Adsorption properties of Thermally Treated Rice Husk for removal of Sulfamethazine antibiotic from pharmaceutical wastewater

Abstract: Equilibrium sorption of the Thermally Treated Rice Husk (TTRH) for Sulfamethazine (SMT) adsorption was studied. The Physico-chemical properties of the modified rice husk were determined. The equilibrium sorption data were fitted into Langmuir, Freundlich and Dubinin–Radushkevich isotherms. Of the three adsorption isotherm, the R^2 value of Langmuir isotherm model was the highest. Also compared to other isotherms the AARE coefficient for the Langmuir isotherm is low, which indicates favorable sorption. The maximum monolayer coverage (q_m) from Langmuir isotherm model was determined to be 19.11 mg/g, the separation factor indicating a favorable sorption experiment is 0.446. Also from Freundlich Isotherm model, the sorption intensity (n) which indicates favorable sorption and the correlation value are 1.84 and 3.79 respectively. The mean free energy was estimated from Dubinin–Radushkevich isotherm model to be 9.18 KJ/mol which clearly proved that the adsorption experiment followed a physical process.

Keywords: Isotherm Model, Thermally Treated Rice Husk, Sulfonamide antibiotics, AARE

Introduction: In recent years, increasing awareness of water pollution and its far reaching effects has prompted concerted efforts towards pollution abatement (1-3). Pharmaceuticals constitute a large group of human and veterinary medicinal compounds which have long been used throughout the world (4, 5). The most important pharmaceuticals found in the waters are antibiotics, analgesics, painkillers, and hormonal drugs (6). These chemicals find their way into the water via sewage systems of drug manufacturing plants, hospitals, and private households (7, 8). Although the amount of pharmaceuticals in the aquatic environment is low, but many decades, the worldwide consumption of antibiotics has increased continuously with the aim of improving human and animal health (9). Antibiotics are widely used to as effective clinical pharmaceuticals to prevent and treat diseases, and they are mainly excreted into the aquatic and soil environments in unchanged and active forms (10, 11).

Therefore, over the past few years these compounds are considered to be an emerging environmental problem. Pharmaceuticals are released to the environment through many ways, including municipal medical and industrial wastewater effluents (12, 13). They are extremely resistant to biological degradation processes and because of their continuous discharge, they remain in the environment for a long time; their presence in the environment has caused increased concern over long-term effect on human health (14, 15). Therefore, the removal of pharmaceuticals before disposal of the wastewater is necessary.

Conventional metal removal techniques such as ion exchange, precipitation, membrane separation, electrochemical precipitation–filtration and reduction followed by chemical precipitation are often expensive or not sufficiently effective in the low concentration range (16, 17). Adsorption is one of the important procedures for the removal of trace antibiotics from aqueous solution. The main properties of the adsorbents for antibiotics removal are strong affinity and high loading capacity (18, 19). Hence, low cost adsorbents with high metal binding affinity need to be investigated. Waste materials from agricultural and food industries used as adsorbents have the dual advantage of waste reuse and low cost (20).

Rice husks are usually used as a low-value energy resource, burned in the field, or discarded, which are unfavorable to environment. The processing and transformation of rice husks with good adsorption properties would alleviate problems of disposal and management of these waste by-products, while producing value added products from rice husks for water and wastewater treatment , etc., to expand the cheap materials market to adsorption pollutants (21, 22).

In the present study, we have prepared a novel adsorbent with thermally process and this new adsorbent was used for removal of Sulfamethazine (SMT) from aqueous solutions. Adsorption isotherms on the adsorption of SMT were studied in a batch system. The effects of the SMT concentration, temperature and contact time were studied to determine the optimal adsorption conditions

Materials and Methods

All chemicals used in this work were of GR grade and was obtained from Sigma Aldrich (Darmstadt, Germany). The chemical structure of SMT antibiotics (molecular weight: 278.33, EC Number 200-346-4 and CAS Number 57-68-1 and Molecular Formula $C_{12}H_{14}N_4O_2S$) is shown in Fig. 1. The pH of the solution was adjusted by 0.1 M H_2SO_4 or NaOH (model Sartorius Professional Meter PP-50). All experiments were conducted in batch mode in 250 mL conical flasks.

Preparation of sorbent

Rice husk collected from a local rice mill was grounded and washed with ultrapure water several times to eliminate impurities and to obtain constant pH before dried in an oven at 105°C for 24 h. The dried rice husk was sieved to obtain particles size between 300 to 600 μm and then heated in a furnace at 800°C for two hours. The thermally treated rice husk was then put in a desiccators for cooling before kept in a container for the adsorption experiments.

