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DEVELOPMENT OF ADSORBENTS FROM RICE HUSK FOR CESIUM REMOVAL FROM SIMULATED WASTE WATER USING CENTRAL COMPOSITE DESIGN

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ABSTRACT

This paper deals with the production of adsorbents and adsorption studies for the uptake of Cesium (Cs) ions from aqueous solutions using carbonized rice husk composite as adsorbent. The carbonized rice husk and surface properties of the adsorbent were characterized by Scanning Electron Microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and Brauner Emmet and Teller (BET) analyzer. Central Composite Design (CCD) was used to optimize the process variables such as initial metal ion concentration, Contact time, adsorbent dosage and pH of the solution on the performance of percentage removal and adsorption capacity. The experimental data were validated with different isotherms and kinetic models to assess the solute interaction behavior and nature of adsorption. The maximum adsorption capacity for (a) rice husk (8.03mg/g) and impregnated rice husk (b) (13.58 mg/g) adsorbents were fully evaluated. Revealing the reliability and suitability of the optimization approach .In addition, the results of isotherm study show that the Langmuir model can be used to best describe the adsorption behavior of Cs on to the rice husk and impregnated rice husk composite s adsorbents.

Keywords: *Central composite design, Impregnation, Cesium, adsorption, adsorbent, Concentration***.**

INTRODUCTION

Cesium (Cs) is one of the most active components and a significant contributor to the heat in high-level radioactive liquid waste. It has attracted great attention due to its long half-life of 30.17 years, high energy gamma ray emission and high solubility in water (Youli *et al.*, 2017). Because of the chemical similarity of Cs to Potassium, it can be easily incorporated into terrestrial and living organisms where it is deposited in the soil tissues, leading to cancer. (Youli *et al.*, 2017). Hence, development of an efficient and economical removal method is principal for the removal of Cesium from waste water

in view of the environmental risks. To date, various methods have been proposed for removal of radio Cesium from wastewater, the most main used are solvent extraction, chemical precipitation and adsorption method. Transition metal (Cu, Fe, Ni, Zn and Co) hexacyanoferrates are considered to be one of the inorganic adsorbents for selective recovery of cesium from wastewater. Among them, Potassium Copper hexacyanoferrate$KCu[Fe(CN)_6]$ is chosen as the agent in practical application. Due to its availability in powdery and granular form compared to other metal hexacyanoferrates. Among these methods, adsorption has been proved to be an excellent way to treat wastewater, offering significant advantages, like the low-cost, availability, profitability, easy operation, and efficiency (Yang, *et al*. 2013).0ptimisation of the process variables is needed to achieve the maximum adsorption capacity and removal efficiency. RSM, a statistical experimental design provides statistical models, helps in understanding the interactions among the factors that have been optimized and also reduces the number of experiments. Central composite design (CCD) is a useful method to optimize the responses shaped under the influence of process variables (Abdullah *et al.* 2009; Martin- Lara *et al.* 2011; Cronje *et al.* 2011; Singh *et al*. 2011; Park *et al*. 2011).Hence, in this present study rice husk was chosen as the precursor for carbonization and Impregnation was done using Potassium Copper hexacyanoferrate, Adsorption studies were performed using rice husk and rice husk activated carbon composites for the removal of Cs ions from aqueous solutions. Adsorption isotherms were established to explain the mechanism. Kinetic models were used to determine the rate and order of the adsorption process. The optimization of process variables was done using four factor central composite experimental designs combined with Response Surface Methodology. When compared to other similar adsorption studies, the novelty of using RSM in this work is to reduce the number of experiments, to study the effect of factor interactions and to develop the statistical mathematical model equation, to identify optimum conditions where the high uptake capacity was obtained for the removal of Cs ions using rice husk adsorbent, to ensure the high uptake capacity at low adsorbent dosage and high metal ion concentration of Cs ions using rice husk adsorbent and to reduce the uptake period.

