG^o becomes more negative with decreasing temperature, which suggests that lower temperature makes the adsorption easier.

The negative value of ΔH^o implies that the adsorption is exothermic. The positive value of ΔS^o indicates that there is an increase in the randomness in solid/solution interface during the adsorption process and the process in not enthalpy driven.

3.7.1 Activation energy

The activation energy (E_a) usually provides important information on the mechanism of adsorption reaction using the pseudo-second order rate constant, k_2 in Table (1). The activation energy E_a for the adsorption of phenol on MR3 is determined using the Arrhenuis equation.

$$\ln k_2 = \ln A - \frac{E_a}{RT}$$

where k_2 is the rate constant, A is the Arrhenuis constant, E_a is the activation energy (KJ mol^{-1}), R is the gas constant (8.314 mol^{-1} K^{-1}) and T is the temperature (K).

By plotting ln k_2 versus 1/T as in Fig.(14), E_a is obtained from the slope of the linear plot. The activation energy is very significant to evaluate whether the entire adsorption reaction is physisorption or chemisorption. If the value for activation energy lies between 8-16 KJ mol^{-1}, it is chemical sorption and when it is < 8 KJ mol^{-1}, it is physisorption [45] . Our results [E_a= -18.70KJ] proved that adsorption is physisorption.

4. CONCLUSION

In this study, we concluded that rice husks are non-active for the removal of phenol from solution but modification with oxidizing reagent such as $KMnO_4$ improved their adsorption efficiency. Adsorption of phenol was influenced by various parameters such as adsorbent dose, pH, contact time and initial concentration of phenol. Amount adsorbed was decreased with increasing adsorbent dose and pH and increased with increasing initial phenol concentration. Furthermore, the adsorption isotherms follow both the Langmuir and Redlich-peterson models. It was found that the pseudo-second- order equation was fitted in describing the adsorption kinetics of phenol on modified rice husks. The data obtained from adsorption isotherms at different temperatures were used to calculate thermodynamic quantities such as ΔG^o, ΔH^o and ΔS^o of adsorption. The results revealed that adsorption process is spontaneous and physical in nature.

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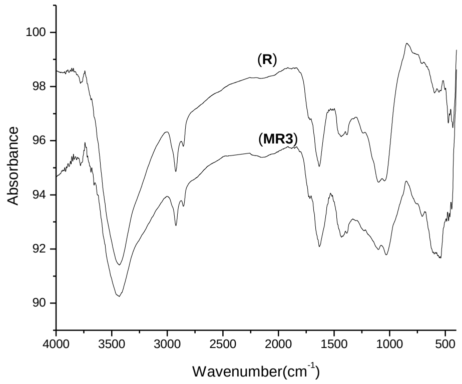

Figure 1: FT-IR spectra of R and MR3.

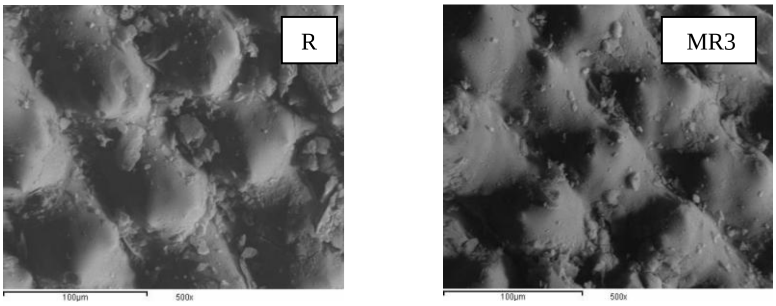

Figure 2: SEM images of R and MR3.

