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Adsorption of Zn (II) Ion from Aqueous Solution by Activated Carbon from Banana Flower and Sorghum Bicolor

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ABSTRACT

The adsorption studies include the manufacture of Adsorbents and adsorption studies by using any of the chief cultivated waste material, Banana Flower Activated Carbon [BFAC] and Sorghum Bicolor Activated Carbon [SBAC]. The heavy metal treatment processes of wastewater by using adsorbent which contain Zn (II) ion. The adsorption experiment study includes the variation with Initial concentration, contact time, adsorbent dose, temperature and pH of the experimental solution. The equilibrium adsorption capacity was measured by means of linear models of Langmuir and Freundlich isotherm. The kinetics study helps to find pseudo first order rate factors for Zn (II). This Gibbs free energy change (ΔG°), the entropy Change (ΔS°) and enthalpy change (ΔH°) were calculated. The best fit with the isotherms Langmuir and Freundlich indicating the applicability of the chosen adsorbent for the removal of Zn (II) ions successfully.

***Key words*:** Heavy metal, Zn (II) ion, Adsorption, Activated carbon, BFAC, SBAC, Isotherm

The ecological difficulties in the world create knowledge about heavy metal pollution in waste water. The industrial waste water which contains different byproducts of heavy metals such as copper, zinc, chromium, lead and nickel are the major sources causing pollution to the environment and significant toxic impact on the living beings. The zinc (II) ion present in natural atmosphere level when exceeds causing damage to humanoid fitness. Zn (II) could be the reason for illnesses counting, infantilism obliteration of red blood cells, high blood pressure, kidney damage and impaired wound curative [1]. The poisonous and damaging nature of Zn (II) compels the authors to prefer the heavy metal, Zn (II). Some of the available treatment methods are Osmosis, electrocoagulation, ultrafiltration, solvent extraction, dialysis/electro dialysis [2-5]. The purpose of this study is using Banana flower activated carbon (BFAC) and sorghum Bicolor activated carbon (SBAC) for the adsorption of Zn (II) from aqueous solution. In Banana flower activated carbon and Sorghum bicolor activated carbon, the pore size can be enlarged so that to adsorb heavy metal easily. There are lot of search for cheap adsorbents from agricultural waste materials as alternative methods [6]. But they also produce sludge and require high energy [7]. Several agricultural waste materials studied and developed for the removal of heavy metal ions [8]. The present study is to analyze ability of Banana flower activated Carbon and Sorghum Bicolor Activated Carbon bio-adsorbent for removal of heavy metal Zn (II) ions from aqueous solution. The adsorption capacity of the bio sorbent can be improved by physicochemical properties and modifying its surface [10]. The adsorption procedure is affected by contact time, initial concentration, pH of the solution, temperature, adsorbent dose and size of the adsorbent. The characteristics of the chosen adsorbent were analyzed by using Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy [FTIR].

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MATERIALS AND METHODS

Preparation of adsorbate

Adsorbate containing Zn (II) was prepared by dissolving 4.39 g of ZnSO4 in 1000 ml of distilled water to get the stock solution of 1000 ppm $ZnSO_4$. Other concentrations (100-900ppm) were obtained from stock solution by diluting the solution.

Preparation of adsorbent

Banana flower and *Sorghum bicolor* were collected and used as sorbent for the bio sorption of Zn (II) ions. [BF] and [SB] sample were collected from Trichy district. Samples were washed several times using deionized water to removal inessential waste and dust. They were then kept in an oven at 70-90°C. The dried adsorbents were then sieved to the desired particle sizes (0-63, 63-125, 125-250 and 250-

400µm) and the adsorbent prepared was used throughout the experimental work.