MATERIALS AND METHODS

Materials

Raw rice husk was sourced from ABU farms shika. The Chemicals used in this study such as Potassium hexacyanoferrate and Copper tetraoxosulphate (vi) pentahydrate, Phosphoric acid,Sodium hydroxide,$CsNo_{3,}$etc., were purchased from Cardinal Scientific Supplies Zaria, Nigeria. Distilled water was used to prepare all the solutions

Methods

Rice husk was heated to 400 ^oC at the rate of 10^oC/min for about four hours under Nitrogen atmosphere and then cool down to room temperature at the same rate. This is labeled as pre-carbonized carbon (PCC). The pre-carbonized carbon was then subjected to chemical activation. In chemical activation process 50g of the pre-carbonized material was agitated with 250g of aqueous solution containing 85% H_3P0_4 by weight. The ratio of chemical activating agent pre-carbonized carbon was fixed at 4.2.The chemical activant and pre-carbonized carbon were homogeneously mixed at 85% for 4 hours in a mixer. After mixing, the pre-carbonized carbon slurry was dried under vacuum at 110 ^oC for 24 hours. The resulting samples were then activated in a vertical cylindrical furnace under Nitrogen N_2 at a flow rate of 100mL/min. This is followed by heating to 800 ^oC to optimize the heat treatment. This was done at a heating rate of 5^oc /min and it was then maintained at a constant temperature for one hour before cooling. After cooling, the activated carbon was washed successively for several times with distilled water until pH becomes neutral. The washed sample was dried at 110 ^oC to obtain the final product(G. Sekaran *et al.,* 2011)

Preparation of impregnated rice husk composite adsorbent

Activated carbon from rice husk with particle size (355µm) was treated with H_3P0_4 (15M) for 24hr at room temperature, washed with distilled water until the pH was found to be neutral, followed by air drying at 90 ^oC .The pretreated activated carbon (1g) was impregnated with $10cm^3$ solution of $CuSO_4$ (0.5M) under Vacuum condition for 4hr. The supernate was decanted, and $5cm^3$ solution of $k_4[fe(CN)_6]$(0.5M) was added drop-wise under agitation at room temperature. The obtained reddish-brown slurries were aged at 353 K for 12hr, then washed with distilled water, filtered using a Buchner funnel with suction, followed by being dried in the air at 373 K for 4hr. (Wang *et al*., 2014)

Characterization of the adsorbent

Surface area analysis. Surface morphology and functional groups were determined using BET, SEM and FTIR

Adsorption Experiment

The stock solutions was diluted appropriately to get the working solution; these solution was mixed as shown in the design of experiment matrix. The pH of the solution was adjusted to the required value using 0.01M HCl and 0.01M NaOH, the appropriate mass of the adsorbent was added to the solutions after which the mixture was loaded on a mechanical shaker and shaken for the required contact time at constant speed of 250rpm at room temperature of 27^oC.The batch adsorption experiment were conducted to investigate the effect of initial concentration, adsorbent dosage, contact time and pH. After shaking, the mixture was then filtered with a filter paper and the residual concentrations of Cesium in the mixture was determined using Microwave plasma atomic emission spectrophotometer.

The percentage removal of Cesium was calculated using the expression below:

$$\%Removal\ or\ adsorption\ efficiency = \frac{C_o - C_t}{C_o} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{(i)}$$

Where: C_0= Initial concentration of Cesium

C_t= Concentration of Cesium after shaking for time, t

The gram of a particular metal adsorbed per unit gram of adsorbent otherwise known as adsorption capacity after a given time was calculated using the expression below:

$$q_t = \frac{(C_o - C_t)V}{W} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \text{(ii)}$$

Where: V= Volume of the solution

W= Mass of the rice husk adsorbent

Central composite design (CCD)