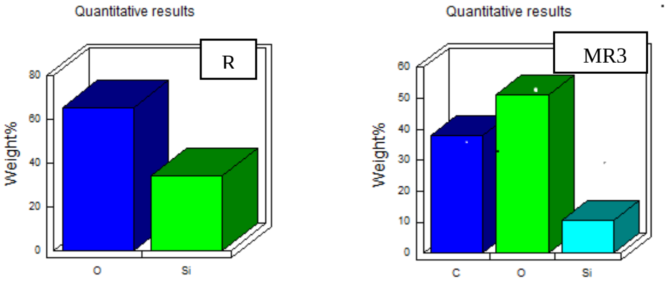

Figure 3: EDX analysis of R and MR3.

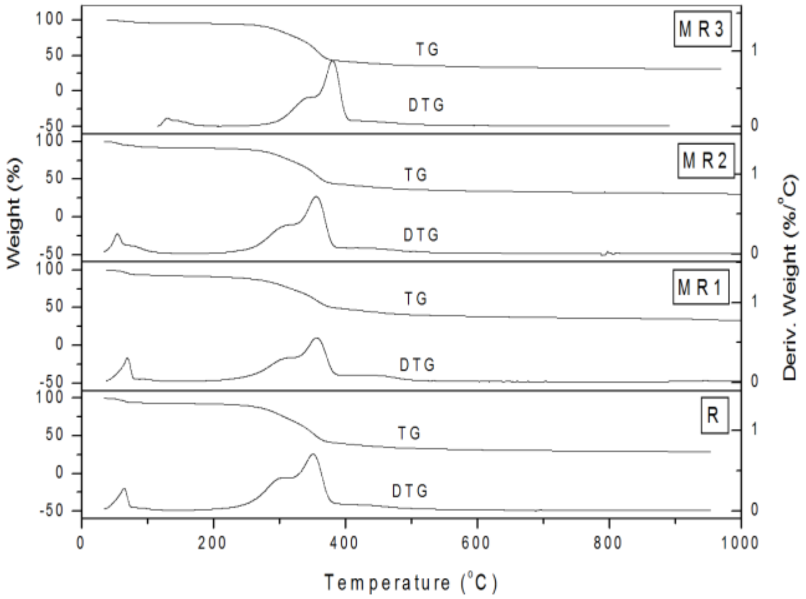

Figure 4: TG and DTG analysis of R, MR1, MR2 and MR3 in atmosphere at 10 ˚C min^{-1}.

