Sorption of Zinc (II) Ions onto Modified Jute Fibers (MJF): Application of Two-Parameter Equilibrium Isotherms

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Abstract - *In the present study, adsorption of Zinc ion on modified Jute fiber (MJF) was done and the equilibrium isotherms were studied. The raw jute fibers were treated by sodium hydroxide and sodium chlorite in order to remove lignin, coloring substances and other alkali soluble compounds from the surface of the fiber. It was then modified by sulfuric acid to increase the proportion of hydroxyl group in the MJF. The MJF samples were characterized by Fourier Transform Infrared Spectroscopy and Scanning Electron Microscopy. The MJF samples were later applied as a potential adsorbent for the removal of Zn (II) ion from aqueous solution. The equilibrium sorption data ware fitted into Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms. The Langmuir isotherm was best fitted with the experimental data and the maximum monolayer sorption of 142.85 mg/g for Zn (II) ion onto MJF adsorbent was found. The favorability of the adsorption process was indicated by separation factor (R_L) and sorption intensity (n) constants of Langmuir and Freundlich isotherms respectively. The Temkin isotherm indicates that the heat of sorption was positive and the process was exothermic. The mean free energy determined by using Dubinin-Radushkevich was 69 KJ/mol which clearly shows that the system followed chemisorption process.*

***Key Words*: Modified Jute Fibers (MJF), Heavy metals, Zn (II) ion, Adsorption, Isotherm**

1. INTRODUCTION

Heavy metals are toxic and carcinogenic in nature, which poses serious threats on the natural environment and living organisms. They are released in natural aqueous system due to different human activity such as industrial activity, smelting operations, agriculture and mining work. The major pollutants released from different industries are lead (Pb), zinc (Zn), copper (Cu), arsenic (As), cadmium (Cd), chromium (Cr), nickel (Ni) and mercury (Hg) [1]. There are different techniques for removal of heavy metal ions from solutions including chemical precipitation [2, 3], solvent extraction [4]; coagulation and flocculation [5], and membrane processes [6], osmosis [7] and adsorption [8, 9, 10]. Among these methods, adsorption is one of the most efficient physico-chemical treatment for heavy metal removal as it has overcome inherent limitations of other

techniques such as high cost, large amount of sludge formation, low efficiency, and sensitive operating conditions [11, 12]. There are several commercial adsorbent such as graphene oxide [13] and activated carbon [14, 15, 16] widely used for the removal of heavy metals. Despite their high efficiency, they are not affordable for many small-scale industrial concerns in many less developed countries [17]. To overcome this issue, Researchers are trying different low cost, naturally available adsorbents and found that agriculture waste material such as sugarcane bagasse [18, 19], raw rice bran[17], sawdust [20], ricehusk [21], neem bark [22], coconut husk [23] and pine bark [24] to be a viable alternative. To establish an adsorbate-adsorbent system, the role of a well suited equilibrium isotherm is unavoidable as it gives information about the maximum adsorption capacity, adsorption system design etc. [25, 26, 27].

Jute fiber is one of the most produced natural fibers in India (mainly West Bengal), Bangladesh, China, and Myanmar. The abundance of jute fibers accounts for the feasibility of choosing it as raw material in this paper. The principal constituents of jute fiber are mainly cellulose (58-63 %), hemicellulose (20-24 %), lignin (12-15 %), and some other small quantities of constituents like fats, pectin, aqueous extract etc. [28]. The hydroxyl and carboxyl functional group present in cellulose helps to bind the metal ion by forming complex [29, 30]. The raw cellulose fibers are reported to have low efficiency compared to the treated one [31, 32, 33].

In this work jute fiber had been modified using chemical treatment method. Biomass characterization was determined with Fourier transform infrared (FT-IR) spectrum and scanning electron microscope (SEM). The modified jute fibers were then used to remove Zn (II) from the aqueous solution and different two-parameter equilibrium isotherms (Langmuir, Freundlich, Temkin and Dubinin- Radushkevich) were studied to define the Jute fiber-Zn (II) system.

2. MATERIAL AND METHOD

2.1. Materials

The modified jute fiber (MJF) was prepared from raw Jute (*Corchorus capsularis)* which is the most available fiber of Bangladesh. The jute fiber was purchased from the local market of Bangladesh. Sulphuric acid (H_2SO_4) and Acetic acid

(CH_3COOH) were purchased from E. Merck, Germany. Sodium hydroxide (NaOH) and Sodium chlorite ($NaClO_2$) were collected from UPL Ltd, India.

