

Kinetic, isotherm and thermodynamic studies of Fe (II) ion removal using activated carbon derived from *Alocasia indica*

^[1]Reenarani Wairokpam, ^[2]Potsangbam Albino Kumar

^{[1][2]}Department of Civil Engineering, National Institute of Technology Manipur- 795004

^[1]reena.wairokpam@gmail.com, ^[2]albinoiit@gmail.com

Abstract: In this study, activated carbon derived from *Alocasia indica* (Taro) was used for the removal of Fe(II). pH of 6, dosage of 3g/L with time of contact 80 mins were the optimal conditions obtained in the batch experimentation process. The adsorbent surface area was identified by BET technique and characterized by Scanning electron microscopy (SEM) and Energy dispersive X-ray measurements (EDAX). The adsorption kinetics study reveals that the kinetic data follows Pseudo-2nd-order with higher R² of 0.99 and lesser chi square value of 0.001. From the experimental data, it was observed that isotherm model fitted well with Langmuir isotherm with maximum adsorption capacity of 4.975 mg/g and R² value of 0.98, indicating chemical adsorption and formation of homogenous surface. Thermodynamic studies revealed that the adsorption process is spontaneous and endothermic.

Index Terms: *Alocasia indica*, Isotherms, Kinetics and Thermodynamic parameters.

I. INTRODUCTION

Groundwater is used as a source of drinking water throughout the world and India is the largest user of groundwater. Groundwater is a vital resource for rural areas in India. Due to inadequate municipal water supplies, the dependence on groundwater for urban residents also increases rapidly. Removing of heavy metals is a major concern as they possess a great risk to both public and environmental health. Iron which is a heavy metal also possess the same risk as it can easily enter the food chain. Iron is the common constituent of groundwater since iron is found abundantly in the earth's crust [1]. Iron is usually concentrated in groundwater due to the dissolution of iron bearing rocks and minerals and seepage of domestic sewage effluents. This makes the quality of water differ from one place to another. The iron content in groundwater depends on natural processes and anthropogenic activities [2]. Normal amount of iron is essential for human nutrition but larger amount adversely affect the human health. According to Bureau of Indian Standard (BIS) as well as World Health Organisation (WHO), the desirable limit for iron content is 0.3mg/l and the permissible limit is 1mg/l. In concentration above 0.3mg/L, iron imparts to water a yellowish coloration, bitter taste and also stains material [3]. Application of activated carbon as adsorbent has become attractive field of studies due to low cost, easy operation and high efficiency. Activated carbon derived from bio-adsorbent is considered as effective adsorbent due to its unique structure, larger surface area, highly developed pore volume and huge number of active sites for adsorbing Fe(II) ion [4].

This study is to investigate the removal of Fe (II) ion from the contaminated groundwater of Tuibong of Churachandpur district, Manipur, India using activated carbon prepared from *Alocasia indica* (Taro). Taro is grown all over Manipur and is easily available at low cost throughout the year [5]. The iron content is more than 6mg/L, which is very much above the permissible limit. The effect of pH, adsorbent doses, contact time and effect of co-ions on the adsorption capacity were investigated by batch process. The kinetic studies, isotherm models and thermodynamics were also studied to know the adsorption behavior.

II. METHODOLOGY

A. Preparation of Adsorbent

Taro was procured from local market, washed, oven dried at 110°C for 15 hours. Dried Taro was powdered, sieved (Indian Standard Sieve) and treated with phosphoric acid for 24 hrs. The activated carbon was then washed thoroughly and dried in an oven at 150^o C till it reached constant density and humidity. The activated carbon derived from Taro (ACT) was then stored in desiccators for further use.

B. Adsorbent characterization

The adsorbent surface area, pore volume and pore size distribution were obtained using BET technique. SEM and EDAX were used for the determination of the adsorbent characteristics. The surface morphology of the adsorbent before and after the adsorption process was obtained from SEM (Sigma - 300) operated at 20.00 KV along with EDAX (Zeiss Gemini) which determines the elemental analysis and composition evaluation of the sample.

