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Original Research Article

Removal of Cadmium from Wastewater using Rice Husk Activated Carbon

***[1]Adamu, A., [1]Adie, D.B., [1]Okuofu, C.A. and [2]Giwa, A.**
[1]Department of Water Resources and Environmental Engineering, Ahmadu Bello University, Zaria, Nigeria.
[2]Department of Textile and Polymer Engineering, Ahmadu Bello University, Zaria, Nigeria.
*adamualiyu@abu.edu.ng

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ABSTRACT

The availability of significant quantities of rice husk in the environment and the pollution they generate is disturbing, hence the need to put them to a useful application. Rice husk activated carbon was produced using both thermal and chemical methods. The rice husk was subjected to carbonization temperature of 400 ^oC for a period of 1 hour in an electric furnace. It was then impregnated with 1M tetraoxophosphate (V) (H_3PO_4) in a ratio of 2:1 for a period of 3 hours. Batch adsorption study was conducted using adsorbent dosage of 1-5g, initial cadmium concentration of 5-25mg/l, shaking time of 0-120 mins, solution pH of 2-10 and temperature of 30-50 ^oC. The results showed that the optimum dosage was 3g while the initial cadmium concentration, shaking time, pH and temperature were 25 mg/l, 10 mins, 6 and 30 ^oC, respectively. The adsorption isotherm investigation revealed that the adsorption process followed Freundlich, Duvinin Radushkevich and Temkin models with corresponding R^2 values of 0.9468, 0.9468 and 1.0000, respectively. The adsorption kinetics followed intra particle diffusion model with R^2 value of 1.0000. The adsorption thermodynamic data obtained indicated that the adsorption process was exothermic. It was concluded that rice husk can be effectively used for the production of activated carbon and its application for cadmium removal from wastewater was also efficient.

1. INTRODUCTION

Rice is ranked as the third most significant cereal crop and is grown in many countries in the world (Song *et al*., 2011; Mohammed, 2015). Rice husk is the by-product left after the paddy rice has been processed and it serves as protective shell for the rice grain. It has been reported that about 20% of the paddy rice is composed of rice husk, meaning that every 1000kg of the paddy rice produces 200kg of rice husk. The chemical constituents of rice husk are: 32.2% cellulose, 21.3% hemicelluloses, 21.4% lignin, 8.1% water, 1.8%

extractives and 15.1% mineral ash; in which the mineral ash contains about 94 – 97% silica (Mohammed, 2015).

Currently, several researches have been conducted on the use of agricultural by-products that are readily found in the environment, because they are cheap in processing, environmentally friendly for the adsorption of heavy metals and other pollutants present in wastewater (Martincigh *et al.*, 2013). This could be attributed to the fact that the commercial activated carbons are expensive coupled with their regeneration difficulty, hence researches are tilted towards the use of agricultural waste to produce a low cost activated carbon.

Cadmium is one the most toxic heavy metals found in the environment as well as industrial effluents. It could lead to many health challenges such as: hypertension, kidney failure, spoiling of red blood cells, lung failure, cancer, destruction of bones and testicular tissues (El Said *et al.,* 2012; Niu *et al.,* 2014).

The aim of this research is to produce activated carbon from rice husk and use it in the removal of cadmium from simulated wastewater using batch adsorption method.

2. MATERIALS AND METHODS

2.1. Materials

The materials employed in this research are grouped into: glassware, chemical reagents as well as equipments or apparatus (Table 1).

Table 1: Materials used in the study

Glassware	Chemical reagent	Equipment/apparatus
Measuring cylinder (50, 100 and 1000ml), Pipette (25ml) and 250 ml conical flask.	Distilled water, de-ionized water, 0.1M NaOH, 0.1M HCl, 1M H_3PO_4 all of analytical grade.	Electrical weighing balance (Mettler P160N), electric furnace, centrifugation machine, magnetic stirrer, pH meter (Pocket size, Hanna), Atomic Absorption Spectroscopy (AA6800 Shimadzu), Membrane micro filter (0.45µm), Whatman filter paper, 30 mesh sieve (0.60mm)

2.2. Methods

2.2.1. Collection and preparation of rice husk

The rice husk was collected from local millers at Zaria City market, in Zaria Local Government Area of Kaduna State, Nigeria. The rice husk was severally washed with tap water followed by distilled water to remove impurities and then placed into electrical oven where it was oven dried overnight at 100^{o}C (Gaikwad and Mane, 2013; Mohammed, 2015). It was grinded using an electric blender and then sieved using standard sieve test (30 mesh sieve).

