



Water remediation using Rice shell-based activated carbon for removal of Sulfamethoxazole: Error analysis

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Abstract The Rice shell was used as a low cost adsorbent to produce activated carbon (AC) for the removal of sulfamethoxazole (SMZ) from aqueous solution at batch systems. Equilibrium data were fitted to Langmuir, Freundlich, Redlich–Peterson and Sips isotherms. The equilibrium data were best represented by the Langmuir isotherm. maximum monolayer capacity of AC obtained from Langmuir is 78.25 mg/g. The adsorption kinetics was found to be best represented by Pseudo second order kinetic model. Equilibrium and Kinetic Studies further supported by the error analysis functions (ARE, EABS, X² and MSDP), where the pseudo second order Kinetic and Langmuir isotherms has the smallest values. The results indicate that the Rice shell-based activated carbon is a promising low cost technology adsorbent for the removal of antibiotics.

Keywords Sulfamethoxazole, Rice shell, Activated carbon, Adsorption Isotherms, Kinetics

Introduction

In the last decades, the presence of emerging contaminants in different types of water appeared as a new environmental threat which needs to be faced by several governments around the world [1-3]. Among the emerging contaminants found in waters, the class of pharmaceuticals has been detected in surface water and sewage wastewater treatment plants (SWTP) effluents [4-5]. Antibiotics occupy an important place due to the high amounts consumed in both veterinary and human medicine [6-7]. Although the amount of these pharmaceuticals waste in the aquatic environment is low, the accumulation of pharmaceuticals waste constitutes a potential risk for the aquatic and terrestrial organisms at long-term [8-10].

According to statistics, nearly 70% of antibiotics are used in agriculture and animal husbandry and aquaculture every year [11-12]. It is reported that most antibiotics cannot be absorbed and digested well by organisms, about 25–75% of the content outflow *in vitro* in the form of precursor with excrement and urine [13-14]. Studies show that the residual antibiotics in the soil environment can induce the increase of the resistance of the microorganism [15-16].

Removing antibiotics is difficult and requires expensive process. In recent years, there has been an increasing interest to the treatment of pollution generated by drug residues, including antibiotics [17-18]. Physical and physico-chemical techniques have proved their efficiency for this purpose [19]. Amongst the Physical techniques adsorption, flocculation, electro-flocculation, reverse osmosis, ultrafiltration, coagulation have been applied to remove recalcitrant pollutants [20-22]. These most conventional methods are non-destructive and merely transfer pollutants from one phase to the other, which always result in secondary pollution [23].

Adsorption, since it is a non-destructive tertiary process, has been revealed as one of the most advantageous physicochemical technique in wastewater treatment processes [24]. In the research practice, it is very important to find a material showing high binding affinity towards the contaminant, and high selectivity and adsorption capacity properties [25]. Commercial activated carbons possess most of these features, since they show a desirable affinity to hundreds of organic and inorganic compounds. Since the pore diffusion seems to be the controlling mechanism in



activated carbons adsorption, the use of commercial adsorbents is usually associated with high expensive and environmental undesirable regeneration operations [26-29].

In this study, Rice shell was used for activated carbons prepared and applied as a biosorbent to remove SMZ as a target pollutant from aqueous solution. The kinetics and isotherms studies have been performed and the results have been analyzed by applying Error analysis theoretical methods.

Materials and Methods

Materials

The Sulfamethoxazole (99%) were obtained from Sigma-Aldrich Ltd., USA and used as received without any further purification. All the other chemicals were obtained from Merck Co. (Germany). All the chemicals used for the study were of analytical grade. The chemical structure and characteristics of SMZ are presented in Fig 1 and Table 1, respectively. The drug SMZ solution was prepared by dissolving accurately weight SMZ in distilled water to the concentration of 1 g/L. The experimental solutions were obtained by diluting the SMZ stock solution in accurate proportions to needed inlet concentrations.