2.2 Preparation of modified Jute fiber (MJF)

Jute fibers were subjected to a washing pre-treatment to remove impurities and other substances from the external surface of fiber cell walls. The fibers were cut into small size (about 2 cm) by using scissors and then milled into fine size by using a mechanical milling machine. These fibers (25 g) were dispersed in distilled water (500 mL) for 10 min at room temperature and stirred for2 h at 50°C using a glass rod and filtered in order to remove soluble extractives in water. The dried fiber was mercerized with 2 % NaOH solution at 80°C for 6 h with mechanical stirring followed by thorough washing until neutralized and drying. This treatment can remove natural and artificial impurities and produce rough surface topography. Therefore, the mechanical interlocking at the interface would be improved. The dried fibers were then bleached with 2 wt.% $NaClO_2$ at 80 °C for 4h with mechanical stirring, washed and dried in an oven. It was done to remove the coloring substance by reacting with chromophores. When a solution of sodium chlorite is acidified, bleaching species i.e. chlorine dioxide (ClO_2) and hypochlorous acid ($HClO_2$) and non-bleaching species i.e. sodium chlorate ($NaClO_3$) and sodium chloride (NaCl) are formed. The produced chlorine oxide (ClO_2) has higher bleaching property. The bleached fibers were further treated in a concentrated sulfuric acid solution (40 wt% sulfuric acid in water) at 45°C for 10 h with mechanical stirring. After the treatment, the hydrolyzed MJF samples were neutralized by 30 wt% NaOH solution in water, and then washed for four times. After each washing step, the fibers were separated from the solution by centrifugation at 8,000 rpm for 10 min. Finally, the MJF was obtained after a freeze drying for 48 hours.

2.3 Preparation of Zn (II) ion solution

The stock solution of Zn (II) ion was prepared by dissolving zinc nitrate ($Zn(NO_3)_2$) in de ionized water. By following the dilution process, working concentrations in the range of 50 to 400 mg/L were prepared from 1000 mg/L of stock solution.

2.4 Characterization

The Fourier transform infrared (FT-IR) spectrum of MJF was measured in a JASCO FT/IR-4100 spectrophotometer in the range of 4000-400 cm^{-1}. The morphological structure of MJF was examined using scanning electron microscope (SEM) (Carry Scope JCM-5700, Jeol, Japan).The Atomic Absorption Spectrophotometer (AA-6200, Shimadzu, Japan) was used to

determine the concentration of Zn (II) ion during the adsorption studies.

2.5 Adsorption studies

The equilibrium sorption of the Zn (II) ions on MJF was carried out by contacting 0.1g of the adsorbent with 0.1 L of different concentrations from 50 mg/L to 400mg/L in 250 mL conical flask intermittently for 120 minutes on the reciprocating shaker. The mixture was filtered and the residual concentration of the filtrate was analyzed using Atomic Absorption Spectrophotometer (AAS). The amount of adsorbed Zn (II) ion (mg/g) was calculated using the following formulae:

$$q_e = \frac{(C_o - C_e)V}{W} \tag{1}$$

Where, q_e = the amount of Zn (II) ion adsorbed from the solution at equilibrium, V = Volume of Zn (II) ion containing solution, C_0 = the concentration before adsorption, C_e = the concentration at equilibrium and W = the weight in gram of the adsorbent. The adsorption data was fitted into different isotherms such as Langmuir, Freundlich, Temkin and Dubinin-Radushkevich. The removal efficiency was determined by computing the percentage sorption using the following formulae:

$$\% \ Sorption = \frac{(C_o - C_e) \times 100}{C_o} \tag{2}$$

Where, C_0 = the concentration before adsorption, C_e = the concentration at equilibrium.

3. RESULT AND DISCUSSION

3.1. Fourier Transform Infrared (FT-IR) Spectroscopy

The FT-IR spectrum of MJF has been shown in chart-1. The major characteristic peaks of MJF have been indicated which resemble all the functional groups present in the chemical structure of cellulose in Jute fiber (Fig-1). The major characteristic peak for MJF assigned in the FTIR are 3332 cm^{-1} (O-H stretching bond of OH group) [34, 35], 2897 cm^{-1} (C-H stretching in SP^3 hybridized bond)[34, 35], 1631 cm^{-1} correspond to vibration of water molecule absorbed in cellulose [34, 35], 1429 cm^{-1}(C-H bending in cellulose) and 1037 (C-O stretching) [36]. The presence of these functional groups in the following chemical structure strengthens the evidence for using modified jute fiber as natural adsorbent.
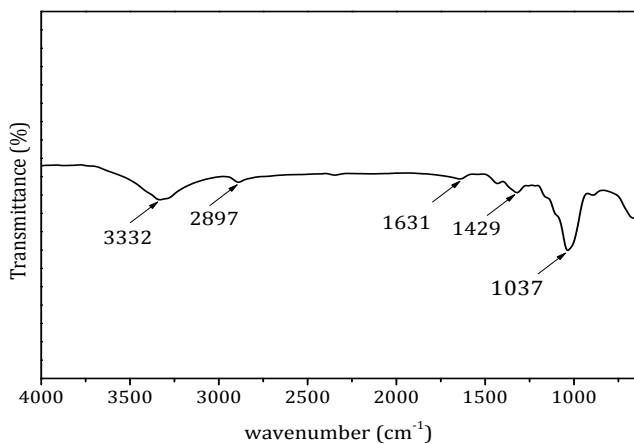
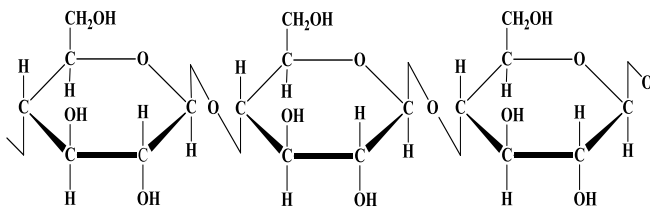Chart-1: FT-IR spectrum of modified jute fiber (MJF)