2.2.2. Production of rice husk activated carbon

The prepared rice husk was then placed into an electrical furnace and heated to a carbonization temperature of 400 ^{o}C at a heating rate of 10^{o}C/min for a residence time of 1 hour. The carbonized rice husk was impregnated with concentrated H_3PO_4 (1M) at the ratio of 2:1 and stirred continuously for period of 3 hours (Pradhan, 2011; Mohammed, 2015). It was then filtered with whatman filter paper and washed thoroughly

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with distilled to remove excess acid until the pH was 7. It was then placed into the oven and dried at a temperature of 100ºC for the period of 4 hours.

2.2.3. Preparation of stock solution of cadmium

The stock solution of cadmium (100mg/l) was prepared by dissolving 0.2774g of cadmium trioxonitrate (V) tetrahydrate ($Cd(NO_3)_2.4H_2O$) in 10ml of 0.1M trioxonitrate (V) acid (HNO_3) in a 1000ml volumetric flask. De-ionized water was added to make it 1000ml. From this, working solutions of 5mg/l, 10mg/l, 15mg/l, 20mg/l and 25mg/l of cadmium were prepared through dilution of the stock solution.

2.2.4. Determination of BET surface area and surface morphologies

The surface functional group for the rice husk activated carbon was obtained using Fourier transform infrared spectroscopy (FTIR-8400S, Shimadzu); while the BET surface area and pore size were obtained using gas sorption analyzer (NOVA 4200e Quantachrome). The rice husk activated carbon was initially degassed within the vacuum at temperature of 200ºC for 3 hours before measurement. The nitrogen gas had been used as the analysis gas and the adsorption - desorption data had been recorded at the liquid nitrogen temperature of 77.35K at the equilibrium time of 60 seconds.

2.2.5. Batch adsorption of cadmium onto rice husk activated carbon

The batch adsorption was carried out by placing 1.0, 3.0 and 5.0g of rice husk activated carbon into 250 ml flask containing 100ml of: 5, 10, 15, 20 and 25mg/l of cadmium solution and agitated continuously in a magnetic stirrer at the speed of 150rpm. In addition, 10ml of cadmium solution was withdrawn at shaking times of: 10, 30, 60, 90 and 120mins, respectively. It was then centrifuged at 2000rpm for 20 minutes and then allowed to decant for about 30 minutes after which the cadmium was extracted and the residual cadmium concentration was analyzed using Atomic Absorption Spectrophotometer (AA 6800). This experiment was also carried out at pH values of 2, 4, 6, 8 and 10 and process temperatures of 30, 40 and 50 ºC at the optimum conditions.

3. RESULTS AND DISCUSSION

Figures 1 and 2 showed the SEM micrographs of the raw rice husk and rice husk activated carbon, respectively. From Figure 1, it can be observed that the raw rice husk possessed little pores which could be attributed to non-carbonization. In view of this, moisture contents as well as volatile matters occupied most pores (Mohammad, 2015). In Figure 2, it could be observed that unlike in Figure 1, there was significant improvement in the pores present after the production of rice husk activated carbon. The improvement in the pores could be attributed to the removal of moisture content as well as volatile matter that initially occupied the pore spaces as a result of the carbonization of the rice husk (Mohammad, 2015). This could also translate into increase in the adsorptive performance of the rice husk activated carbon.