C. Batch experiment and Analysis

The study to determine the adsorption of Fe (II) on activated Taro was performed in Jar-test apparatus (Phipps and Bird Model PB-600,USA). The test was done by mixing fixed amount of ACT adsorbent with 500 ml of sample in a beaker and stirred at 250 rpm at room temperature until equilibrium is attained. The effect of pH was studied from pH (2 – 10) and ACT dose of 1 – 4g. The desired pH of the solutions were adjusted by adding 0.1N NaOH and 0.1N HCl using pH meter (PCS Tester 35). Thereafter, the supernatant were separated and absorbance of the solutions were determined for Fe (II) by using UV-Visible Spectrophotometer (Thermo Scientific-Evolution 201,USA) at a fixed wavelength of 510 nm. All the chemicals used were of analytical grade without purification. The amount of Fe (II) ion adsorbed by adsorbent can be calculated from the following equation:

$$q_t = \frac{C_o - C_t}{m} V \quad (1)$$

where, q_t (mg/g) is the quantity of Fe(II) ions adsorbed at time t , C_o is the initial concentration and C_t is the concentrations of Fe (II) ions (mg/L) at time t , V (L) is the volume of Fe(II) ions sample and m (in gram) is the mass of the adsorbent.

III. RESULTS AND DISCUSSION

A. Characterisation of adsorbent

The SEM images of the ACT adsorbent prior to adsorption and after the adsorption process are shown in Fig.1 and Fig.2 respectively. The adsorbents prior to adsorption of Fe (II) ion have a smooth surface and homogenous pores as seen in Fig. 1, but after the adsorption, the surface and pores are completely filled due to the deposition of iron on it. The EDAX images are also shown in Fig. 3 and Fig. 4 respectively. The EDAX image after adsorption shows the iron uptake on the surface of the adsorbent ACT. To understand the pore size distribution of ACT adsorbent, BET analysis was examined. The surface area, pore volume and pore size of the adsorbent was found to be 4.929 m²/g, 0.011 cc/g and 3.507 nm respectively.