The CCD was applied in this present study to determine the optimum process variables for adsorption of Cs ions using rice husk adsorbents. The CCD was used for fitting a second-order model which requires only a minimum number of experiments for modeling (Tanyildizi 2011; Ahmad *et al*. 2009). Basically the optimization process involves three major steps: (1) performing the statistically designed experiments, (2) estimating the coefficients in a mathematical model, and (3) predicting the response and checking the adequacy of the model (Sahu*et al.* 2009; Kumar *et al*. 2009). An empirical model was developed to correlate the response to the adsorption process and is based on second order quadratic model for removal of Cs ions using (a) Rice husk (b) Impregnated rice husk adsorbents (Bashir *et al.,* 2010)

RESULTS AND DISCUSSION

Characterization of adsorbents

The prepared adsorbents were characterized by BET, SEM, and FTIR analysis.

BET and SEM analysis; The specific surface area, pore volume and pore width of the rice husk and impregnated rice husk were found to be (1779.80 m^2/g, 610.75 m^2/g.) (0.62 cm^3/g, 0.24 cm^3/g) and (6.5 nm and 5.83 nm).The surface morphology of the rice husk and impregnated rice husk adsorbents were observed using SEM. The images are given in figure 1.the images indicated that the adsorbents of the rice husk had an irregular and hollow cavity surface while the impregnated rice husk surface morphology indicated highly porous surface which leads to better uptake removal of metal ions. While the SEM image after adsorption shows a clear metal crystals of Cesium on the surface.

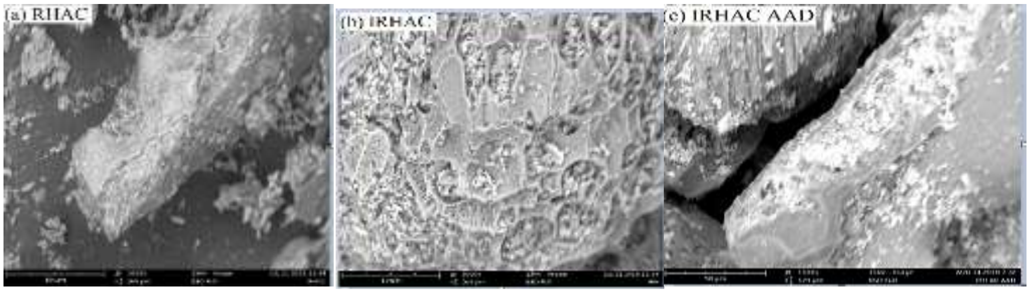

Fig.1:*SEM* images of (a) Rice husk activated Carbon (b) impregnated rice husk activated carbon
(c) Impregnated rice husk adsorbent after Cesium uptake