Batch mode absorption study

The batch mode equilibrium experiments were carried out proceeding the adsorption of Zn (II) on BFAC and SBAC. The adsorption experiments were carried out in 50ml reagent bottle with 50ml of 1000 ppm Zn (II) solution and 200 mg of adsorbent were taken in a mechanical shaker with constant temperature. The effect of initial metal ion concentration (100, 200, 400, 600, 800, 1000 and 1100 mg/L), contact time (15, 30, 45, 60, 75, and 120 minutes), pH of the solution (1, 2, 3, 4, 5, 6, and 7), adsorbent dose (200, 400, 600, 800, and 1000 mg), and temperature (30, 40, and 50°C) were studied. The pH of the experimental solution is adjusted to the level by addition of HCl, for, more than 7, NaOH. The adsorbed phase concentration (q_t, in mg/g) at time (t) is calculated expending equation:

$$q_e = \frac{(Co - Ct)}{Co} \times 100 \text{ ……….. (1)}$$

C_o, and C_t are the initial and at contact time, t Zin (II) ion concentration (mg/L)

RESULTS AND DISCUSSION

Effect of contact time initial concentration

The Zinc (II) ion adsorption at different concentration [BFAC] (100-mg to 1400 mg/L) and [SBAC] (100-mg/L to 1200 mg/L) were calculated and it could be understood that the adsorption increase from contact time 15 to 120 min [BFAC] and the maximum 60% removal efficiency for Zn (II) and the adsorption increases from 15 and 120 min [SBAC] and the maximum 57% removal of Zn (II) ion were displayed in (Fig 1).

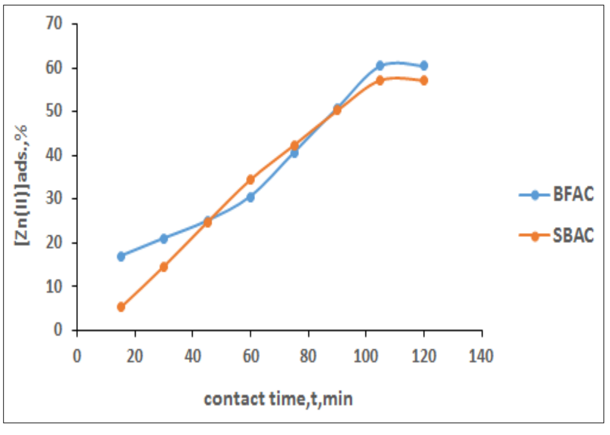

Fig 1 Effect of contact time on Zn (II) adsorption: dose: 0.2mg. pH:7.5

Results of pH on metal ion removal

The adsorption specific capacity is favored through increasing the pH value [11]. The test was conducted using 50ml of Zn (II)ion solution containing an initial concentration of 1000mg/L, dose 200 mg adsorbent [BFAC] at a temperature of 30°C mean while solution of the pH is varied from 1.0 to 7.0 and they were monitored for 15-120 min. Maximum adsorption occurred at pH 5.0 for BFAC and pH 1 for SBAC and the adsorption is 80.3% and 7.5% respectively as showed in (Fig 2).

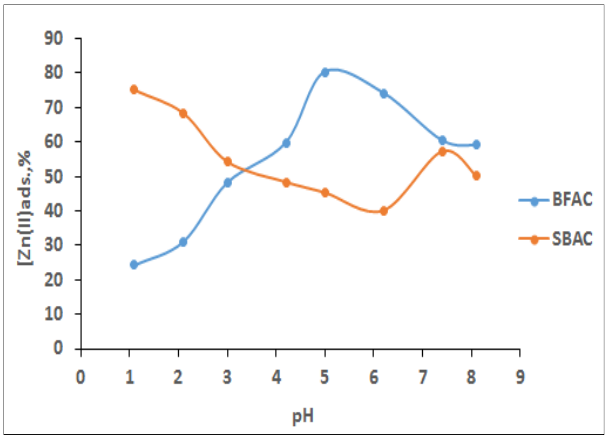

Fig 2 Effect of pH on Zn (II) adsorption: dose: 0.2mg. pH: pH1.1 and 5.0

Adsorption isotherm studies

Freundlich and Langmuir isotherms were tested. The Langmuir and Freundlich form of the equation studied is given below [12].

$\log q_e = \log_{kf} + (1/n) \log_{ce}$ derivated from $q_e = k_f C_e 1/n$ ……… (2)

Where;

q_e(mg/g) represent zinc adsorbed at equilibrium

C_e denotes equilibrium concentration in (mg/L)

k_f is Freundlich adsorption constant

The corresponding values are presented in (Table 1) and shown in the (Fig 3-4).