Sorption study: Adsorption tests were carried out by using batch experiments. For each test, 2 g of the adsorbent was placed in screw-capped Erlenmeyer flasks containing 100 mL of SMT solution. The flasks were shaken constantly for a sufficient period to achieve equilibrium using an orbital shaker at 180 rpm and 28°C. Then the solution was filtered using Whatman filter paper ($0.45\ \mu$). The dye uptake was monitored with a spectrophotometer by maximum wave length of 290 nanometer. The adsorption at the equilibrium, q_e (mol/g), was calculated using the following equation (23, 24):

$$q_e = (C_0 - C_e)\frac{V}{M}$$

Where C_o and C_e (mol/L) are the initial and the equilibrium liquid-phase concentrations of the dye, respectively. V is the volume of the solution (in liters), and M is the mass of the dry adsorbent (in grams). The equilibrium adsorption data were fitted with three isotherm models, the Langmuir and Freundlich and Dubinin–Radushkevich models.

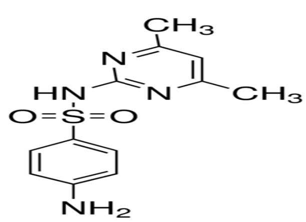

Fig.1. Molecular structure of Sulfamethazine (SMT)

Results and Discussion

Adsorption isotherm

For the analysis of equilibrium data for SMT adsorption onto the TTRH, Langmuir isotherm model and Freundlich isotherm model were used. Langmuir isotherm model is assumed monolayer adsorption onto surface with a finite number of identical sites (25, 26). Linearity of the plots indicated the applicability of the adsorption isotherm. Weber expressed the essential characteristics and feasibility of the Langmuir isotherm in terms of a dimensionless constant, separation factor or equilibrium parameter, R_L. The linear form of the Langmuir adsorption isotherm and R_L constant can be defined by Eqs. 2 and 3. If this value ranges in between 0 and 1 then the adsorption process is favorable (27). All the experimental data were lying between 0 and 1 indicated favorable adsorption. The Freundlich isotherm is an empirical equation based on the adsorption on the heterogeneous surface (29, 30). The linear form of the Freundlich adsorption isotherm can be defined by Eq. 4. The Freundlich isotherm constant n was an empirical parameter that varies with the degree of heterogeneity and K_F was related to adsorption capacity. The constants K_F and n were calculated from Eq. 4 and Freundlich plots (Figs 2b). Table 1 indicates the Langmuir and Freundlich constants along with the statistical parameters. The values of n lies between 1 and 10 represent favorable adsorption.

$$\text{Ln } q_e = \text{Ln } K_F + \frac{1}{n} \ln C_e \qquad (2)$$

$$R_L = \frac{1}{1+C_0 K_L} \qquad (3)$$

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b} \qquad (4)$$

Calculation of sorption energy

The Dubinin–Radushkevich isotherm model was used to predict the nature of adsorption process as physical or chemical by calculating sorption energy. The linear from of the model was described as (31, 32):

$$\text{Ln } C_{abs} = \text{Ln } X_m - \gamma \varepsilon^2$$

The Polanyi potential which is equal to (33, 34):

$$\varepsilon = RT + \text{Ln}\left(1 + \frac{1}{C_e}\right)$$

From Fig 2 C, a plot of Ln C_{abs} versus ε^2 gave a straight line from which the values of γ and X_m for all the adsorbents were calculated. Using the value of γ, the mean sorption energy, E, was evaluated as (35, 36):

$$E = \frac{1}{\sqrt{-2\gamma}}$$

where ϵ is Polanyi potential, γ is Dubinin-Radushkevich constant, R (8.314 J/mol.K) is the gas constant, T (K) is the absolute temperature, X_m (mg/g) is the D-R maximum adsorption capacity of IPF, and E (J/mol) is mean free energy of adsorption per molecule of the adsorbate.

The Dubinin–Radushkevich isotherm relates the heterogeneity of energies close to the adsorbent surface. If a very small sub-region of the sorption surface was considered and assumed to be approximately by the Langmuir isotherm, the quantity $\sqrt{-\gamma}$ can be related to the mean sorption energy, E, which indicated the information about adsorption mechanism. If

E<8 kJ/mol, the adsorption process was physical in nature and in the ranges from 8 to 16 kJ/mol, it was chemical in nature. The estimated values of E are shown in Table 1 which suggested the adsorption process was chemical in nature.

The average absolute value of relative error, AARE, was used to compare the predicted results with experimental data. This is defined as follows (37, 38):

$$\%\text{AARE}=\frac{1}{N}\sum_{i=1}^{N}(\frac{Prid\ value-\text{Exp}\ value}{\text{Exp}\ value}\times 100$$

Which N is the number of data points. From Table 1, it can be concluded that the adsorption of SMT onto TTRH follow Langmuir adsorption isotherm model (according to high value of the R^2 coefficient or and the low value of the AARE coefficient).