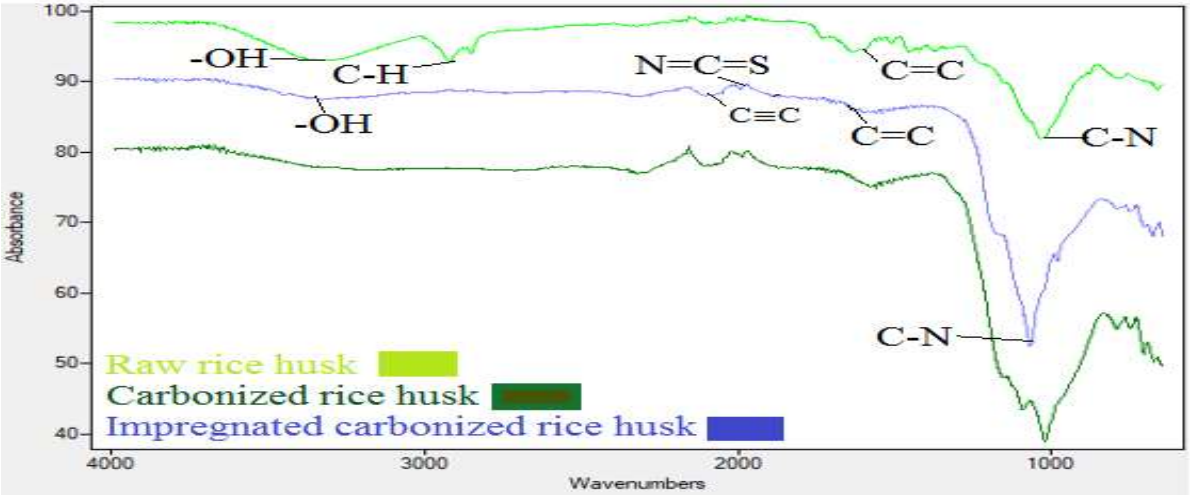

Fig.2: FTIR Spectra of (a) Raw rice husk (b) Impregnated rice husk (c) Carbonized rice husk

Development of regression model analysis

Development of regression model analysis In this present investigation, the CCD of four variables such as adsorbent dosage (g), pH, initial metal ion concentration(mg/l), and contact time (min) each with two levels were chosen as independent variables with designated factors are presented in Table1 respectively. The software used for CCD is Design expert 11.0. A total of 30 experiments were necessary to estimate the coefficients of each model using linear regression analysis. The two dependent output responses of percentage removal were obtained from the independent input variables for CCD and are presented in Table 1. The quadratic models was suggested by the software for percentage removal of Cs ions using (a) Carbonized rice husk (b) impregnated Carbonized rice husk adsorbent due to the higher order polynomial and are reported in Tables 1,respectively

TABLE 1: EXPERIMENTAL DESIGN MATRIX AND RESPONSES

Runs	Initial Conc. (mg/l)	Acidity (pH)	Adsorbent dosage (g)	Contact time (Min)	%Cs removal A	%Cs removal B	% Cs removal C
1	100	4	0.2	30	52.20	96.80	72.88
2	130	6	0.3	45	15.27	96.00	79.77
3	70	6	0.3	75	62.28	96.00	69.99
4	40	8	0.4	30	41.50	95.70	59.99
5	70	2	0.3	45	59.35	98.00	67.88
6	70	6	0.3	45	57.38	97.15	66.99
7	40	4	0.2	60	54.32	97.00	68.88
8	10	4	0.4	30	48.69	97.00	73.11
9	40	4	0.2	30	52.30	96.00	62.96

10	70	6	0.3	45	54.71	97.90	66.11
11	70	6	0.3	45	60.01	97.50	66.88
12	70	6	0.3	45	60.07	97.60	67.22
13	70	6	0.3	15	59.00	97.20	67.99
14	40	8	0.2	60	48.00	93.00	58.97
15	100	8	0.2	60	49.13	94.00	69.88
16	70	6	0.3	45	60.64	96.90	70.77
17	70	10	0.3	45	40.21	92.50	68.11
18	100	4	0.4	60	49.12	97.75	70.88
19	100	8	0.4	60	45.77	95.00	6989
20	70	6	0.3	45	47.68	97.40	70.00
21	100	8	0.2	30	49.09	96.95	69.99
22	40	8	0.2	30	50.55	94.00	62.09
23	70	6	0.1	45	57.38	97.00	67.09
24	40	4	0.4	60	47.67	97.37	57.09
25	10	6	0.3	45	16.01	94.50	53.11
26	100	8	0.4	30	45.01	96.50	67.89
27	40	8	0.4	60	49.70	95.00	55.99
28	40	4	0.4	30	56.67	97.60	59.88
29	100	4	0.2	60	44.29	98.60	72.88
30	70	6	0.5	45	62.23	97.20	56.09

TABLE 2: MODEL SUMMARY OF STATISTICS FOR PERCENTAGE REMOVAL OFCS

Adsorbent	Model	R^2	Adj. R^2	Pred. R^2
A	Quadratic	0.9105	0.8270	0.6319
B	Quadratic	0.9403	0.8846	0.6952
C	Quadratic	0.9375	09245	0.8866