Table 2 shows the characteristics of the rice husk activated carbon. The Table indicates the surface area, micro pore volume, average pore diameter and pH of the rice husk activated carbon. From the Table, the surface area, micro pore volume, average pore diameter, pH moisture content and Ash content of: 1730.53m^2/g, 0.766cm^3/g, 5.349nm, 7.3, 3.30 and 3.88, respectively were obtained for rice husk activated carbon produced. Meanwhile, the possession of average pore diameter of 5.349nm also signified that it is mesoporous.

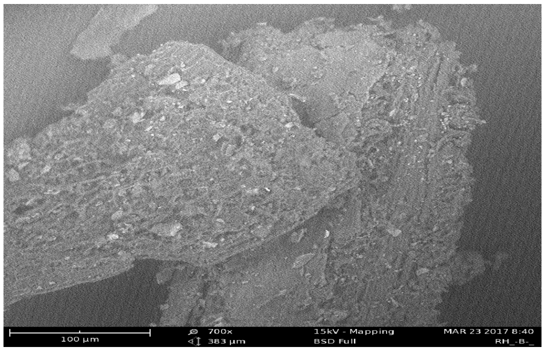

Figure 1: SEM micrograghs for raw rice husk

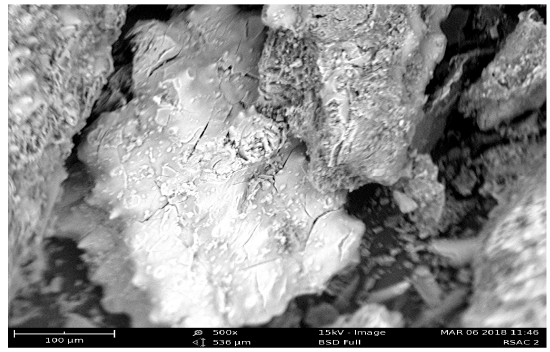

Figure 2: SEM micrograghs for rice husk activated carbon

Table 2: Characteristics of the rice husk activated carbon

Characteristics	Results
Surface area (m^2/g) single point BET	1338.00
Surface area (m^2/g) multi point BET	1730.53
Micro pore volume (cm^3/g)	0.766
Average pore diameter (nm)	5.349
pH	7.3
Moisture content (%)	3.30
Ash content (%)	3.88

Figures 3 and 4 show the effect of initial cadmium concentration on adsorption capacity and removal efficiency of cadmium onto rice husk activated carbon. From Figure 3, when the initial cadmium concentration increased from 5 to 25mg/l, the adsorption of cadmium also increased 0.4963 to 2.4926mg/g for the constant adsorbent dosage of 1.0g. Similarly, for the constant adsorbent dosages of 3.0 and 5.0g, the adsorption of cadmium increased from 0.1651 to 0.8319mg/g and 0.0991 to 0.4990mg/g, respectively when the initial cadmium concentration increased from 5 to 25mg/l. The increase in the adsorption capacity with increase in the initial cadmium concentration could be due the fact that a rise in the initial adsorbate concentration translates into a rise in the driving force to overcome the resistance of the solute transfer and such increased the adsorption of cadmium. This observation was also reported by Mohammed (2015) and Mopoung et al. (2015).

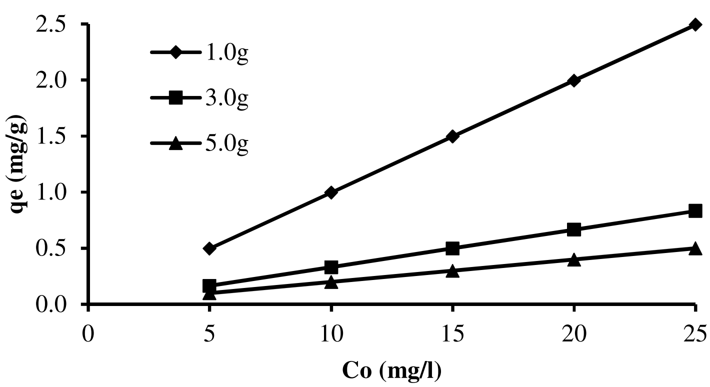

Figure 3: Effects of initial cadmium concentration on adsorption capacity

In Figure 4, when the initial cadmium concentration increased from 5 to 25mg/l, the removal efficiency also increased from 99.26 to 99.70%, 99.06 to 99.83% and 99.14 to 99.80%, respectively for the constant adsorbent dosage of: 1.0, 3.0 and 5.0g, respectively. The increase in the removal efficiency of cadmium onto the rice husk activated carbon could be attributed to the presence of multilayer adsorption, in which a solute could be absorbed in a layer that is already occupied by another solute. This observation was also reported by Mohammed (2015).