Fig-1: Chemical structure of cellulose in jute fiber

3.2. Scanning Electron Microscopy (SEM)

Scanning Electron Microcopy (SEM) gives very important information about the morphological structure of MJF. The SEM image of the MJF is shown in fig-2. This SEM image gives the clear external appearance of the MJF. It can be seen from the figure that the MJF appeared in rod like structure.
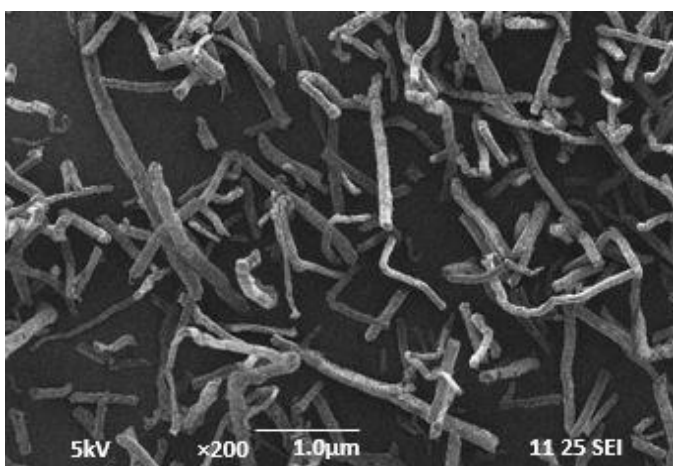

Fig-2: SEM image of modified jute fiber (MJF).

3.3. Equilibrium Isotherms

In the present study, four different equilibrium isotherms (Langmuir, Freundlich, Temkin and Dubinin- Radushkevich) were studied and the results are shown in table-1. The linear

least-squares method was used to correlate the sorption data. The first two isotherms are important for optimizing the design of the system and the latter two provide insights on the sorption energy of the system.

3.3.1. Langmuir isotherm

One of the most widely used equilibrium isotherm is Langmuir isotherm. This isotherm was derived under the assumption that each active site of the adsorbent can host a single molecule (monolayer) and have no lateral interaction or steric hindrance among the adsorbed molecules. The adsorption system is further presumed to be homogenous i.e. all active sites have equivalent affinity [37, 38, 39]. The equation is expressed as

$$q_e = q_\infty \frac{KC_e}{1 + KC_e} \tag{3}$$

Where, q_∞ (mg/g) is the maximum adsorbed capacity, K (L/mg) represents the Langmuir equilibrium constants, q_e is the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g) and C_e is the equilibrium concentration. Equation is linearized to determine the parameters

$$\frac{C_e}{q_e} = \frac{1}{q_\infty K} + \frac{1}{q_\infty} C_e \tag{4}$$

The equilibrium constant can be used to characterize a dimensionless constant; separation factor R_L to define the feasibility of the system [40].

$$R_L = \frac{1}{1 + KC_O} \tag{5}$$

The system is unfavorable if $R_L > 1$; linear when $R_L = 1$; favorable when $0 < R_L < 1$ and it indicates irreversibility of the process for $R_L = 0$.

For this study, equation (4) was used to determine the equilibrium parameters (Chart-2). The maximum adsorption capacity and the Langmuir equilibrium constants were found to be 142.85 mg/g and 0.012 L/mg respectively. R^2 value (Table-1) shows that the data is completely in agreement with the Langmuir model. . The adsorption capacity of MJF and several other natural adsorbents for Zn (II) ion are shown in Table-2. The adsorbent capacity of MJF is much greater than any other adsorbents, proving the viability of using MJF for this purpose. The R_L values for different initial concentrations are shown in chart-3. It shows that for the concentrations 50, 100, 200, 300, 400 mg/L, the values of R_L are smaller than 1 indicating that the system is

favorable. It also shows that, as the initial concentration increases, the R_L value become smaller expressing that as the initial concentration increases, the favorability of the system increases.
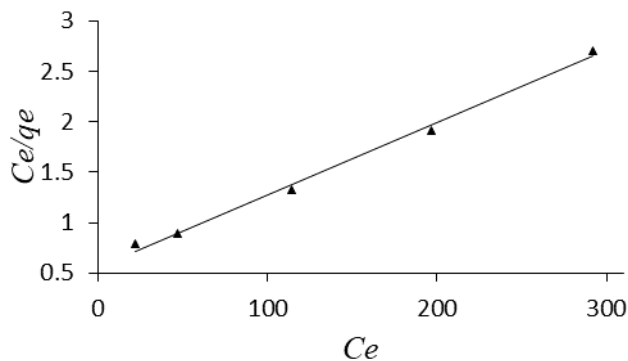