TABLE 3: ANALYSIS OF VARIANCE (ANOVA) FOR PERCENTAGE REMOVAL OF CESIUM IONS USING ADSORBENT A

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	2493.67	5	498.73	57.78	< 0.0001	significant
A-Initial Conc.	54.45	1	54.45	6.31	0.0191	
B-pH	147.76	1	147.76	17.12	0.0004	
AB	19.69	1	19.69	2.28	0.1440	
A^2	2260.80	1	2260.80	261.93	< 0.0001	

B^2	73.52	1	73.52	8.52	0.0075	
Residual	207.15	24	8.63			
Lack of Fit	174.17	19	9.17	1.39	0.3833	not significant
Pure Error	32.99	5	6.60			
Cor Total	2700.83	29				

TABLE 4: ANALYSIS OF VARIANCE (ANOVA) FOR PERCENTAGE REMOVAL OF CESIUM IONS USING ADSORBENT B

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	61.24	8	7.65	24.08	< 0.0001	significant
A-Initial Conc.	3.85	1	3.85	12.10	0.0022	
B-pH	34.09	1	34.09	107.23	< 0.0001	
C-Adsorbent Dosage	1.63	1	1.63	5.12	0.0343	
D-Contact Time	1.40	1	1.40	4.42	0.0478	
AC	1.86	1	1.86	5.85	0.0248	
BD	4.38	1	4.38	13.77	0.0013	
A^2	6.98	1	6.98	21.97	0.0001	
B^2	6.98	1	6.98	21.97	0.0001	
Residual	6.68	21	0.32			
Lack of Fit	6.06	16	0.38	3.10	0.1082	not significant
Pure Error	0.61	5	0.12			
Cor Total	67.91	29				

Modified quadratic model

The modified quadratic model obtained for the percentage removal of Cesium ions using (a) Carbonized rice husk(b) Impregnated carbonized rice husk in terms of coded factor was reported in equation (iii) and (iv) respectively.

Adsorbent A = $59.72 + 1.51A - 2.48B + 1.11AB - 8.92A^2 - 1.61B^2$…………………………………..(iii)

Adsorbent B = $97.15 + 0.40A - 1.19B + 0.26C - 0.25D - 0.34AC - 0.55BD - 0.50B^2$ ….. (iv)

Adsorbent C = $67.29 + 5.95A – 0.98B – 1.91C + 1.01AC – 1.61C^2$ ………………….. (v)

Where:

A-Initial Conc.

B-pH

C-Adsorbent Dosage

D-Contact Time

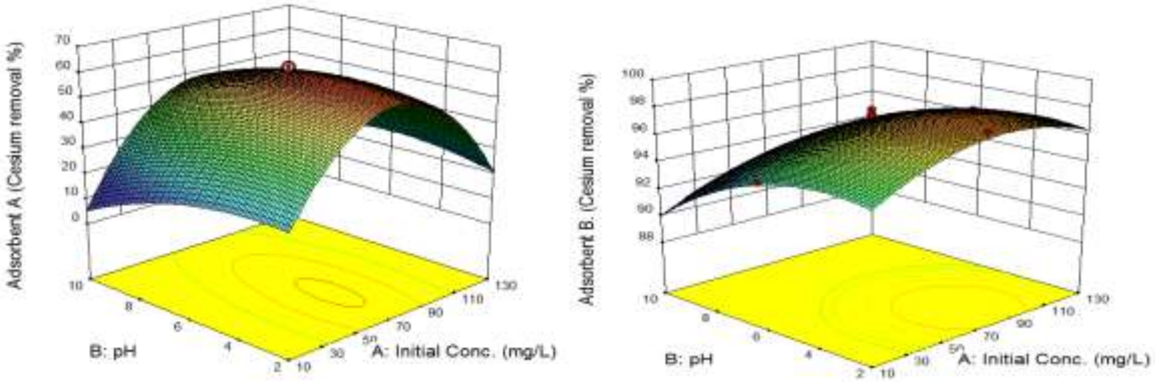

Fig. 3: The combined effect of pH and Initial concentration on percentage removal of Cesium ions using rice husk activated carbon and impregnated rice husk activatedcarbon