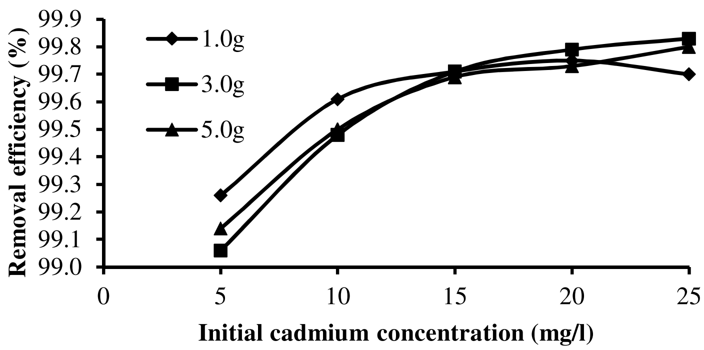

Figure 4: Effects of initial cadmium concentration on removal efficiency

Figures 5 and 6 show the effects of adsorbent dosage on adsorption capacity and removal efficiency at constant initial cadmium concentrations of 5, 15 and 25mg/l, respectively. From Figure 5, it could be seen that when the adsorbent dosage increased from 1.0 to 5.0g, the adsorption capacity also decreased from 0.4963 to 0.0991mg/g, 1.4957 to 0.2991mg/g and 2.4926 to 0.4990mg/g, respectively for fixed initial cadmium concentrations of 5, 15 and 25mg/l. This could be attributed to the fact that increase in adsorbent dosage at constant cadmium concentration results into a decrease in the ratio of solute to adsorbent in solution, which in turn decreased the amount in which a unit mass of the adsorbent adsorbs from solution. This result in agreement with Mohammed (2015) and Parate and Talib (2015).

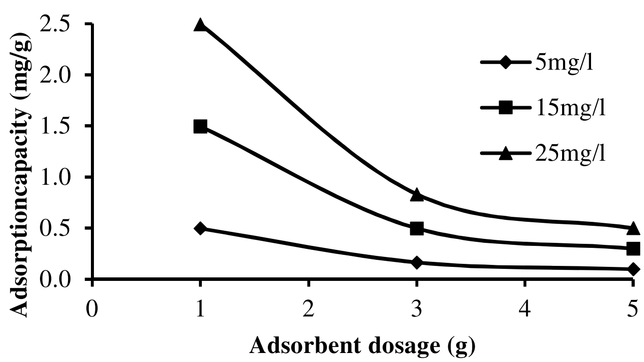

Figure 5: Effects of adsorbent dosage on adsorption capacity

In Figure 6, the increase in the adsorbent dosage was accompanied with the increase in the removal efficiency. This could be attributed to the fact that, increase in the sorption sites that become available for removal of solute from the aqueous solution. However, the removal efficiency was more pronounced at higher initial cadmium concentration. In addition, for initial cadmium concentrations of 5 and 15mg/l, the optimum dosage recorded was 1.0 g, in which 99.26 and 99.71% of cadmium ion, respectively were removed after which there was no appreciable change in the removal efficiency which could be related to saturation. However, at the initial cadmium concentration of 25mg/l, the removal efficiency of cadmium increased from 99.70 to 99.80%. This result is in agreement with Ali and Abdel-Satar (2017); Mohammed (2015).