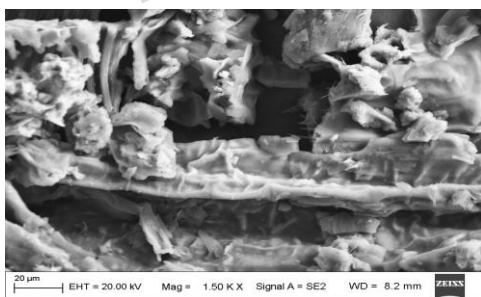


Fig.1: SEM images of ACT adsorbent before Fe(II) ion adsorption

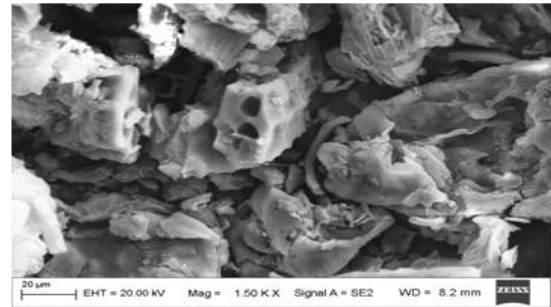


Fig.2: SEM images of ACT adsorbent after Fe(II) ion adsorption

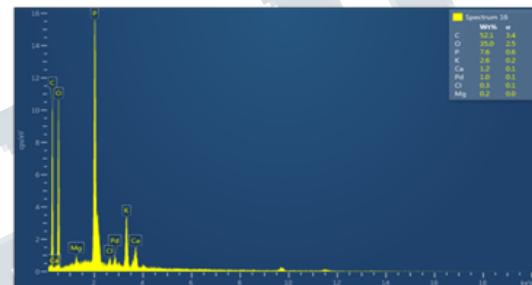


Fig.3: EDAX images of ACT adsorbent before Fe(II) ion adsorption

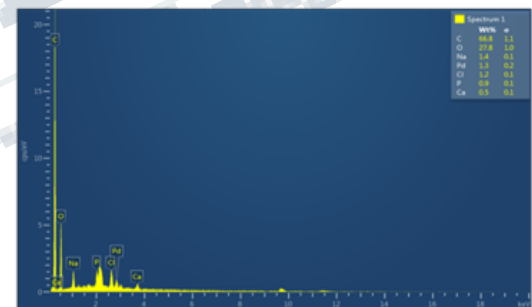


Fig.4: EDAX images of ACT adsorbent after Fe(II) ion adsorption

B. Effect of pH:

The effect of pH was examined at different pH ranging from 2-10 and the test solutions were adjusted to different pH values accordingly to find the optimal pH. The amount of ferrous iron adsorbed increases with increasing pH and reaches its peak at pH of 6 as shown in Fig. 5. On further increasing the pH the rate of adsorption decreases which may be due to attainment of saturation point. So, the optimal pH was set at 6 where the maximum removal of Fe(II) ion was found to be 90%.

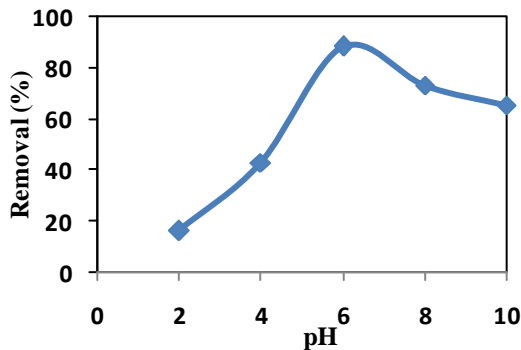


Fig.5: pH effect for the removal of Fe(II) ion by ACT adsorbent.

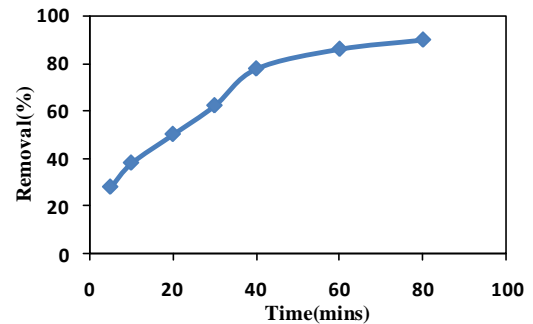


Fig.7: Effect of contact time on Fe(II) ion removal by ACT adsorbent.

C. Effect of adsorbent dosage:

The adsorbent dosage controls the capacity of adsorbent and thus, is an important parameter in adsorption studies [6]. The adsorbent dosage were varied from 1 to 4g. From Fig. 6, it is seen that the adsorption capacity increase with increase in dosage of the adsorbent due to significant accessibility of adsorbent sites. However, with further increase in the adsorbent dosage, no significant affect in the removal of Fe (II) was seen due to overcrowding of adsorbent particles. Hence, the optimum dosage was achieved at 3 g/L with a removal percentage of 95%.

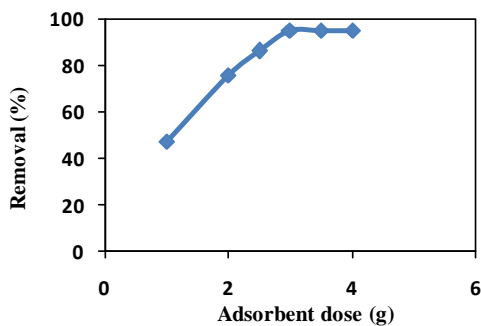


Fig.6: Effect of adsorbent dosage on the adsorption of Fe(II) ion by ACT adsorbent.

D. Effect of contact time

The kinetics studies were performed to determine the adsorption rates of the adsorbent and the minimum time required for adsorption [7]. In this experiment, contact time ranges from 0, 5, 10, 15, 20, 30, 40, 60, 80, 100 and 120 minutes with pH 6, dose of 3g/L. It was observed that, the percentage removal of Fe (II) ion increases with increase in contact time as shown in Fig.7. Equilibrium was reached at 80 min with a maximum removal efficiency of 89.95% for Fe(II) ion removal using ACT adsorbent.

