

Identification of adsorption mechanism for Iron uptake by activated carbon derived from *Alocasia indica*

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Abstract

The present study assess the potential of activated carbon derived from *Alocasia indica*, Taro, (ACT) for the removal of Fe(II) from the groundwater of Yaingangpokpi, Imphal East District, Manipur, India. The ground water was observed to be having Fe (II) concentration of 4.34 mg/L which is very much above the permissible limit of 1 mg/L. The adsorbent was activated using phosphoric acid and characterized by scanning electron microscopy (SEM) and energy dispersive X-ray measurements (EDAX). Adsorption kinetics study reveals that the kinetic data were better obeyed the Elovich kinetic model with correlation coefficient (R²) of 0.992 as compared to that of diffusion model with 0.93. Though, activated carbon are predominately physical adsorption due to the presence of large surface area, the study reveals a major chemical based adsorption due to the presence of functional groups in *Alocasia indica* (Taro). Adsorption isotherm studies reveals the adsorption was able to explained by both the non-linear Langmuir and Freundlich isotherm with insignificant error Chi square value of 0.05 and 0.003 respectively. The maximum adsorption capacity obtained was 4.03 mg Fe (II)/g ACT. These results proved that the adsorbent ACT is effective for the removal of Fe (II) from ground water.

Keywords: *Alocasia indica*, Elovich model, Fe(II), intraparticle diffusion

Introduction

Heavy metal causes enormous threat to environment and public health, being a pollutant in source and treated water. The iron content in groundwater depends on weathering of rocks and minerals and man-made activities [1]. Most iron contamination occurs mainly due to these man-made activities. Iron is important for the human health, especially for proper functioning of body cells. Iron deficiency causes Anaemia and excess consumption leads to cirrhosis of liver, heart diseases, liver cancer, and infertility etc. [2]. The presence of higher concentrations of iron changes color, taste, odour of water, staining of clothes and utensils and corrosion of water pipes [3]. Fe (II) in the dissolved form is colorless, but on oxidation Fe(II) oxidizes to Fe(III) forming precipitates which is reddish in color causing unpleasant odour in groundwater. According to Bureau of Indian Standard (BIS) as well as World Health Organisation (WHO), the desirable limit for iron content is 0.3 mg/L and the permissible limit is 1 mg/L, whereas, the desirable limit is 0.1mg/L according to Indian Council of Medical Research (ICMR) [4]. As stated by the Central Groundwater Board, the extent of iron contamination was found maximum in the Northeast. Therefore, it is necessary to remove excess iron in order to procure safe drinking water.

Many treatment techniques were employed by different researchers in the past few decades for iron removal from contaminated groundwater namely, precipitation and filtration, membrane technique, manganese greensand filter, oxidation, ion exchange and biological iron removal [5]. All the mechanism depends on the groundwater quality and the process conditions. And, most of these techniques are either extremely expensive or too ineffective to reduce metal ions from water. Among these techniques, adsorption process is widely used in recent years due to its cost effectiveness, easy operation and ample availability of adsorbents.

This study aims to investigate the removal of Fe (II) ions from groundwater samples using *Alocasia*

indica(Taro). It is a tropical plant which is also a traditional food and is widely cultivated throughout the year and is easily available at low cost all over Manipur. The samples for the estimation of iron were collected from the groundwater of Yaingangpokpi area, Imphal East, Manipur. For this study, the non-linear regression form was used to analyse the kinetic and isotherm models.

Methodology

Preparation of Adsorbent

Alocasia Indica (Taro) was collected from local market, washed thoroughly with distilled water to remove dirt and other impurities. It is then peeled and dried in an oven at 1500 C for 15 hours. Dried Taro were 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 1000 C till it reached constant density and humidity. The activated carbon derived from Taro (ACT) was then stored in desiccators for further use.

Adsorbent characterization

The Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray Analysis (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 5.00 KV, magnification 300X along with EDAX (Zeiss Gemini). EDAX determines the elemental analysis and composition evaluation of the sample. BET technique was also used to analyse the surface area, pore volume and pore size of the adsorbent.