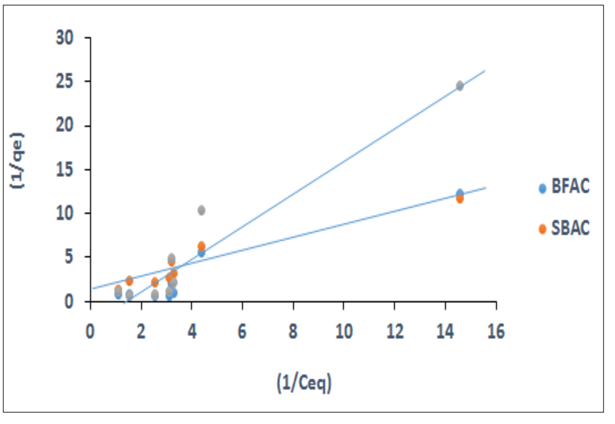

Fig 3 Langmuir Isotherm for the adsorption of Zn (II)

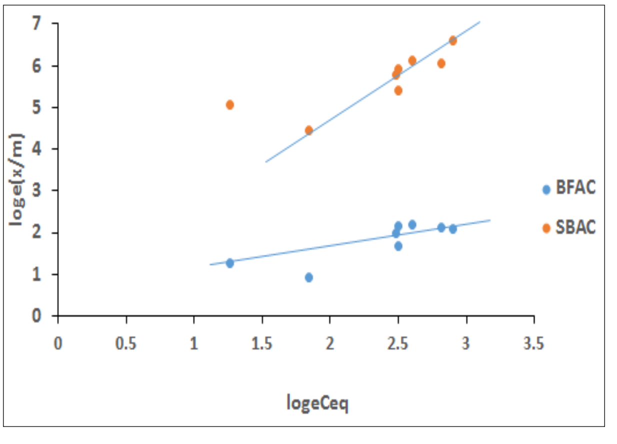

Fig 4 Freundlich isotherm for the adsorption of Zn (II)

Table 1 Adsorption isotherm (Langmuir and Freundlich)

1	Temperature °C	Langmuir isotherm				Freundlich isotherm		
		q_m	B	R_L	r^2	k_f	1/n	r^2
BFAC	30	0.1454	0.46	0.0107	0.9556	0.1643	0.3130	0.8491
2	Temperature °C	Lagmuir isotherm				Freundlich isotherm		
		q_m	B	R_L	r^2	k_f	1/n	r^2
SBAC	30	0.6153	0.1	0.0476	0.9766	0.3802	1.2000	0.9368

Kinetics study

The kinetic model for pseudo first order reaction was calculated. The corresponding equation for adsorption process [13] is:

$t/q_t = [1/k_2q_e^2] + t/q_e$ …………………. (3)

The above pseudo-first order kinetic modal is linearized [14] as:

$\log(q_e-q_t) = \log q_e - K_{ad}/2.303\ t$ ……………… (4)

The study was carried out at 30°C with the initial concentration of 1000mg/L for 120 minutes for both Banana flower activated carbon and Sorghum Bicolor Activated carbon, [BFAC] and [SBAC]. The adsorption process best fits pseudo- first order model for both [BFAC] and [SBAC]. {[BFAC] (R^2= 0.9203) and [SBAC] R^2 = 0.9735}. This pseudo- first order kinetic modal was compared to the pseudo second order model. {[BFAC] (R^2= 0.7556) and [SBAC] (R^2 = 0.5035)}.

From the above value, it is very clear that this process undergoes pseudo first order kinetics and the corresponding values are showed in (Table 2).

Table 2 Adsorption kinetics for Zn (II) [Pseudo First Order and Pseudo Second Order Rate Constants]

	Pseudo first order-rate constant			Pseudo second order-rate constant		
BFAC	q_e(mg/g)	K_{ad} (min-1)	r^2	q_e (mg/g)	k_2(g/mg min-1)	r^2
	162.18	12.56	0.9203	0.1409	0.2008	0.7556
	Pseudo first order-rate constant			Pseudo second order-rate constant		
SBAC	q_e(mg/g)	K_{ad}(min-1)	r^2	q_e(mg/g)	k_2(g/mg min-1	r^2
	204.17	0.023	0.9735	1.13	0.1512	0.5035

Thermodynamic parameters and activation energy

The thermodynamic parameters were calculated for the adsorption of Zn (II) ion. The temperature dependence on Gibbs free energy for both Banana Flower Activated Carbon and Sorghum Bicolor Activated carbon were calculated using equation [14].