Effect of temperature and contact time

The effect of temperature on the SMT adsorption onto TTRH was carried out at 10, 25, 40 and 55 $^{\circ}$C and the results are illustrated in Fig. 3. An increase in the temperature led to an increase in the adsorption capacity, q_e, from 11.78 to 15.8 mg/g corresponding to a temperature change from 10 to 55 $^{\circ}$C, indicating that SMT adsorption onto TTRH may be a kinetically controlled process. The higher temperature increases the reaction rate and decreases the particle density, which forms voids, resulting in a reduced equilibrium time (39, 40). The obtained result is consistent with observations made by Ahmadi (10) on a study of the adsorption of antibiotics by nano-particle. The observed increase in the adsorption capacity with increasing temperature is a kinetic effect resulting from the increased monomer concentration in the solution.

Contact time is another important variable in adsorption processes. Fig. 4 shows the effect of contact time on adsorption for various SMT concentrations. The results show that with increasing SMT concentration, the time required to reach equilibrium increased accordingly. For initial dye concentrations of 25, 50, 100 and 200 mg/L, the times reaching equilibrium were 45, 60, 75 and 90 min, respectively. At low initial concentrations, the SMT adsorption by TTRH was very intense and reached equilibrium very quickly. However, during the adsorption process, the adsorbent surface was progressively blocked by dye molecules, becoming covered after some time. The hindrance enhanced with increasing SMT concentration, and thus the time for adsorption equilibrium increased accordingly (41).

When Mahvi *et al* (42), investigated the adsorption of tetracycline antibiotics onto Azolla, similar results were also observed. The time attaining equilibrium increased with increasing concentrations. Their study found that 75 min was sufficient to achieve complete recovery of the Penicillin G at initial concentrations below 100 mg/L. However, for the highest concentration (200 mg/L), 90 min was necessary to reach equilibrium. In this work, in order to achieve adsorption equilibrium, the data were measured in 90 min for adsorption isotherms.

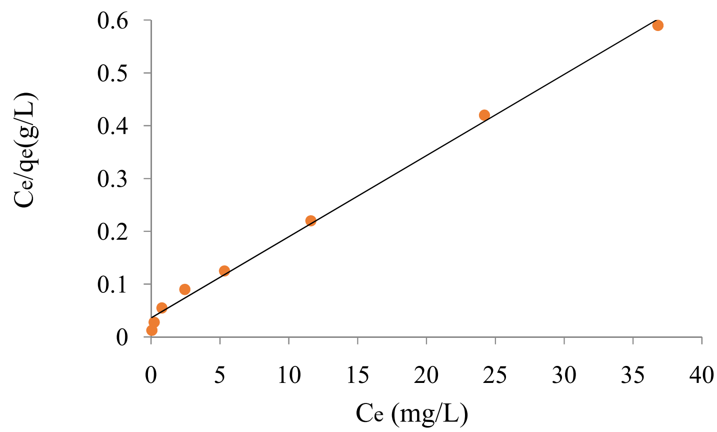

Fig.2 a. Langmuir isotherm models for the adsorption of SMT adsorption onto TTRH

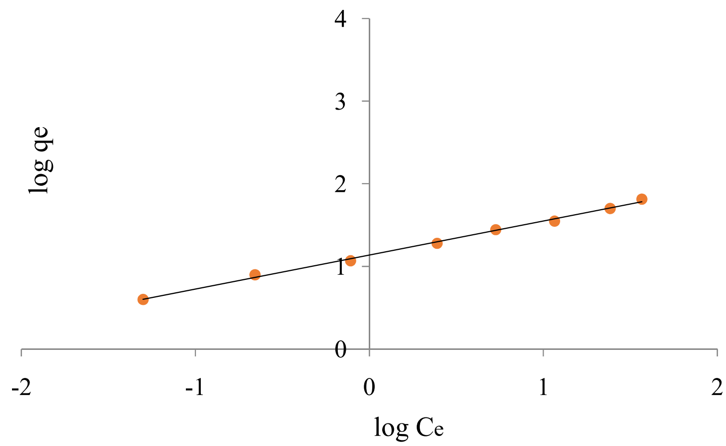

Fig. 2b. Freundlich isotherm models for the adsorption of SMT adsorption onto TTRH