Preparation of Activated Carbon

Rice shell was washed with hot distilled water to remove dust-like impurities, then dried in an oven at a temperature of 105 °C for 24 h and then crushed and sieved. The chemical activation method 5 g of precursor was impregnated by a certain amount of 40 % weight concentration ZnCl₂ with occasional stirring. The amount of ZnCl₂ solution used was adjusted to give a certain impregnation ratio (weight of activating agent: weight of precursor) of 1:1. After impregnation, the samples were placed for 24 h in an oven at a 105 °C until completely dried. Activation of ZnCl₂ impregnated precursor was carried out into a vertical furnace at a 450 °C and time 2 h under nitrogen flow (300 cm³/min) at a heating rate of 5 °C/min. After the activation, the samples were cooled to the room temperature and then were washed with a 0.05 M HCL solution. Subsequently, the samples were washed sequentially several times with distilled water until the pH of the washing solution reached 6–7. Finally, the samples were dried in an oven at 105 °C for 24 h and pack for further used.

Batch experimental: Initial SMZ solutions with different concentrations were prepared by diluting a SMZ stock standard solution of 1000 mg/L with distilled water. All glassware and plastics used were soaked in 10% (v/v) nitric acid solution for 1 day before being used and then cleaned repeatedly with deionized water. In the adsorption experiment, content of the biosorbent was added to a standard-joint pyrex glass bottle (250 ml) containing 100 ml wastewater sample with concentration 25-200 mg/L and at the desired pH=7. The tube was then shaken at 250 rpm on an electrically thermostatic reciprocating shaker for 75 min at a temperature of 303 K. After equilibrium, the suspension was filtered through 0.45 μm nitrocellulose membrane. SMZ analysis was performed using an Agilent 1200 series HPLC equipped with a C18 column, a UV detector (at wavelength 267 nm), and a methanol/water (50/50 v/v) mobile phase at a flow rate of 0.6 ml/min.

The amount of SMZ adsorbed per gram of AC, q_e (mg/g), was calculated using [30-31]:

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

Where C_0 is the initial SMZ concentration (mg/L), C_e is the equilibrium SMZ concentration (mg/L), V is the volume of SMZ solution used (L), and m is the mass of AC used (g). The percentage removal of the SMZ is represented by [32, 33]:

$$R\% = \frac{C_0 - C_e}{C_0} \times 100$$

Table 1: General characteristics of SMZ

CAS No.	Chemical formula	Molecular weight	pK _{a1} , pK _{a2}	Water solubility
723-46-6	C ₁₀ H ₁₁ N ₃ O ₃ S	400.39 (g/mol)	1.7 and 5.6	281 mg/L

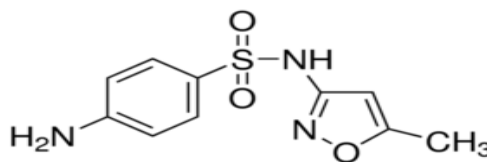


Figure 1: The chemical structures of SMZ



Results and Discussion

Adsorption is a physiochemical process that involves the mass transfer of a solute (adsorbate) from the fluid phase to the adsorbent surface. A study of kinetics of adsorption is desirable as it provides information about the mechanism of adsorption, which is important for efficiency of the process. The applicability of the pseudo-first-order and pseudo-second-order model was tested for the adsorption of SMZ onto AC particles. The best-fit model was selected based on the linear regression correlation coefficient, R^2 , values.

First-order kinetic model

The Lagergren rate equation is one of the most widely used adsorption rate equations for the adsorption of solute from a liquid solution. The pseudo-first-order kinetic model of Lagergren may be represented by [34]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

Integrating this equation for the boundary conditions $t=0$ to $t=t$ and $q=0$ to $q=q_t$, gives(35):

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

Where q_e and q_t are the amounts of SMZ adsorbed (mol/g) at equilibrium and at time t (min), respectively, and k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}). The validity of the model can be checked by linearized plot of $\ln(q_e - q_t)$ versus t . The rate constant of pseudo-first-order adsorption is determined from the slope of the plot.