E. Adsorption Kinetics:

To investigate the rate of the adsorption process, the adsorption kinetic data were simulated with Pseudo-1st-order and Pseudo-2nd-order models, which is expressed as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where q_e and q_t (both in mg/g) are adsorption capacity at equilibrium and time t and k_1 (min^{-1}) and k_2 (g/mg min) are rate constants of Pseudo-1st-order and Pseudo-2nd-order adsorption respectively [8]. Fig. 8 and 9 represents the plot of Pseudo-1st-order and Pseudo-2nd-order kinetic model. The correlation coefficient (R^2) for Pseudo-2nd-order R^2 was found to be 0.99, as compared to Pseudo-1st-order (R^2 of 0.822), indicating that Pseudo-2nd-order fits better for the kinetic model. The parameters for kinetic models are shown in Table1.

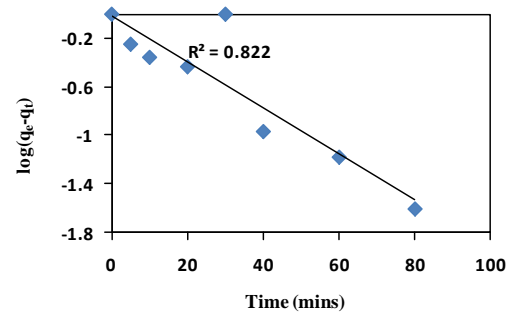


Fig.8: Pseudo-1st-order kinetic model for Fe(II) ion adsorption.

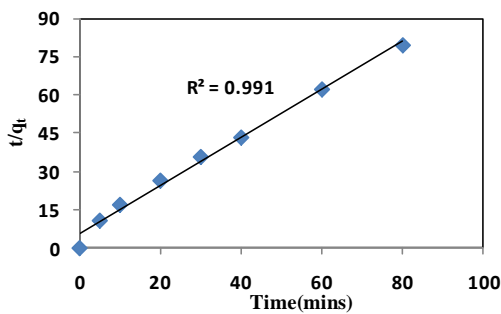


Fig.9: Pseudo-2nd-order kinetic model for Fe(II)ion adsorption.

Table 1: Kinetic Parameters for Fe(II) ions removal.

| Kinetic Model | Parameters | R ² | χ ² |
|-------------------------------|--|----------------|----------------|
| Pseudo-1 st -order | k ₁ (min ⁻¹) = 0.0132 q _e (cal) = 4.031mg/g | 0.822 | 0.15 |
| Pseudo-2 nd -order | k ₂ (g/mgmin) = 0.1174 q _e (cal.) = 5.490mg/g | 0.991 | 0.001 |

F. Adsorption Isotherm Studies:

Adsorption isotherm describes the equilibrium relationships between adsorbent and adsorbate [3]. The most commonly used isotherms are Langmuir and Freundlich isotherms were used to fit the equilibrium data. Its applicability was judged with the correlation coefficient (R²).

The linearized form of the isotherm is given by: [1]

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (4)$$

Where, C_e is the equilibrium concentration of adsorbate in groundwater sample after adsorption (mg/L), q_e is the amount of metal adsorbed per unit mass of adsorbent(g), q_m is the monolayer adsorption capacity(mg/L) and b is the Langmuir constant.

The linear expression of the isotherm is as follows:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (5)$$

where, q_e is the amount of adsorbate adsorbed at equilibrium(mg/g), K_f and n are Freundlich constants and C_e is the equilibrium concentration of adsorbate in the solution(mg/L).

Chi-square test was also done to evaluate the better fit isotherm using the equation:[8]

$$\chi^2 = \sum \frac{(q_e - q_{em})^2}{q_{em}} \quad (6)$$

where q_e and q_{em} (mg/g) are iron adsorbed at equilibrium evaluated from experiment and predicted isotherm models respectively.