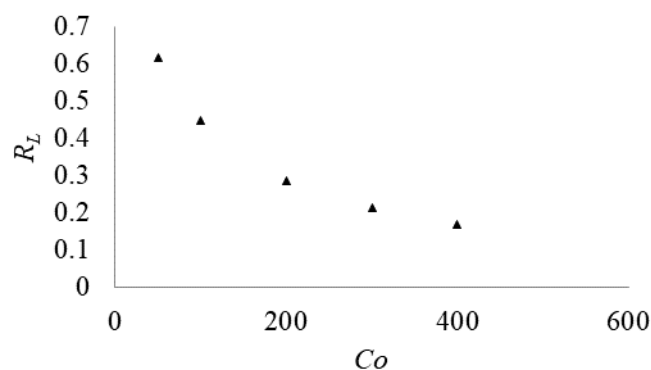Chart-2: Langmuir equilibrium isotherm for MJF-Zn (II) ion adsorption system

Chart-3: Plot of separation factor versus initial zinc solution concentration.

3.3.2. Freundlich isotherm model

This equilibrium isotherm can be applied to adsorption processes on heterogeneous, non-uniform surface and not limited to monolayer formation [41]. This model assumes that the stronger sites are occupied first in the process and the adsorption affinity decreases as the system proceed forward [37]. The model may be represented as follow [42]:

$$q_e = K_f C_e^{\frac{1}{n}} \qquad (6)$$

Where K_f represents Freundlich isotherm constant (mg/g), the adsorption intensity is expressed as n. The linear form of equation (6) is

$$log q_e = log K_f + \frac{1}{n} log C_e \qquad (7)$$

The value of K_f and n can be determined from a plot of log q_e versus $log\ C_e$. The value of n signifies the adsorption strength and type of adsorption. If the value of n is larger than one, it signifies lower bond energy, indicating unfavorable adsorption system. Chart-4 represents the Freundlich isotherm fitting of Zn-MJF system. The value of 1/n is found to be 0.524 and can be concluded that the system follows normal adsorption [43, 44]. It is also well established that if the value of n is within the range of 1-10, the sorption process is favorable. In the discussed Zn-MJF system the value of n is 1.908, indicating the system is favorable.
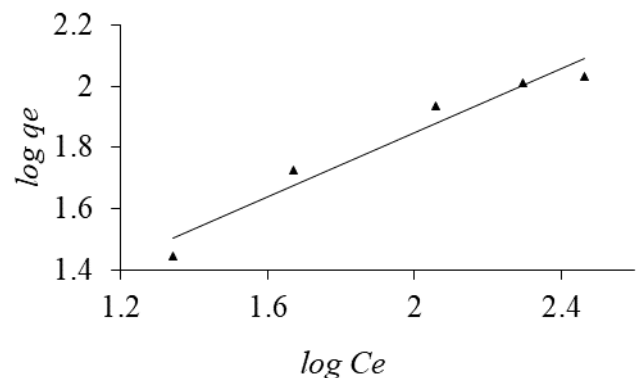

Chart-4: Freundlich equilibrium isotherm for MJF-Zn (II) ion adsorption system

3.3.3. Temkin isotherm

Temkin isotherm discusses Adsorption–desorption relation. Excluding extreme low and high concentration, the model assumes that the heat of adsorption of all molecules will decrease linearly rather than logarithmic with the increase of surface coverage [45, 46]. This can be expressed by the following relation [45]:

$$q_e = B ln(A_T C_e) \qquad (8)$$

Equation (8) can be express in the following linear form,

$$q_e = B ln A_T + B ln C_e \qquad (9)$$

$$B = \frac{RT}{b_T} \qquad \qquad 9(a)$$

Where, A_T is Temkin isotherm equilibrium binding constant (L/g), b_T is Temkin isotherm constant, B is the constant related to heat of sorption (J/mol), R is universal gas

constant (8.314 J.K/mol) and T indicates Temperature at 298K.