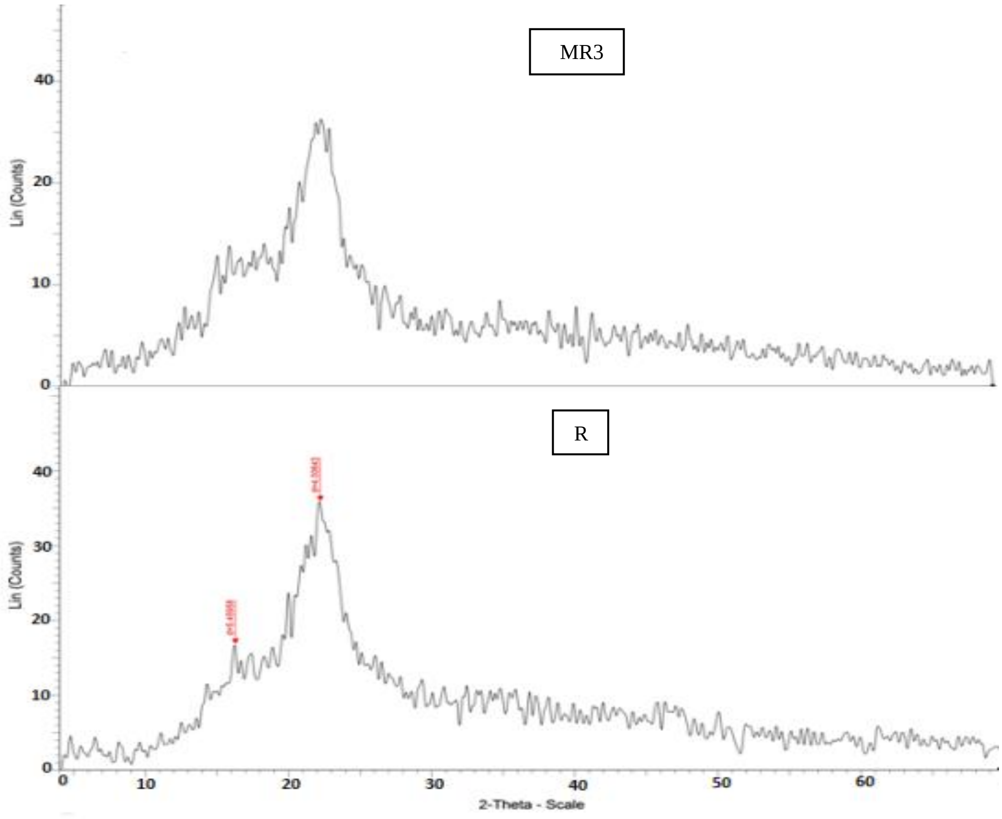

Figure 5: XRD spectra of R and MR3.

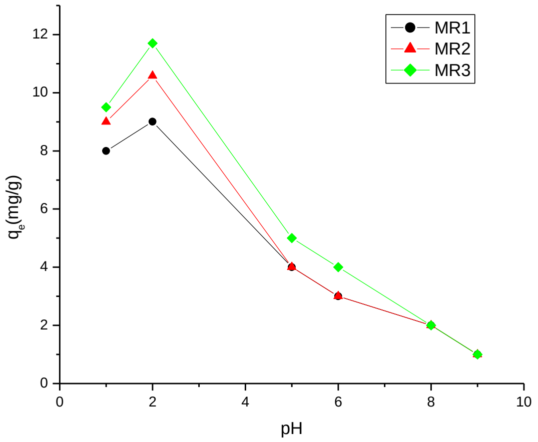

Figure 6: Effect of initial pH phenol solution onto MR1, MR2 and MR3.

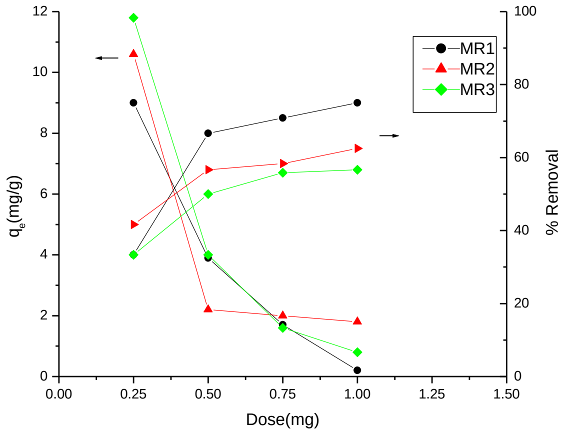

Figure 7: Effect of adsorbent doses on the phenol adsorption by MR1, MR2 and MR3.

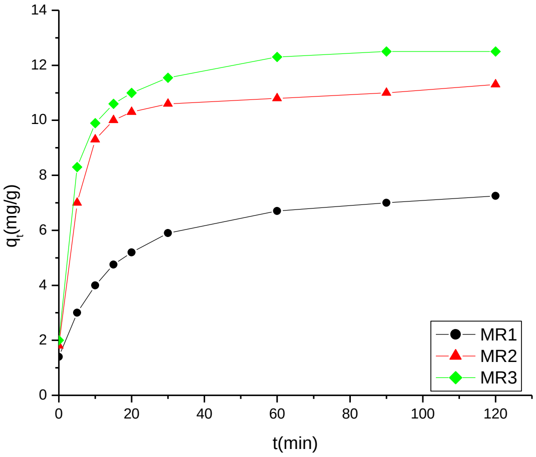

Figure 8: Effect of contact time on the uptake of phenol solution at 30˚C by MR1, MR2 and MR3.