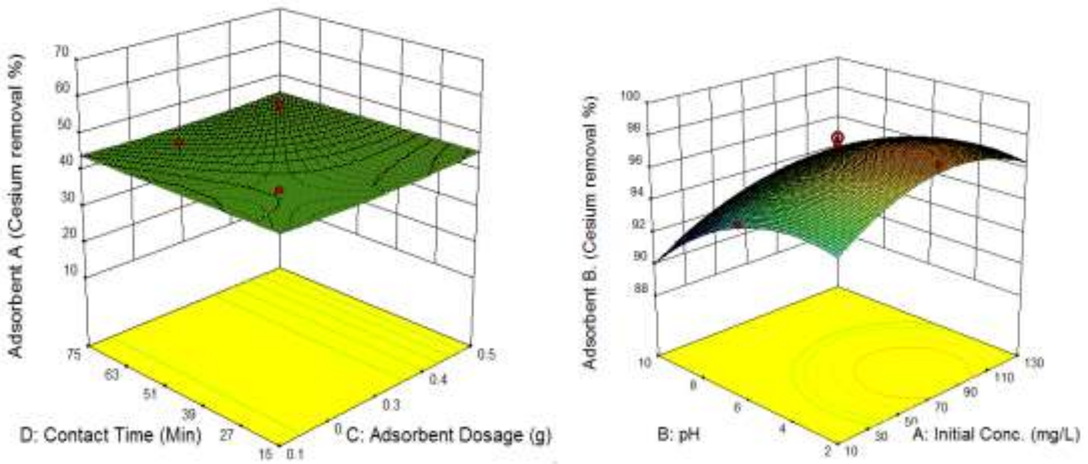

Fig. 4: The combined effect of contact time and adsorbent dosage on percentage removal of Cesium ions using rice husk activated carbon and impregnated rice husk activated carbon composite

TABLE 5: PREDICTED AND ACTUAL OPTIMUM RESULTS FOR ADSORPTION OF CS IONS

Source	Adsorbent dosage (g)	Ini. Conc. (mg/L)	pH	T (min)	%Removal Predicted	%Removal Experiment
Adsorbent A	0.24	109.09	3	45	41.54	42.80
Adsorbent B	0.20	69.47	2	30	97.94	96.80

TABLE 6: LANGMUIR AND FREUNDLICH ISOTHERM CONSTANT FOR CS

adsorbent	Langmuir isotherm coefficient				Freundlich isotherm coefficient		
	$q_{m\ (mg/g)}$	$K_{L\ (L/mg)}$	R^2	R_L	k_f(mg/g).[(L/mg)]$^{1/n}$	I/n	R^2
A	8.244	0.081	0.9973	0.087	0.6014	0.6504	0.8435
B	21.35	0.0128	0.9955	0.73	9.504	0.9828	0.9603

From Table 6, above (R_L) is one of the essential characteristics of the Langmuir isotherm modeling, which is defined in the following equation: $R_L = 1/1 + K_L C_o$ where K_L(L/mg) is the Langmuir constant and C_o(mg/L) is the highest metal ion concentration. The type of the adsorption isotherm is determined by the value range of R_L: unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) and irreversible ($R_L = 0$). On the other hand, the Freundlich model assumes that molecules are adsorbed on the heterogeneous surfaces of adsorbent based on different sites with different adsorption energies (Han *et al.*, 2015., ; Alslaibi, *et al.*, 2014) This model takes into account the mutual interaction between adsorbed molecules. The application of the Freundlich equation also suggests that sorption energy exponentially decreases upon the completion of the sorption centers of the adsorbent. The linear form of Freundlich equation is given as: $\ln q_e = \ln K_F + 1/n \ln C_e$ where 1/n and $K_F[(mg/g).(L/mg)^{1/n}]$ are Freundlich constants related to the favorability of adsorption process and the adsorption capacity of the adsorbate, respectively. 1/nis the heterogeneity factor indicating the adsorption intensity of the adsorbent (Alslaibi *et al.*, 2014)