A plot of q_e versus $ln\ C_e$ (Chart-5) provides the value of B and A_T. In the present study, the value of b_T was positive (32.25 J/mol), which indicates that the system is exothermic.
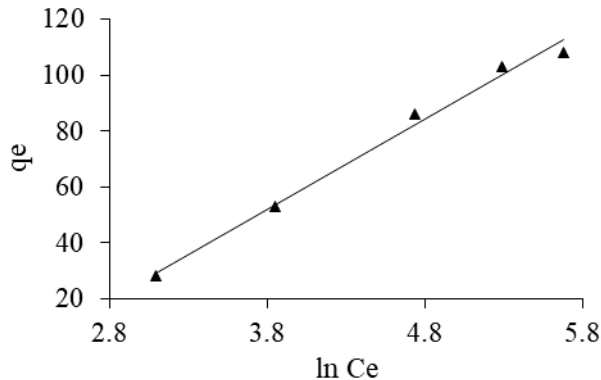

Chart-5: Temkin isotherms for MJF-Zn (II) ion adsorption system

3.3.4. Dubinin-Radushkevich Isotherm

Dubinin–Radushkevich isotherm determines the adsorption process with a Gaussian energy distribution onto a heterogeneous surface and usually suitable for data within intermediate concentration [47, 48].

$$q_e = q_s \exp(-K_r \varepsilon_D^2) \tag{10}$$

Where,

$$\varepsilon_D^2 = RT ln(1 + \frac{1}{C_e}) \tag{11}$$

Equation (10) can be expressed as follow [52]

$$ln q_e = ln q_s - K_r \varepsilon_D^2 \tag{12}$$

Here, q_s represents Dubinin–Radushkevich model constant (mg/g); K_r expresses the Dubinin–Radushkevich model constant (mol^2/kJ^2) and ε_D is the Polanyi potential. The Dubinin–Radushkevich model constant can be used to determine mean energy of sorption, E, by the following relation:

$$E = (2K_r)^{-0.5} \tag{13}$$

The mean energy of adsorption can be used to predict the adsorption mechanism. If the value of E is less than 8, the system follows physisorption [49]. However, if mean energy of adsorption, E within the range of 8 to 16, the adsorption process is indicated to be ion exchange [50] and if the value of E is greater than 16, the system indicates toward the chemisorption [51]. In the present study, a plot of $ln q_e$ versus ε^2 (Chart-6) was done to determine the value of q_s and K_r. Mean energy of adsorption, E was calculated using equation (13). The values are enlisted in table-1. The value to E (69 KJ/mol) indicates that the adsorption mechanism follows chemisorption.
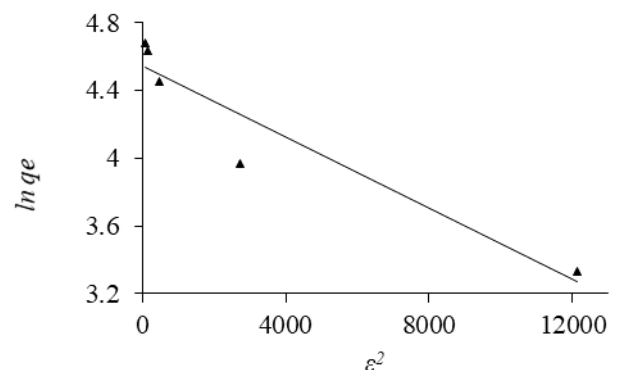
Chart-6: Dubinin-Radushkevich Isotherm for MJF-Zn (II) ion adsorption system

Table-1: Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm parameters obtained by linear fitting for the MJF adsorbents

Langmuir Isotherm				Freundlich Isotherm			
q_∞(mg/g)	K(L/mg)	R_L	R^2	1/n	n	K_f (mg/g)	R^2
142.85	0.012	0.167	0.994	0.524	1.908	6.295	0.949

Temkin Isotherm				Dubinin-Radushkevich Isotherm			
A_T (L/mg)	b_T	B (J/mol)	R^2	q_s (mg/g)	K_r (mol^2/KJ^2)	E (KJ/mol)	R^2
0.1125	76.82	32.25	0.990	93.69	$1.05*10^{-4}$	69	0.906

Table-2: Maximum adsorption capacities (q_∞) for some natural adsorbent for Zn (II) ion removal

Adsorbent	q_∞(mg/g)	Reference
Phosphoric Acid Modified Rice Husk	101.01	[53]
Sulfuric acid modified Bagasse	31.11	[54]
Bael Leaves	2.083	[55]
Clarified sludge	15.53	[56]
Rice husk ash	14.30	[56]
Neem bark	13.29	[56]
Bark	5.965	[57]
Bagasse	8.228	[57]
Bark+Bagasse	7.481	[57]
CaCl$_2$ treated Dried marine green macroalga	128.8	[58]
HCl treated Carrot residues	29.61	[59]
Modified Jute fiber (MJF)	**142.85**	**This study**

3.4 Effect of initial concentration on the removal of Zn (II) ion

The effect of initial zinc ion concentration on the removal rate of Zn (II) ion is shown in chart-7.
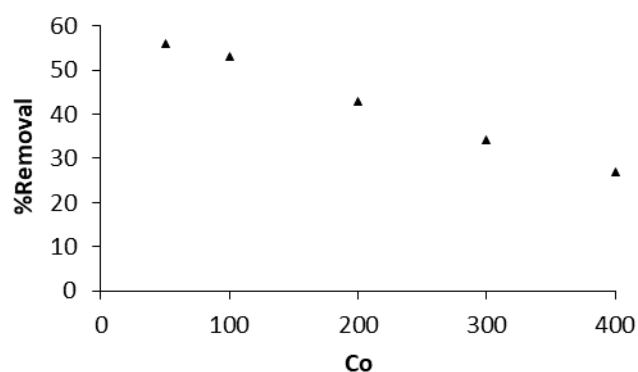

Chart-7: The relation between initial Zn (II) ion concentration and removal rate.