$\Delta G^o = - RT \ln K$ ………………………. (5)

The Gibbs energy change (ΔG^o), the entropy change (ΔH^o) and enthalpy change (ΔS^o) are relating at constant temperature as in the following equation [15].

$\Delta G^o = \Delta H^o - T\Delta S^o$ ……………………. (6)

The Arrhenius equation is useful to calculate activation energy, Ea from equation following:

$K=Ae^{-Ea/RT}$ ……………………. (7)

Where, Ea is activation energy, k is the constant, A is Arrhenius factor, and T is the temperature (K) and R is gas constant. The adsorption process for the Zn (II) ions is feasible and spontaneous. The value of Gibbs free energy change in negative. ΔH^o also has negative value. These values designate that the adsorption of Zn (II) ions on Banana Flower Activated Carbon and Sorghum Bicolor Activated Carbon is exothermic. The positive values of ΔS^o suggest that increase randomness leads to become more negative with increase in temperature.

Table 3 Thermodynamic parameter calculation

BFAC				SBAC			
Temperature °C	$\Delta_{ads}G°$	$\Delta_{ads}S°$	$\Delta_{ads}H°$	Temperature °C	$\Delta_{ads}G°$	$\Delta_{ads}S°$	$\Delta_{ads}H°$
303	-16,321.5	52.14		303	-16,657.8	54.73	
313	-14,833.0	45.75	-511.3	313	-18,157.1	57.77	-72.5
323	-13,496.9	40.20		323	-20,378.8	62.86	

Fig 5 SEM-Before adsorption (a)- BFAC

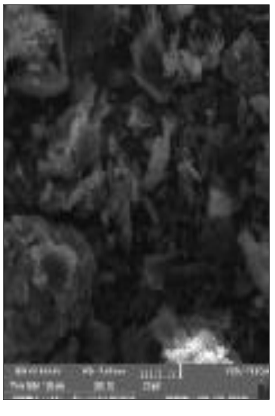

Fig 5 SEM-After adsorption (b)- BFAC

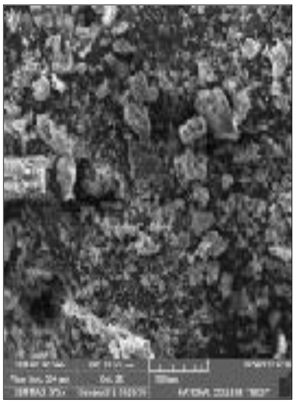

Fig 6 SEM-Before adsorption (a)- SBAC

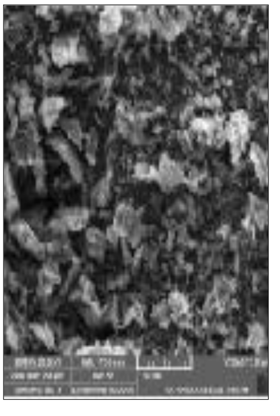

Fig 6 SEM- After adsorption (b)- SBAC

Morphological study on bio sorbent surfaces

Scanning Electron Microscopy (SEM) examination of bio sorbent has been completed and the results were analyzed. From this, we can know the morphology on the superficial of the bio sorbent. Banana Flower Activated Carbon (Fig 5a,b), (Fig 6a,b) represent the SEM images of before and after adsorption for both BFAC and SBAC. The adsorbent pore sizes showed figure.

FTIR- analysis

From the figures (Fig 7a,b), (Fig 8a,b), it is very clear that the presence of functional groups such as FTIR – (BFAC) adsorbent before adsorption peak range (1573 - NO_2 stretch, 1403 - C = C bend, 1259 C-F strong, 579 –C-Br strong) and (SBAC) adsorbent before adsorption peak range (1082 – C – O –C stretch, 1579 – NO_2 stretch, 599 – C – Br strong) showed FTIR.