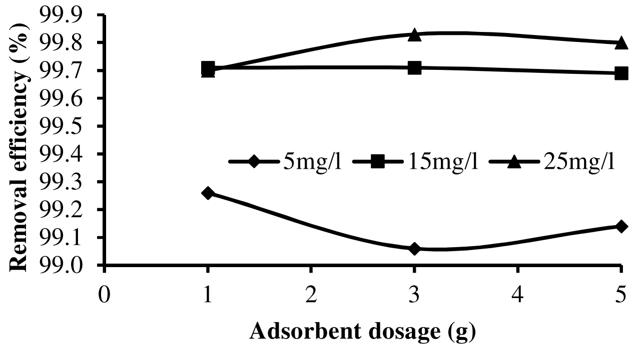

Figure 6: Effects of adsorbent dosage on removal efficiency

Figures 7 and 8 depict the effect of contact time on the adsorption capacity and removal efficiency of cadmium onto rice husk activated carbon. From the Figures, it could be noticed that the adsorbent dosages were kept constant at 1.0, 3.0 and 5.0g while the contact time was varied from 0 to 120 mins. In addition, the maximum adsorption capacity and removal efficiency of 2.4911mg/g and 99.644%, respectively were achieved within 10 mins of contact time as shown in the Figures. The adsorption of cadmium was very rapid at the initial stage due to the availability of vacant sorption sites which reduced as the contact time increase until an optimum time was reached after which there was no appreciable increase in the adsorption capacity and removal efficiency. This result agrees with the observations of Mohammed (2015) and Galleti et al. (2012).

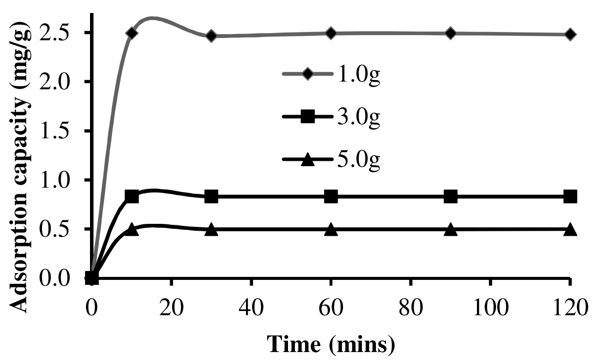

Figure 7: Effects of contact time on adsorption capacity

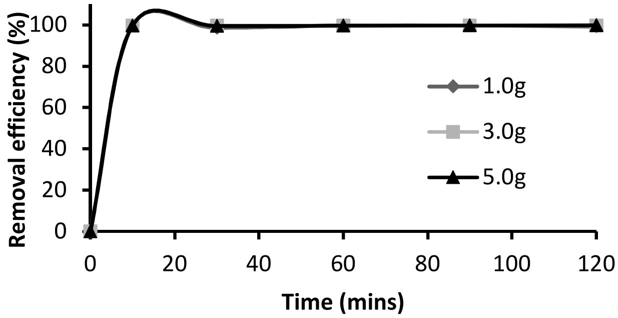

Figure 8: Effects of contact time on removal efficiency

Figures 9 and 10 showed the effect of pH on the adsorption capacity and removal efficiency of cadmium onto rice husk activated carbon. From Figure 9, it could be noticed at the solution pH of 2, the adsorption capacity recorded a value of 2.4989mg/g, but increased to 2.4990mg/g when the pH increased to 4 after which the maximum adsorption capacity of 2.4992mg/g was obtained at pH of 6. This could be attributed to the fact at very low pH; the hydrogen ion in the aqueous solution competes with the metal ion in the sorption sites thereby decreasing adsorption of the metal ions by the adsorbent. Similarly, at higher pH, there are more hydroxyl ions in the aqueous solution which neutralized the hydrogen ions, thereby enhancing the adsorption of the metal ions. This result is in agreement with those of Ali and Abdel Satar (2017) and Mas Haris et al. (2011).