In the experiment it was observed that as the initial concentration increases, the rate of removal of Zn^{2+} decreases linearly. The observations were made from a range of 50 to 400mg/L and were found that as the removal rate decreased from 56% to 27%. The probable reason for this phenomenon is as the concentration increases, the available sites on the adsorbent decreases, causing a decline in the removal rate.

4. CONCLUSIONS

In this paper, Adsorption capacity of MJF was found to be very high and can be concluded that MJF can be used as a potential adsorbent for the removal of Zn (II) ion from waste water. The equilibrium data of the experiment was fitted in four two-parameter isotherms. The Langmuir isotherm model showed the best fit indicating towards monolayer formation. From Freundlich, Temkin and Dubinin-Radushkevich isotherms, the system was found to be favorable, exothermic and follow chemical adsorption mechanism respectively.

REFERENCES

[1] Mehdipour, S., Vatanpour, V. and Kariminia, H.R., 2015. Influence of ion interaction on lead removal by a polyamide nanofiltration membrane. Desalination, 362, pp.84-92.

[2] Abid, B.A., BrbootI, M.M. and Al-ShuwaikI, N.M., 2011. Removal of heavy metals using chemicals precipitation. Engineering and Technology Journal, 29(3), pp.595-612.

[3] Esalah, J. and Husein, M.M., 2008. Removal of heavy metals from aqueous solutions by precipitation-filtration using novel organo-phosphorus ligands. Separation Science and Technology, 43(13), pp.3461-3475.

[4] Černá, M., 1995. Use of solvent extraction for the removal of heavy metals from liquid wastes. Environmental monitoring and assessment, 34(2), pp.151-162.

[5] Charerntanyarak, L. Heavy metals removal by chemical coagulation and precipitation. Water Sci. Technol. 1999, 39, 135–138.

[6] Algureiri, A.H. and Abdulmajeed, Y.R., 2016. Removal of Heavy Metals from Industrial Wastewater by Using RO Membrane. Iraqi Journal of Chemical and Petroleum Engineering, 17(4), pp.125-136.

[7] Vital, B., Bartacek, J., Ortega-Bravo, J.C. and Jeison, D., 2018. Treatment of acid mine drainage by forward osmosis: heavy metal rejection and reverse flux of draw solution constituents. Chemical Engineering Journal, 332, pp.85-91.

[8] Sarkar, S. and Adhikari, S., 2018. Adsorption Technique for Removal of Heavy Metals from Water and Possible Application in Wastewater-Fed Aquaculture. In Wastewater Management Through Aquaculture (pp. 235-251). Springer, Singapore.

[9] Santhy, K. and Selvapathy, P., 2004. Removal of heavy metals from wastewater by adsorption on coir pith activated carbon. Separation Science and Technology, 39(14), pp.3331-3351.

[10] Aksu, Z.,Equilibrium and kinetic modelling of cadmium(II) biosorption by C. 6ulgaris in a batch system: effect of temperature, Separation and Purification Technology 21 (2001) 285–294.

[11] Sardella, F., Gimenez, M., Navas, C., Morandi, C., Deiana, C. and Sapag, K. (2015) 'Conversion of viticultural industry wastes into activated carbons for removal of lead and cadmium', Journal of Environmental Chemical Engineering, Vol. 3, No. 1, pp.253–260.

[12] Renu, Agarwal, M. and Singh, K., 2017. Methodologies for removal of heavy metal ions from wastewater: an overview. Interdisciplinary Environmental Review, 18(2), pp.124-142.

[13] Thangavel, S. & Venugopal, G. (2014) Understanding the adsorption property of graphene-oxide with different degrees of oxidation levels. Powder Technology 257, 141–148.

[14] Shen, W., Li, Zh. and Lieu, Y. (2008) Recent Pat. Chem. Eng. 1, 27.

[15] Vinitnantharat, S., Rattanasirisophon, W. and Ishibashi, Y. (2007) Water Sci. Technol. 55, 145.

[16] Hema, M. and Srinivasan, K. (2010) Indian J. Eng. Mater. Sci. 17, 373.

[17] Oliveira, E., Montanher, S., Andrade, A., Nobrega, J., Rollemberg, M., 2005. Equilibrium studies for the sorption of chromium and nickel from aqueous solutions using raw rice bran. Process Biochem. 40 (11), 3485–3490.