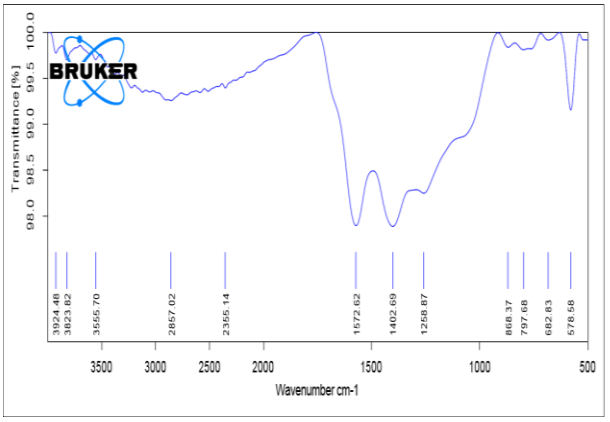

Fig 7 FTIR-Before adsorption (a)- BFAC

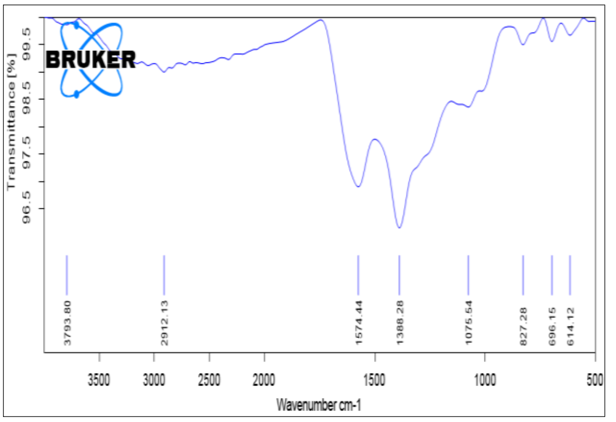

Fig 7 FTIR-After adsorption (b)- BFAC

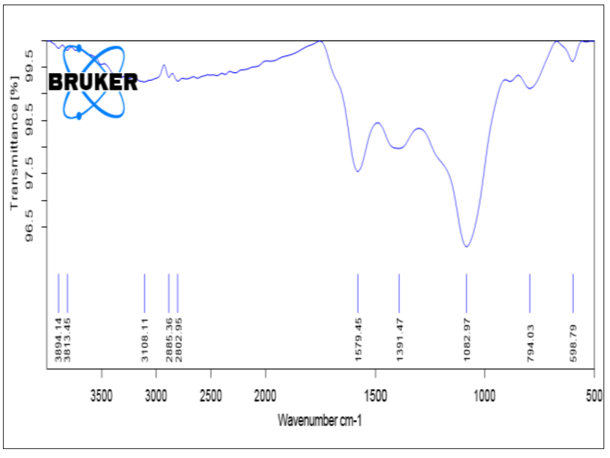

Fig 8 FTIR-Before adsorption (a)- SBAC

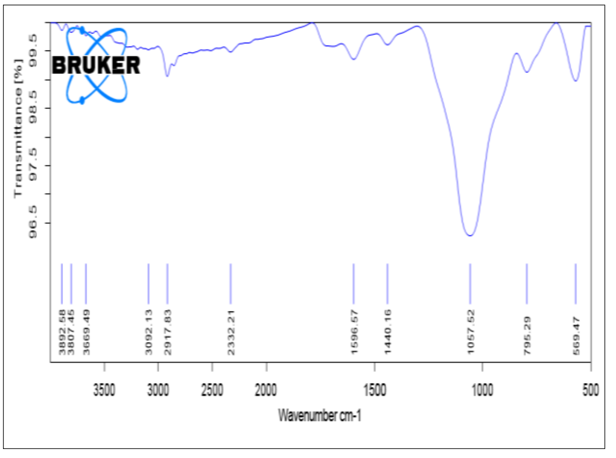

Fig 8 FTIR-After adsorption (b)- SBAC

CONCLUSION

The adsorption of Zn (II) ion on both BFAC and SBAC was investigated. The equilibrium times for both adsorbents were measured. The optimum pH, dose, size, concentration and temperature variations are calculated. The isotherms such as Langmuir and Freundlich were tested and their constant were reported. From the kinetic study, it is clear that the present study follows adsorbent pseudo first order for both the adsorbents. The thermodynamic parameters and activation energy were calculated. The negative sign of both ΔG^0 and ΔH^0 reveals that the process is spontaneous and exothermic.

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