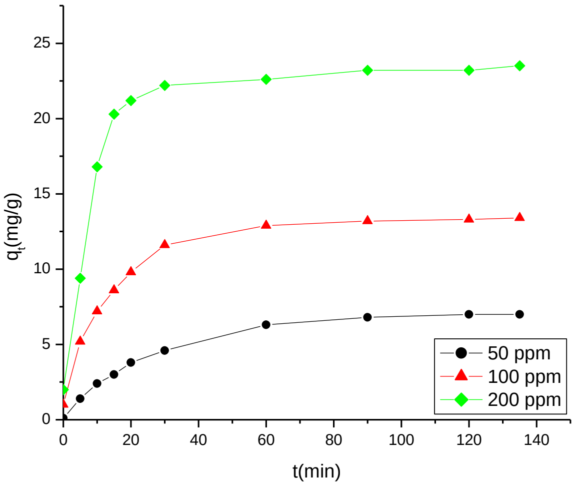

Figure 9: Effect of initial phenol concentration on the kinetic studies on MR3.

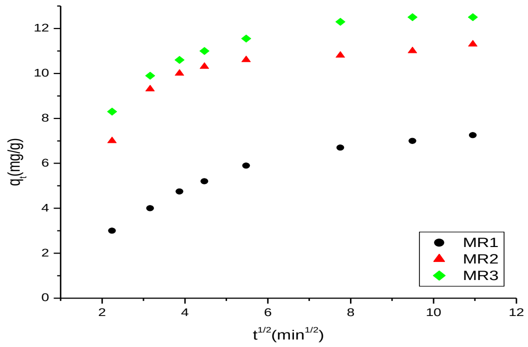

Figure 10: Intra-particle diffusion of phenol sorption at 30˚C onto MR1, MR2 and MR3.

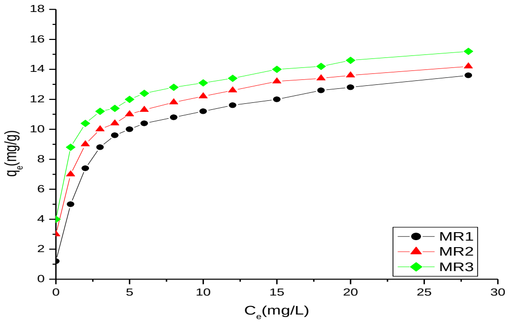

Figure 11: Adsorption isotherms at 303K for phenol onto MR1, MR2 and MR3.

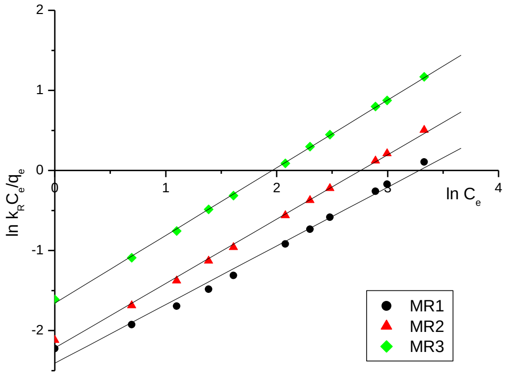

Figure 12: Linear plots of Redlich-Peterson equation on MR1, MR2 and MR3.

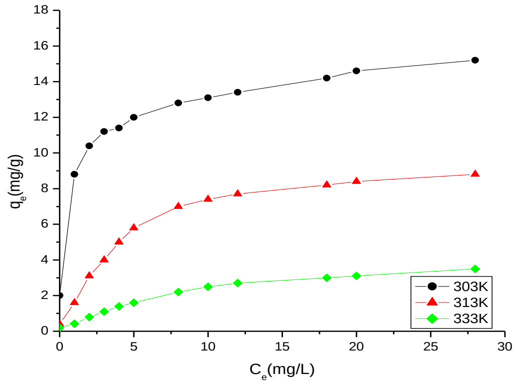

Figure 13: Effect of temperature on the phenol adsorption on MR3.