[18] D. Mohan, K.P. Singh, Single and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse – an agricultural waste, Water Res. 36 (2002) 2304– 2318.

[19] N.A. Khan, S.I. Ali, S. Ayub, Effect of pH on the removal of chromium (Cr) (VI) by sugar cane baggase, Sci. Technol. 6 (2001) 13–19.

[20] Karthikeyan, T., Rajgopal, S. and Miranda, L.R., 2005. Chromium (VI) adsorption from aqueous solution by Hevea Brasilinesis sawdust activated carbon. Journal of hazardous materials, 124(1-3), pp.192-199.

[21] Ajmal, M., Rao, R.A.K., Anwar, S., Ahmad, J. and Ahmad, R., 2003. Adsorption studies on rice husk: removal and recovery of Cd (II) from wastewater. Bioresource technology, 86(2), pp.147-149.

[22] S. Ayub, S.I. Ali, N.A. Khan, Efficiency evaluation of neem (Azadirachta indica) bark in treatment of industrial wastewater, Environ. Pollut. Control J. 4 (4) (2001) 34–38.

[23] W.T. Tan, S.T. Ooi, C.K. Lee, Removal of chromium (VI) from solution by coconut husk and palm pressed fibre, Environ. Technol. 14 (1993) 277–282.

[24] Montes-Atenas, G. and Schroeder, S.L., 2015. Sustainable natural adsorbents for heavy metal removal from wastewater: lead sorption on pink bark (Pinus radiate D. Don). Surface and interface analysis, 47 (10), pp.996-1000.

[25] V.V. Srivastava, M.M. Swamy, I.D. Mall, B. Prasad, I.M. Mishra, Adsorptive removal of phenol by bagasse fly ash and activated carbon: equilibrium, kinetics and thermodynamics, Colloids Surf. A 272 (2006) 89–104.

[26] Y.S. Ho, J.F. Porter, G. Mckay, Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: copper, nickel and lead single component systems, Water Air Soil Pollut. 141 (2002) 1–33.

[27] M.I. El-Khaiary, Least-squares regression of adsorption equilibrium data: comparing the options, J. Hazard. Mater. 158 (2008) 73–87.

[28] Wang, W.M., Cai, Z.S., Yu, J.Y. and Xia, Z.P., 2009. Changes in composition, structure, and properties of jute fibers after chemical treatments. Fibers and Polymers, 10(6), pp.776-780.

[29] J. R. Deans, B.G. Dixon, Uptake of Pb2+ and Cu2+ by novel biopolymers, Water Res. 26(1992) 469-472.

[30] K. Kurita, T. Sannan, Y. Iwakura, Studies on Chitin. VI. Binding of Metal Cations, J. Appl. Polym. Sci. 23(1979) 511-515.

[31] Li, X.; Tang, Y.; Xuan, Z.; Liu, Y.; Luo, F. Study on the preparation of orange peel cellulose adsorbents and biosorption of Cd^{2+} from aqueous solution. Sep. Purif. Technol. **2007**, 55, 69– 75.

[32] Zhou, Y.; Lu, J.; Zhou, Y.; Liu, Y. Recent advances for dyes removal using novel adsorbents: a review. Environ. Pollut. **2019**, 252, 352– 365.

[33] Daochalermwong, A., Chanka, N., Songsrirote, K., Dittanet, P., Niamnuy, C., & Seubsai, A. (2020). Removal of Heavy Metal Ions Using Modified Celluloses Prepared from Pineapple Leaf Fiber. *ACS omega*, *5*(10), 5285-5296.

[34] Rosa, M.F., Medeiros, E.S., Malmonge, J.A., Gregorski, K.S., Wood, D.F., Mattoso, L.H.C. and Imam, S.H. (2010) Cellulose Nanowhiskers from Coconut Husk Fibers: Effect of Preparation Conditions on Their Thermal and Morphological Behavior. Carbohydrate Polymers , 81, 83-92.

[35] Poletto, M., Pistor, V., Zeni, M. and Zattera, A.J. (2011) Crystalline Properties and Decomposition Kinetics of Cellulose Fibers in Wood Pulp Obtained by Two Pulping Processes. Polymer Degradation and Stability, 96, 679-685.

[36] Fackler, K., Stevanic, J.S., Ters, T., Hinterstoisser, B., Schwanninger, M. and Salmén, L. (2011) FT-IR Imaging Spectroscopy to Localise and Characterise Simultaneous and Selective White-Rot Decay within SprudeWoodcell. Holzforschung ,65, 411-420.

[37] K. Vijayaraghavan, T.V.N. Padmesh, K. Palanivelu, M. Velan, Biosorption of nickel(II) ions onto Sargassum wightii: application of two-parameter and three parameter isotherm models, J. Hazard. Mater. B133 (2006) 304– 308.

[38] Ayawei, N., Ebelegi, A.N. and Wankasi, D., 2017. Modeling and Interpretation of adsorption isotherms. Journal of Chemistry, 2017.