Second-order kinetic model

The second-order kinetic model is expressed as [36]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

Rearranging the variables in following Eq gives [37]:

$$\frac{dq_t}{(q_e - q_t)^2} = k_2 dt$$

Taking into account, the boundary conditions $t=0$ to $t=t$ and $q=0$ to $q=q_t$, the integrated linear form of Eq. can be rearranged to obtain following Eq [38-39]:

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

The equilibrium adsorption capacity (q_e), and the second-order constants k_2 (g/mol min) can be determined experimentally from the slope and intercept of plot t/q_t versus t .

Error analysis

The model that best fits the equilibrium data was chosen based on the coefficient of determination (R^2) value, fitting of the non-linear regression and error analyses using the average relative error (ARE), sum of absolute error (EABS), chi-square test (X^2), and Marquardt's percent standard deviation (MPSD). The error analysis equations are represented as follows(40-42):

$$\text{ARE} : \frac{100}{n} \sum_{i=1}^n \left| \frac{q_{e,\text{meas}} - q_{e,\text{calc}}}{q_{e,\text{meas}}} \right|_i$$

$$\text{EABS} : \sum_{i=1}^n |q_{e,\text{meas}} - q_{e,\text{calc}}|$$

$$\chi^2 : \sum_{i=1}^n \frac{(q_{e,\text{meas}} - q_{e,\text{calc}})^2}{q_{e,\text{meas}}}$$

$$\text{MPSD} : 100 \sqrt{\frac{1}{n-p} \sum_i \frac{(q_{e,\text{meas}} - q_{e,\text{calc}})^2}{q_{e,\text{meas}}}}$$

Where $q_{e,\text{meas}}$ is the experimental value while $q_{e,\text{calc}}$ is the calculated value, n is the number of data points in the experiment and p is the number of parameters of the model. Smaller values of these error analyses indicate the better curve fitting. The coefficient of determination, R^2 , of the kinetic models as shown in Table1, is highest for the pseudo second order model, with $R^2 > 0.99$, for all four SMZ concentrations, while the Lagergren first order showed R^2 value of 0.925 for 25 mg/L SMZ, and much lower values with at higher concentration. This shows that the pseudo second order model is a better fit for the experimental data than the first order model. This is further supported by the error analysis functions (ARE, EABS, X^2 and MSDP), as listed in Table 2, where the pseudo



second order has the smallest values. The predicted value of q_e for the pseudo second order is very close to the experimental q_e , whereas the Lagergren first order predicted a value much lower than experimental q_e (Table 2). Hence, taking consideration of the R^2 , Error analysis functions and the value of the predicted q_e , it can be concluded that the pseudo second order model is the best fit model to predict the behaviour for the adsorption process and the adsorption process appeared to be controlled by chemical process.

Table 2: Parameters of kinetics models and their error analysis

Lagergren first order					Pseudo second order				
C_0 (mg/L)	25	50	100	200	C_0 (mg/L)	25	50	100	200
q_{ecal} (mg/g)	9.75	15.29	28.47	61.24	q_{ecal} (mg/g)	11.24	19.46	34.75	71.32
q_{exp} (mg/g)	11.46	20.74	37.61	73.46	q_{exp} (mg/g)	11.46	20.74	37.61	73.46
K_1	0.412	0.118	0.095	0.081	K_2	0.044	0.025	0.012	0.0072
R^2	0.925	0.894	0.876	0.852	R^2	0.998	0.994	0.996	0.997
X^2	19.4	21.95	18.5	14.6	X^2	8.55	8.24	11.5	7.46
EABS	11.8	18.1	21.7	18.9	EABS	9.73	7.11	4.79	8.44
ARE	14.6	19.5	14.6	21.7	ARE	14.58	10.73	8.46	11.65
MSDP	18.7	24.8	22.6	17.49	MSDP	6.89	8.44	11.25	9.84

Adsorption isotherms

Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms. Three adsorption isotherm equations were used in the present study namely, Langmuir, Freundlich, Redlich–Peterson and Sips. The applicability of the isotherm models to the adsorption study done was compared by judging the correlation coefficients values. The linear forms of the Langmuir isotherms are represented by the following equations [43-44]:

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

Where C_e is the equilibrium concentration (mg/L), q_{max} is the monolayer adsorption capacity (mg/g) and K_L is the constant related to the free adsorption energy (Langmuir constant, L/mg).