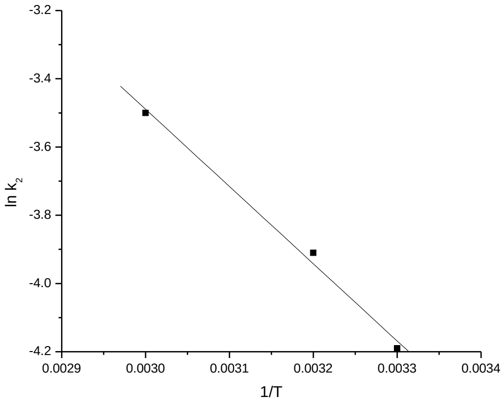

Figure 14: Plot of ln k_2 vs 1/T.

Table 1: Kinetic parameters for the phenol adsorption onto investigated sorbents.

		Pseudo-first-order constant		
		k_1(g/mg min)	**q_e (mg/g)**	**R^2**
Samples				
MR1		0.098	57	0.878
MR2		0.114	17.4	0.860
MR3		0.118	11.48	0.812
Sample	**Temperature °C**			
MR3	30	0.097	53	0.847
	40	0.92	30	0.888
	60	0.084	12	0.877
Sample	**Phenol Conc. mg/L**			
MR3	50	0.077	77	0.890
	100	0.092	144	0.888
	200	0.175	275	0.890
		Pseudo-second-order constant		
		k_2 (g/mg min)	**q_e (mg/g)**	**R^2**
Samples				
MR1		0.015	7.75	0.997
MR2		0.02	11.75	0.996
MR3		0.03	12.67	0.999
Sample	**Temperature °C**			
MR3	30	0.013	13	0.998
	40	0.025	7	0.997
	60	0.013	5.5	0.999
Sample	**Phenol Conc. mg/L**			
MR3	50	0.0046	8.4	0.999
	100	0.008	13	0.999
	200	0.005	26	0.998
		Intra-Particle diffusion Constants		
		k_{id}	**C**	
Sample				
MR1		0.89	11.1	
MR2		1.96	2.7	
MR3		1.6	4.7	
Sample	**Temperature °C**			
MR3	30	0.83	0.1	
	40	0.045	0.55	
	60	2.75	1.8	
Sample	**Phenol Conc. mg/L**			
MR3	50	1.905	-0.2	
	100	1.273	0.8	
	200	0.667	8.0	

Table 2: Langmuir, Freundlich, D-R and Redlich-Petrson parameters for phenol sorption onto investigated sorbents at 303K.

Models	**Sample**	**Isotherm parameters**			
		q_m mg/g	**K_L (L/g)**	**R_L**	**R^2**
Langmuir	MR1	13.14	0.54	0.018	0.998
	MR2	14	0.84	0.012	0.989
	MR3	14.28	1.75	0.006	0.997
		K_F	**n**	**R^2**	
Freundlich	MR1	7.61	6	0.893	
	MR2	8.499	6.67	0.912	
	MR3	9.02	6.25	0.899	
		q_m	**β**	**E_a**	**R^2**
D-R	MR1	11.02	0.42	1.09	0.939
	MR2	12.18	0.44	1.07	0.898
	MR3	13.19	0.43	1.08	0.901
		q_R	**a_R**	**K_R**	**R^2**
Redlich-Peterson	MR1	0.76	12.18	69.29	0.998
	MR2	0.825	9.39	43.47	0.997
	MR3	0.857	5.42	29.30	0.998

Table 3: Thermodynamics parameters for phenol adsorption onto MR3.

Sample	**Temperature (K)**	**$\ln K_L$**	**ΔG° ($Jmol^{-1}$)**	**ΔH° ($Jmol^{-1}$)**	**ΔS° ($Jmol^{-1} K^{-1}$)**
MR3	303	11.7	-29.47	-	-
	313	9.96	-25.91	-8.07	0.062
	333	9.18	-25.41	-	-