[39] S. Kundu, A.K. Gupta, Arsenic adsorption onto iron oxide-coated cement (IOCC): regression analysis of equilibrium data with several isotherm models and their optimization, Chem. Eng. J. 122 (2006) 93–106.

[40] Weber, T.W. and Chakravorti, R.K., 1974. Pore and solid diffusion models for fixed-bed adsorbers. AIChE Journal, 20(2), pp.228-238.

[41] A.W. Adamson, A.P. Gast, Physical Chemistry of Surfaces, sixth ed., WileyInterscience, New York, 1997.

[42] E. Voudrias, F. Fytianos and E. Bozani : Sorption Description isotherms of Dyes from aqueous solutions and Waste Waters with Different Sorbent materials, Global Nest, The Int.J. 2002 4(1),75-83.

[43] Puttamat, S. and Pavarajarn, V., 2016. Adsorption study for removal of Mn (II) ion in aqueous solution by hydrated ferric (III) oxides. International Journal of Chemical Engineering and Applications, 7(4), pp.239-243.

[44] Alene, A.N., Abate, G.Y. and Habte, A.T., 2020. Bioadsorption of Basic Blue Dye from Aqueous Solution onto Raw and Modified Waste Ash as Economical Alternative Bioadsorbent. Journal of Chemistry, 2020.

[45] Tempkin, M.I. and Pyzhev, V., 1940. Kinetics of ammonia synthesis on promoted iron catalyst. Acta Phys. Chim. USSR, 12(1), p.327.

[46] C. Aharoni, M. Ungarish, Kinetics of activated chemisorption. Part 2. Theoretical models, J. Chem. Soc. Faraday Trans. 73 (1977) 456–464.

[47] M.M. Dubinin, L.V. Radushkevich, The equation of the characteristic curve of the activated charcoal, Proc. Acad. Sci. USSR Phys. Chem. Sect. 55 (1947) 331–337.

[48] A. Gunay, E. Arslankaya, I. Tosun, Lead removal from aqueous solution by natural and pretreated clinoptilolite: adsorption equilibrium and kinetics, J. Hazard. Mater. 146 (2007) 362–371.

[49] Monika J, Garg V, Kadirvelu k. Chromium (VI) removal from aqueous solution, using sunflower stem waste. J. Hazardous materials 2009;162:365 – 372.

[50] Çalışkan, E. and Göktürk, S., 2010. Adsorption characteristics of sulfamethoxazole and metronidazole on activated carbon. Separation Science and Technology, 45(2), pp.244-255.

[51] Gereli, G., Seki, Y., Kuşoğlu, İ.M. and Yurdakoç, K., 2006. Equilibrium and kinetics for the sorption of promethazine hydrochloride onto K10 montmorillonite. Journal of colloid and interface science, 299(1), pp.155-162.

[52] Singh, T.S. and Pant, K.K., 2004. Equilibrium, kinetics and thermodynamic studies for adsorption of As (III) on activated alumina. Separation and purification technology, 36(2), pp.139-147.

[53] Dada, A.O., Olalekan, A.P., Olatunya, A.M. and Dada, O.J.I.J.C., 2012. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn^{2+} unto phosphoric acid modified rice husk. IOSR Journal of Applied Chemistry, 3(1), pp.38-45.

[54] D. Mohan and K. P. Singh, "Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse—an agricultural waste," Water Research, vol. 36, no. 9, pp. 2304–2318, 2002.

[55] Kumar, P.S., Kirthika, K. and Kumar, K.S., 2009. Bael tree leaves as a natural adsorbent for the removal of zinc (II) ions from industrial effluents. Adsorption Science & Technology, 27(5), pp.503-512.

[56] A. K. Bhattacharya, S. N. Mandal, and S. K. Das, "Adsorption of Zn(II) from aqueous solution by using different adsorbents," Chemical Engineering Journal, vol. 123, no. 1-2, pp. 43–51, 2006.

[57] Schwantes, D., Gonçalves Jr, A.C., Miola, A.J., Coelho, G.F., Dos Santos, M.G. and Leismann, E.A.V., 2015. < b> Removal of Cu (II) and Zn (II) from water with natural adsorbents from cassava agroindustry residues. Acta Scientiarum. Technology, 37(3), pp.409-417.

[58] L. C. Ajjabi and L. Chouba, "Biosorption of Cu^{2+} and Zn^{2+} from aqueous solutions by dried marine green macroalgaChaetomorphalinum," Journal of Environmental Management, vol. 90, no. 11, pp. 3485–3489, 2009.

[59] B. Nasernejad, T. E. Zadeh, B. B. Pour, M. E. Bygi, and Zamani, "Camparison for biosorption modeling of heavy metals (Cr (III), Cu (II), Zn (II)) adsorption from wastewater by carrot residues," Process Biochemistry, vol. 40, no. 3-4, pp. 1319– 1322, 2005.