Batch experiment and Analysis

The batch study determines the capacity of adsorption of Fe (II) on activated Taro and were conducted in Jar-test apparatus (Phipps and Bird Model PB-600). The tests were conducted by mixing certain amount of ACT adsorbent with 500 ml of sample in a beaker and stirred at 300 rpm at room temperature until equilibrium is reached. The effect of pH was found out by varying the pH (2 – 10) and a dose ACT (1 – 8g). The desired pH of the solutions were adjusted using 0.1N NaOH and 0.1N HCl by pH meter (ESICO-1013). Thereafter, the supernatant were separated and absorbance of the solutions were determined for Fe(II) by UV-Visible Spectrophotometer (Thermo Scientific-Evolution 201) at a fixed wavelength of 510 nm. All the chemicals used were of analytical grade without purification. The sample concentrations were determined by calibration curve. The amount of Fe (II) ion adsorbed by adsorbent can be calculated based on the difference of Fe(II) ion concentration in the groundwater sample before and after adsorption according to the following equation:

$$q_t = (C_o - C_t) / m V \quad (1)$$

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

Error Analysis

It is extensively used for the minimization and maximization of error distributions based on the convergence criteria of the experimental and predicted values. Also, the error analysis presents the fitting of diffusional and adsorption models. The chi square value is measured by the difference between the experimental and

the calculated equilibrium data of the different models used.

$$\chi^2 = \sum_{(i=0)}^n (q_e - q_{(pred.)})^2 / q_{pred} \quad (2)$$

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

Results and discussion

Characterization

The ACT adsorbent has the BET surface area of $4.125 \text{ m}^2/\text{g}$, pore volume of $0.009 \text{ cm}^3/\text{g}$ and pore size of 3.311 nm . The SEM images of ACT adsorbent before and after adsorption are shown in Fig.1 and Fig.2 respectively. The micrograph of the adsorbent shows fractured and rough surface morphology indicating the presence of good adsorbent sites. The EDAX spectra of the same are also shown in Fig. 3 and 4 respectively. The peak on the EDAX image of ACT after adsorption (Fig. 4) confirms the iron uptake on the surface of the adsorbent.

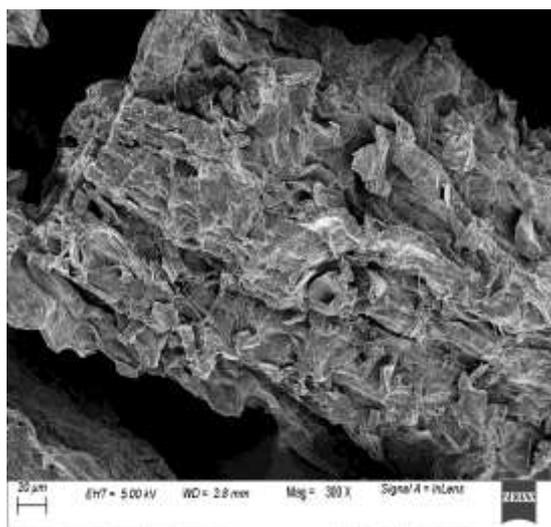


Fig.1: SEM images of ACT before adsorption for the removal of Fe(II) ion.

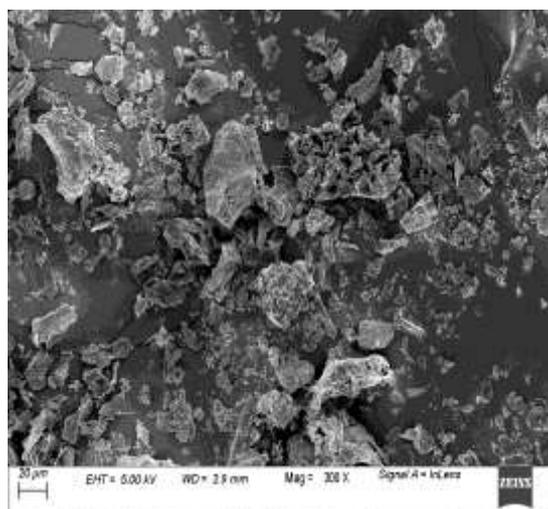


Fig.2: SEM images of ACT after adsorption for the removal of Fe(II) ion.