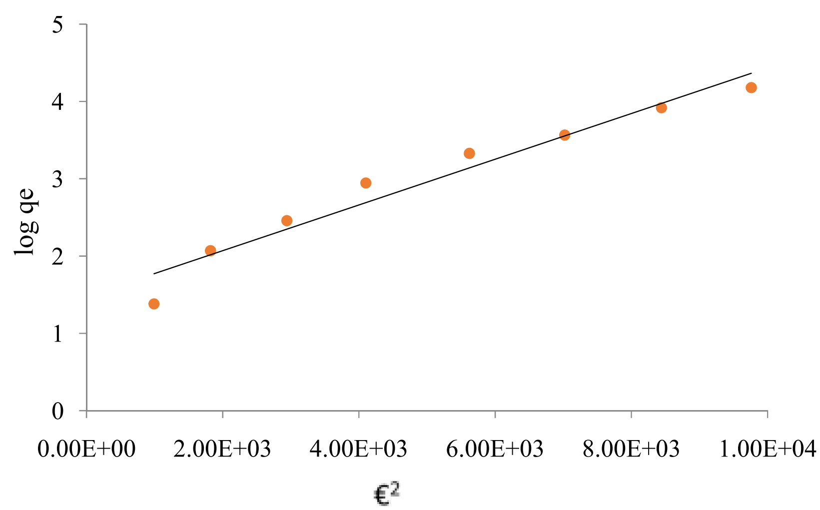

Fig. 2 C. Dubinin–Radushkevich isotherm models for the adsorption of SMT adsorption onto TTRH

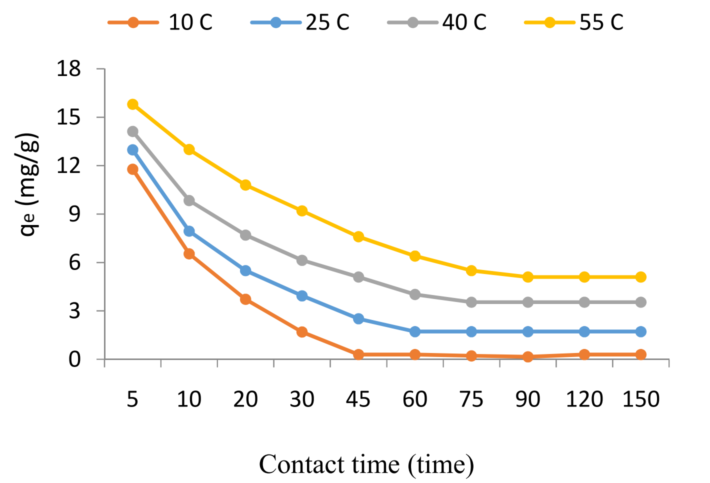

Fig 3. Effect of contact time and temperature on the removal of SMT by TTRH (concentration: 50 mg/L; dose: 2.5 g/L; shaking speed: 180 rpm; pH: 7)

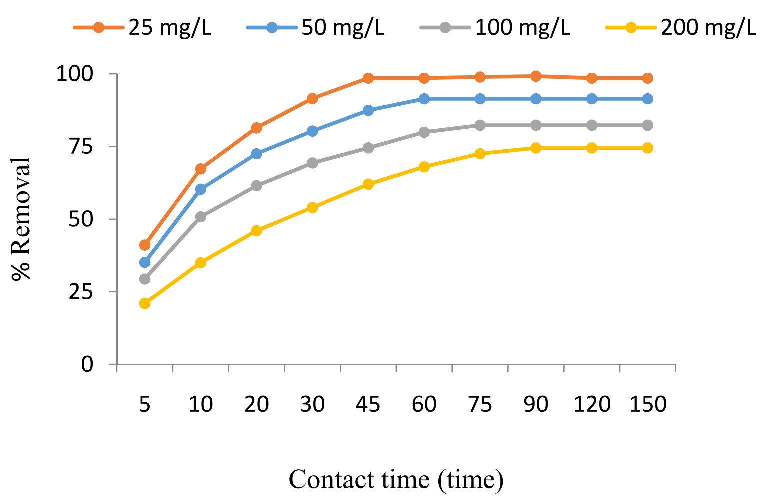

Fig 4. Effect of contact time and concentration on the removal of SMT by TTRH (Temp: 25℃; dose: 2.5 g/L; shaking speed: 180 rpm; pH: 7)

Table 1: Langmuir, Freundlich and Dubinin–Radushkevich Isotherm constants for the adsorption of SMT by TTRH

Langmuir					Freundlich				Dubinin–Radushkevich				
q_m	TTRH	b	R_L	R^2	n	TTRH	K_F	R^2	q_m	TTRH	B ($\times 10^7$ $mol^2 \cdot J^{-2}$)	E	R^2
19.11	1.69	0.029	0.446	0.992	1.84	14.63	3.79	0.972	13.21	26.73	6.25	9.18	0.914

Conclusion: In this paper, investigation of the equilibrium sorption was carried out at 10-55 °C at pH fixed 7. Other physico-chemical parameters were determined and three adsorption isotherm models were studied. The sorption data fitted into Langmuir, Freundlich and

Dubunin–Radushkevich isotherms out of which Langmuir Adsorption model was found to be have the highest regression value and hence the best fit. It could be concluded that rice husk modified with thermally process is a potential and active biosorbent for removal of SMT from its aqueous solution and industrial waste water remediation.

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Conflict of interest: Authors have declared that no competing interests exist.

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