It was found that the Langmuir equation is more suitable than Freundlich model in the description of the adsorption behavior of Cs on the (a) rice husk and (b) impregnated rice husk adsorbent with higher values of correlation coefficients (R^2) (0.9973 and 0.9955) while that of Freundlic are (0.8835 and 0.9603) which shows that the adsorption is more of monolayer adsorption, Hence it favors Langmuir. Moreover, values of R_L were found to be lower than 1, suggesting that the adsorption processes are favorable

TABLE 7: SUMMARY OF PARAMETERS FOR VARIOUS KINETIC MODELS

Kinetic model	Equation	A	B
Pseudo-first order	$In(q_e - q_t) = In\ q_e - K_{Lad}^t$	$R^2=0.9732$ $K_{ad = 0.014min}^{-1}$ $q_{e=0.275mg\ g}^{-1}$	$R^2=0.9822$ $K_{ad = 0.0156min}^{-1}$ $q_{e=0.082mg\ g}^{-1}$
Pseudo-second order	$1/q_t = 1/K_{2nd.qe}^2 + 1/q_e$	$R^2=0.999$ $K_{ad=0.307mg}^{-1}\ min^{-1}$	$R^2=0.999$ $K_{ad=0.1135mg}^{-1}\ min^{-1}$

Adsorption kinetics

The pseudo-first-order and pseudo-second-order kinetic models were tested to investigate the rate of adsorption of Cs ions by Adsorbents A and B The linearized form of adsorption kinetics (Guo *et al.*,2015) and their constants are presented in Table 7 From the Table, it is confirmed that the adsorption of Cs ions using rice husk and impregnated rice husk composites adsorbent followed the pseudo-second order reaction. The pseudo-second order model indicates that the adsorption of Cs ions on the surface of the adsorbents represented two phase reaction such as rapid adsorption for shorter duration in first stage and followed by slow adsorption for longer duration. Several researchers reported that the fast reaction may be due to chemisorption (Saueprasearsit 2011; Hai-Jun *et al.*, 2009

Table 8: Summary of various metal hexacyanoferrates (MHCFS) materials for cesium removal

MHCFs	Carrier	pH	Q_{max}(mg/ g)	Ci,Cs*(mg/L)	Contact time	References
KCoFC	ND	2.0-6.5	227.04	1320	3 days	Moon *et al*., 2004
CuFCN	ND	0.5M HNO_3	421.08	536	4 hours	Wang *et al*., 2014
CuHCF	EDASAMMS	0.1MHNO_3	175.56	2244	2 hours	Lin *et al* ., 2001
NiHCF	PEDTAFS	ND	223.08	594	ND	Chang et al., 2008
KNiFC	Clinoptilolite	ND	ND	198	24 days	Kazemian et al., 2006
KNiFC	Chabazite	3.70-5.83	246.87	13,200	2 Days	Mimura *et al*., 1999
CoHCF	Graphite	1-11	ND	1320	Electrochemically Control	Green and Korshin., (1999)
NiHCF	Carbon Nanotube	ND	ND	ND	Electrochemically Control	Lin and Cui., (2005)
KCuFC	AC	1.5	63.36	246	24 hours	Wang *et al*., 2014
KCuHCF	IRHAC	6	13.58	70	45 min	Present work
KCuHCF	RHAC	6	8.03	70	45 min	Present work

CONCLUSION

Rice husk adsorbents are effective, economic and ecofriendly adsorbents for the removal of 62.28 %, 77.99 % and 98.6 % Cs from 70 ppm 130 ppm and 100 pmm of aqueous solutions respectively. The development of mathematical model and optimization for adsorption of Cs using statistical tool for prediction and understanding of interaction effects between process variables using CCD. Adsorption kinetics was found to fit suitably in a pseudo second order kinetics model and adsorption isotherms followed the monolayer adsorption

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