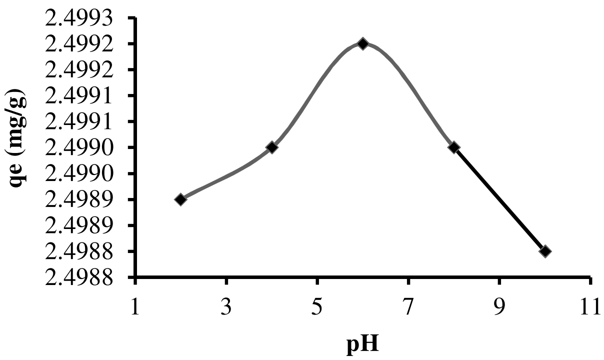

Figure 9: Effect of pH on adsorption capacity

In Figure 10, the removal efficiency increased with the increase in pH until an optimum value of 99.969% was obtained at pH of 6 after which the removal efficiency declined at pH of 8 and 10. The removal efficiencies recorded at pH values of: 2, 4 and 6 were: 99.955, 99.960 and 99.969%, respectively. This implied that the optimum pH for the removal of cadmium from the aqueous solution was 6.

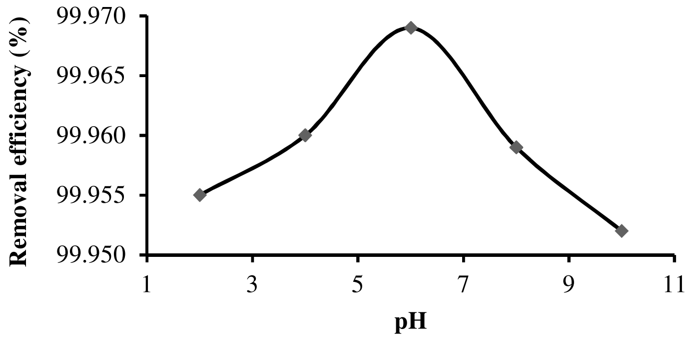

Figure 10: Effect of pH on removal efficiency

Figures 11 and 12 depict the effect of process temperature on the adsorption capacity and removal efficiency of cadmium onto rice husk activated carbon. From the Figures, it could be noticed that the adsorption capacity and removal efficiency decreased with rise in the process temperature signifying that the adsorption process was exothermic. However, when the process temperature increased from 30 to 50^oC, the adsorption capacity and removal efficiency decreased from 2.4988 to 2.4987mg/g and 99.952 to 99.948%, respectively.