The Langmuir isotherm is based on the assumptions that the adsorption is monolayer and takes place at specific homogeneous sites on the adsorbent, where no further adsorption can occur when a site is occupied with adsorbate. The separation factor (R_L) is a dimensionless constant which is an essential indication of the Langmuir model. It is given by the following equation [45-46]:

$$R_L = \frac{1}{1 + K_L C_0}$$

Where C_0 (mg/L) is the highest initial SMZ concentration, and R_L indicates whether the Langmuir isotherm is either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

The Freundlich isotherm model takes account of multilayer coverage where adsorption is still possible on the adsorbate-saturated adsorbent's surface. It is applicable for adsorption on heterogeneous surfaces with uniform energy distribution and reversible adsorption. The linear forms of the Freundlich isotherms are represented by the following equations [45]:

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

Where K_F is a constant indicative of the adsorption capacity of the adsorbent (mg/g) and the constant $1/n$ indicates the intensity of the adsorption.

The Sips isotherm is a combination of the Langmuir and Freundlich expressions and is useful to predict heterogeneous adsorption systems as well as to overcome the limitation of the increasing concentration associated with the Freundlich isotherm model. The linear forms of the Sips isotherms are represented by the following equations [47]:

$$\ln\left(\frac{q_e}{q_m - q_e}\right) = K_F \ln C_e + \ln K_S$$

Where K_S (L/g) and K_F are Sips constant and Sips exponent, respectively.

The Redlich–Peterson isotherm is a parameters model that can be used to represent adsorption equilibrium over a wide range of concentrations and due to its versatility. This model can be applied to either homogeneous or heterogeneous systems. Like The Sips model, it incorporates both elements from the langmuir and freundlich equations. The linear forms of the Redlich–Peterson isotherms are represented by the following equations [48]:

$$\ln\left(K_R \frac{C_e}{q_e} - 1\right) = \beta \ln C_e + \ln \alpha_R$$



Where K_R (L/g) and a_R (L/mg) are the R–P constants, while b is the R–P exponent.

Isotherm model parameters are obtained by determining the slope and intercept of the irrespective linear plots as shown in Table 2. Comparing the R^2 values, The Langmuir has the highest value followed by the R–P, Sips and Freundlich which suggests Langmuir yielded better fit than the other data. From Error analysis, it can be seen that in general, the R–P has the lowest values of error followed by Langmuir, Freundlich and Sips. From these comparisons, it can be said that the Langmuir model is the best fit to the experimental data.

Table 2: Parameters of isotherm models and their error analysis

	Langmuir	Freundlich		R–P		Sips	
q_m (mg/g)	78.25	K_F (mg/g)	7.862	K_R (L/g)	36.4	q_m (mg/g)	91.56
K_L	0.175	$(L/mg)^{1/n}$		β	0.724	K_S (L/mg)	0.225
R_L	0.102	n	3.25	α_R (L/mg)	1.125	K_F	0.465
R^2	0.998	R^2	0.812	R^2	0.958	R^2	0.924
X^2	11.25	X^2	22.4	X^2	9.45	X^2	11.25
EABS	8.42	EABS	25.8	EABS	8.12	EABS	14.85
ARE	6.78	ARE	17.75	ARE	4.65	ARE	12.6
MSDP	9.12	MSDP	14.64	MSDP	7.79	MSDP	9.95

Conclusion

Low cost activated carbon prepared from Rice shell by $ZnCl_2$ treatment, was used as an eco friendly adsorbent for the removal of a sulfamethoxazole from aqueous solution at a Batch adsorption experiments. The kinetics of adsorption process was investigated using pseudo first order kinetic model and pseudo second order kinetic model. The results showed that the adsorption process followed pseudo second order kinetic model. Equilibrium data was fitted to the Langmuir, Freundlich, Redlich–Peterson and Sips adsorption isotherm models and isotherm constants were determined. The equilibrium data were best fitted by the Langmuir isotherm model than other model.

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