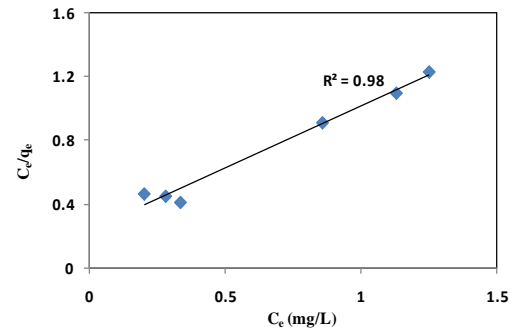


Fig.10:Langmuir Isotherm plot for Fe(II) ion adsorption by ACT.

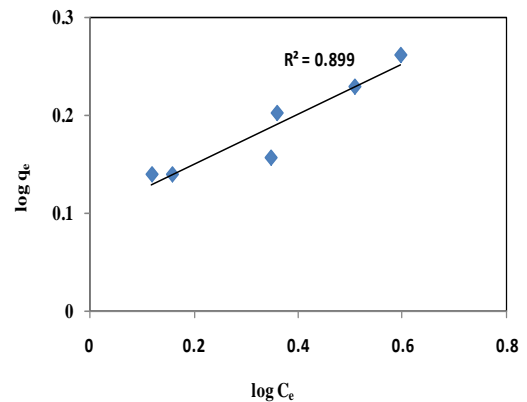


Fig.11: Freundlich Isotherm plot for Fe(II) ion adsorption by ACT adsorbent.

The plot of linear equation of Langmuir and Freundlich isotherms are shown in Fig.10 and Fig.11 respectively. The correlation coefficient (R²) was calculated to examine the fitness of the two isotherm models in the linear form. It was observed that Langmuir model fitted better than Freundlich model since the R² value of Langmuir model is higher and more closer to unity and lesser χ² value as shown in Table 2, indicating chemisorption and formation of monolayer surface. The maximum adsorption capacity was found to be 4.975mg/g.

Table 2. Coefficients of Langmuir and Freundlich isotherms

| Isotherms | Langmuir | | | | Freundlich | | | |
|-----------|----------------|-----------------------|---------|----------------|----------------|----------------|------|----------------|
| | R ² | q _m (mg/g) | b(L/mg) | χ ² | R ² | K _f | 1/n | χ ² |
| Taro | 0.98 | 4.975 | 1.26 | 0.002 | 0.899 | 6.76 | 0.42 | 1.02 |

G. Thermodynamics studies

In order to determine the effect of temperature on adsorption of Fe (II), the study were done at different temperatures i.e., 298K, 308K and 318 K. The thermodynamics parameters were evaluated as:

$$\Delta G^{\circ} = -RT \ln K_L \quad (7)$$

$$\ln K_L = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \quad (8)$$

$$K_L = \frac{q_e}{C_e} \quad (9)$$

where, R (8.314JK⁻¹mol⁻¹) is the universal gas constant, T(K) is the absolute temperature, K_L is the thermodynamic constant, q_e (mg/g) is the amount of Fe(II) adsorbed at equilibrium and C_e (mol/L) is the concentration of Fe(II) at equilibrium time. The negative values of Gibb's energy shows thermodynamic feasibility and spontaneity of the adsorption process. The thermodynamic parameters are shown in Table 3. The values of enthalpy and entropy were calculated from the slope and intercept of the plot of 1/T

versus ln K_L (Fig.12). The enthalpy value is positive thus suggesting that the adsorption of Fe(II) by ACT adsorbent is an endothermic reaction.

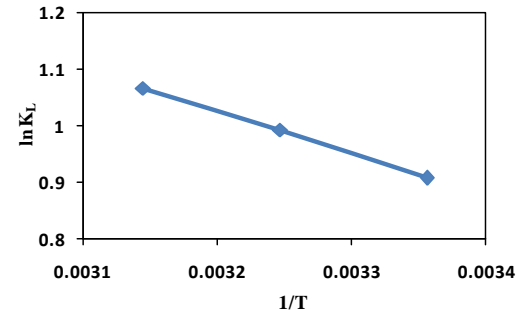


Fig.12: The plot of 1/T versus ln K_L for removal of Fe(II) by ACT.