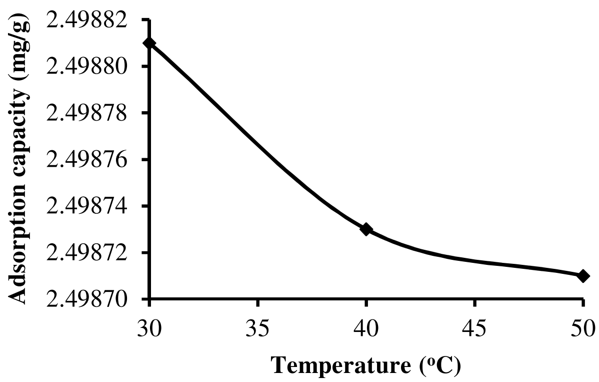

Figure 11: Effect of operating temperature on removal efficiency

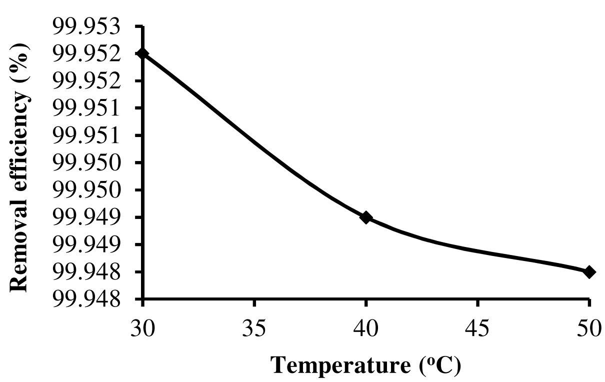

Figure 12: Effect of operating temperature on removal efficiency

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Table 3 shows the adsorption isotherm data for the Langmuir, Freundlich, Temkin and D-R adsorption isotherms. From the Table, it could be observed that the Langmuir, Freundlich, Temkin and D-R isotherms recorded R^2 values of: 0.6534, 0.9468, 1.0000 and 0.9468, respectively implying that the adsorption data fitted well to Freundlich, Temkin and D-R isotherms than the Langmuir isotherm. However, both Freudlich and D-R isotherms recorded the same maximum adsorption capacity value of 0.4000mg/g. More so, the D-R model recorded mean free energy value of 1.1291kJ/mol, implying that the adsorption process was physical adsorption; while 1/n value of 0.1704 indicated by the Freundlich isotherm implied normal and favourable adsorption. In addition, according to Itodo and Itodo, (2010), a free energy of less than 8kJ/mol implied a physical adsorption. On the other hand, the temkin isotherm indicated temkin adsorption potential value of 0.9954l/mg and heat of sorption values of 0.4992J/mol.

Table 3: Adsorption isotherm data

Isotherm model	Parameters	Values
Langmuir isotherm	b (l/mg)	-0.1473
	q_m (mg/g)	96.153
	R^2	0.6534
Freundlich isotherm	1/n	0.1704
	k_f (mg/g)	0.4000
	R^2	0.9468
Temkin isotherm	At (l/mg)	0.9954
	Bt (J/mol)	0.4992
	b	4963
	R^2	1.0000
D-R isotherm	$-B_D$ (mol^2/kJ^2)	0.3922
	q_m (mg/g)	0.4000
	E (kJ/mol)	1.1291
	R^2	0.9468

The adsorption kinetic data are shown in Table 4. It could be observed that the adsorption kinetic followed intra particle diffusion with R^2 of 1.0000.

Table 4: Adsorption kinetic data

Kinetic model	Parameters	Values
Pseudo-first order	K_1 (min^{-1})	0.0048
	q_e (mg/g)	0.0033
Pseudo-second order	R^2	0.0236
	K_2	85.351
	qe (mg/g)	2.4832
Intra particle diffusion	R^2	1.0000
	K_{id} ($mgg^{-1}h^{1/2}$)	0.0002
	C	2.4821
	R^2	0.0016

In Table 5, the enthalpy change (ΔH) recorded was a value of -3.412kJ/mol, revealing that the batch adsorption process was exothermic. In addition, the enthalpy change also suggested that adsorption process was physical as also reported by Rahman and Sathasivam, (2015). In addition, the change in entropy (ΔS) recorded was a positive value of 0.0331 kJ/mol, which suggested increased degree of freedom of the cadmium molecule coupled with increase in affinity at the solute-adsorbent interface as reported by Chowdhury *et al.,* (2015) and Zhang *et al.* (2017). The negative value of ΔG implied that the batch adsorption process was spontaneous and feasible. This observation was also reported by Purkait *et al.* (2007) and Zhang *et al.* (2017).

Table 5: Adsorption thermodynamics data

T (K)	1/T (K^{-1})	ln k (g/l)	∆G (kJ/mol)	∆S (kJ/mol)	∆H (kJ/mol)
303	0.00330	2.871	-13.454	0.0331	-3.412
313	0.00319	2.292	-13.786	0.0331	-3.412
323	0.00310	1.749	-14.117	0.0331	-3.412

4. CONCLUSION

Based on the production of activated carbon from rice husk and the batch adsorption studies carried out on the adsorption of cadmium, it can be concluded that the rice husk was successfully used in the production of low cost activated carbon. The result obtained revealed that the optimum dosage for cadmium removal was 3g; while the optimum initial cadmium concentration, shaking time, pH and process temperatures were 25 mg/l, 10mins, 6 and 30 ^{o}C, respectively. Similarly, the adsorption isotherm study revealed that the adsorption process followed Freundlich, Duvinin Redushkevich and Temkin models with corresponding R^2 values of: 0.9468, 0.9468 and 1.0000, respectively while the adsorption kinetics followed intra particle diffusion with R^2 values of 1.0000. Moreover, the adsorption thermodynamic data obtained indicated that the adsorption process was exothermic, signifying that the adsorption of cadmium decreased with increasing in the process temperature and the adsorption process was physical.

5. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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