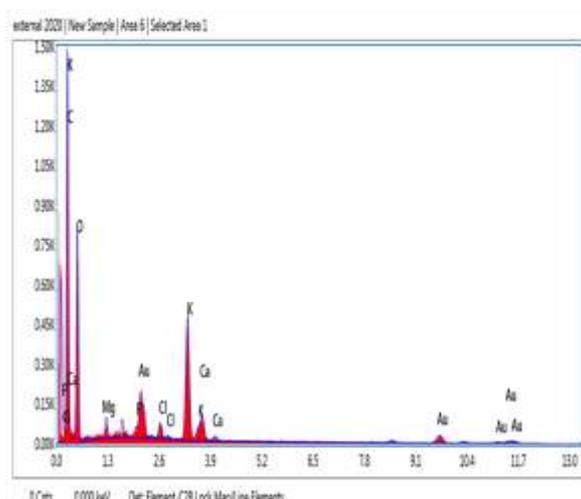


Fig.3: EDAX images of ACT before adsorption for the removal of Fe(II) ion .

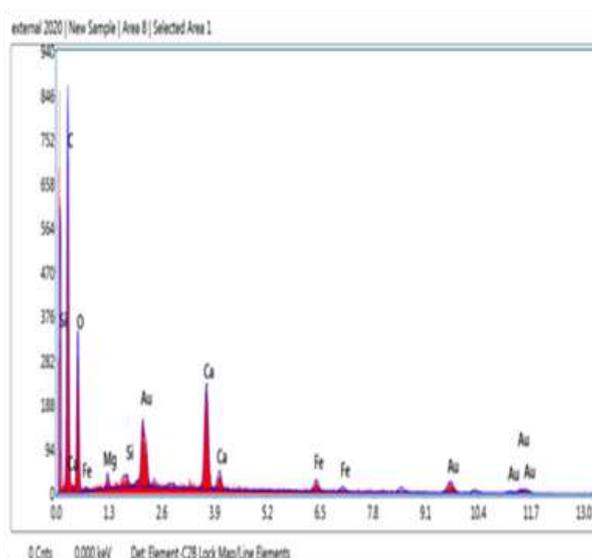


Fig.4: EDAX images of ACT after adsorption for removal of Fe(II) ion .

Adsorption kinetics

The adsorption kinetic models generally determines the potential rate of the process and the mechanism of adsorption [6]. The adsorption kinetics of Fe (II) onto ACT evaluates the experimental data which were analysed using non-linear regression kinetic models, Pseudo-1st-order, Pseudo-2nd-order, intraparticle diffusion model and Elovich model. The intra – particle diffusion determines the rate of the reaction. The Elovich kinetic model describes the chemisorption kinetics of adsorption of adsorbates in aqueous phase onto adsorbents. The expressions of the kinetic models are as follows:

$$q_t = q_e (1 - e^{-k_1 t}) \tag{3}$$

$$q_t = (q_e^2 k_2 t) / (q_e k_2 + t) \tag{4}$$

$$q_t = k_d t^{0.5} \tag{5}$$

$$q_t = 1/\beta \ln(1 + \alpha \beta t) \tag{6}$$

where q_t (mg/g) and q_e (mg/g) are the amount of Fe(II) ions adsorbed at time t (min) and at equilibrium

time respectively, k_1 (min⁻¹) and k_2 (g/mg min) are the Pseudo-1st-order and Pseudo-2nd-order constants respectively, k_d [mg/(g min^{1/2})] is the intraparticle diffusion rate constant, α [mg/(g min)] and β (g/mg) are the Elovich rate constant.