Table 3: Thermodynamics parameters for removal of Fe(II) by ACT adsorbent.

| Adsorbent | Temp(K) | K _L | ΔG ^o (KJmol ⁻¹) | ΔH ^o (KJmol ⁻¹) | ΔS ^o (JK ⁻¹ mol ⁻¹) |
|-----------|---------|----------------|---|---|--|
| Taro | 298 | 3.46 | -3.07 | 20.853 | 22.537 |
| | 308 | 3.72 | -3.35 | | |
| | 318 | 3.99 | -3.66 | | |

IV. CONCLUSION

In this study, activated carbon derived from bio-adsorbent Taro (ACT) was used for the effective removal of Fe (II) ion. It was found that the maximum uptake for iron of ACT adsorbent was observed at pH 6, adsorbent doses of 3g/L and contact time of 80mins for ACT adsorbent. The adsorption process follows the pseudo- 2nd-order kinetic model. The experimental data confirmed that the adsorption of Fe (II) ion by ACT adsorbent follows Langmuir isotherm with the formation of monolayer surface with the correlation coefficient R² of 0.98 and chi square value of 0.002. The maximum adsorption capacity for Fe(II) ion removal was found to be 4.975mg/g. The thermodynamics parameters confirms that the adsorption process is endothermic and spontaneous. Hence, it can be concluded that the locally available and inexpensive adsorbent ACT has potential for the removal of Fe (II) ion from the contaminated groundwater.

REFERENCES

- [1] L. Chandana, K. Krushnamurty, D. Suryakala and C. Subrahmanyam, "Low-cost adsorbent derived from the coconut shell for the removal of hexavalent chromium from aqueous solution," *Materials Today: Proceedings*, vol.26, pp.44-51, July 2019.
- [2] M. O. Borna *et al*, "Batch and column studies for the adsorption of chromium(VI) on low-cost Hibiscus Cannabinus kenaf, a green adsorbent," *Journal of the Taiwan Institute of Chemical Engineers*, vol.68, pp.80-89, Nov.2016.
- [3] S. Khandaker, Y. Toyohara, G. C. Saha, M. R. Awual and T. Kuba, "Development of synthetic zeolites from bio-slag for cesium adsorption: kinetic, isotherm and thermodynamic studies," *Journal of Water Process Engineering*, vol.33, pp.1-10, Feb.2020.
- [4] E. C. Nnadozie and P. A.Ajibade, "Adsorption, kinetic and mechanistic studies of Pb(II) and Cr(VI) ions using APTES functionalized magnetic biochar," *Microporous and Mesoporous Materials*, vol.32, pp.106-292, Oct. 2020.

- [5] G. Ketsela , Z. Animen and A. Talema,” Adsorption of Lead (II), Cobalt (II) and Iron (II) From Aqueous Solution by Activated Carbon Prepared From White Lupine (GIBITO) HSUK,” *Journal of Thermodynamics and Catalysis*, vol.11, pp.1-8, August 2020.
- [6] H. Peng, J. Guo and B. Wang, “Adsorption behavior of Fe (III) in aqueous solution on melamine,” *Water Science and Technology*, vol.82, pp.1848-1857, Nov.2020.
- [7] M. H. Salmani *et al*,” Removal of Cr(VI) oxoanion from contaminated water using granular Jujube stems as a porous adsorbent,” *Groundwater for Sustainable Development*, vol.8, pp.319-323, April 2019.
- [8] A. M. Ahmed, M. I. Ayad , M. A. Eledkawy, M. A. Darweesh and E. M. Elmelegy,” Removal of iron, zinc and nickel-ions using nano bentonite and its application on power station wastewater,” *Heliyon*, vol.7, pp.1-14, Feb.2021.