Parameters of the kinetic model for adsorption of Fe(II) onto ACT are shown in Table 1. From the table, it is found that Elovich kinetic model has higher value of correlation coefficient ($R^2=0.99$) with lower chi square ($\chi^2= 0.001$) as compared to the other kinetic models.. Thus, it can be concluded that Fe (II) ion adsorption onto ACT obeyed the Elovich kinetic model, suggesting that chemical adsorption is predominant. The plot of intra-particle diffusion model for adsorption of Fe (II) ion on ACT is presented in Fig.5. The experimental values were compared with predicted values for Pseudo-1st-order, Pseudo-2nd-order and Elovich kinetic model as shown in Fig.6.

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

Kinetic Model	Calculated Parameters	R ²	χ^2
Pseudo-1 st -order	$k_1=0.0133$ $q_e(\text{cal}) =2.461$ mg/g	0.96	0.26
Pseudo-2 nd -order	$k_2=0.0074$ $q_e(\text{cal}) =2.389$ mg/g	0.97	0.15
Intra-particle Diffusion	$k_d=0.1123$	0.93	0.65
Elovich	$\alpha=2.446$ $\beta=3.15$	0.99	0.001

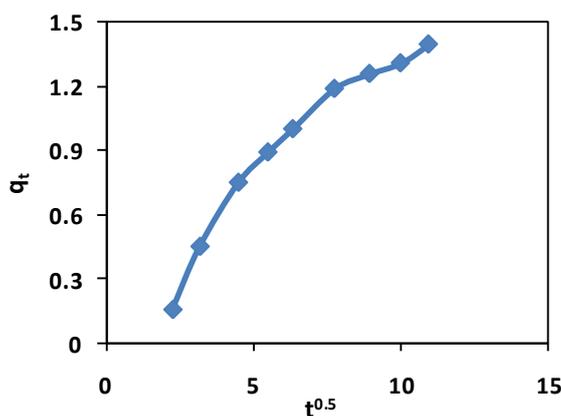


Fig.5: Intraparticle diffusion model for Fe (II) ion adsorption by ACT.

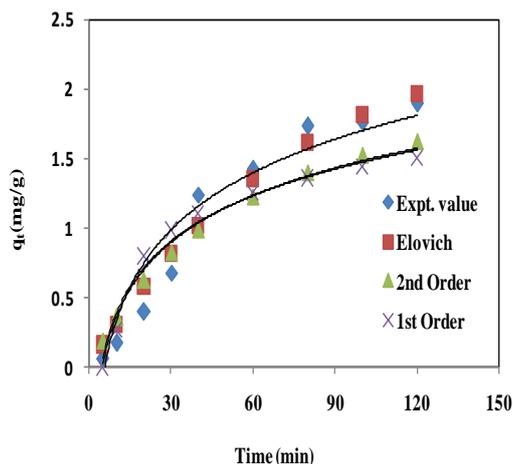


Fig.6: Comparison plot of Experimental and Predicted value of kinetic models for Fe (II) ion removal by ACT.

Adsorption Isotherms

In this study, two mostly applied isotherm models, Langmuir and Freundlich isotherms, were used for non-linear regression analysis. Langmuir isotherm assumes the adsorption of both monolayer and homogenous surface, while Freundlich isotherm describes the exponential adsorption and formation of heterogenous surface and does not assume monolayer adsorption[7]. The non-linear expression of Langmuir isotherm model (Eqn.7) and Freundlich isotherm model (Eqn.8) equations are expressed as follows:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{7}$$

$$q_e = K_F C_e^{1/n} \tag{8}$$

where, q_e (mg/g) is the amount of Fe(II) ions adsorbed at equilibrium, q_m (mg /g) is the maximum adsorption required, C_e (mg/L) is the equilibrium concentration of Fe(II), b (L/mg) is enthalpy constant, and K_f and n are Freundlich constants.

Table 2 listed the parameters of the isotherm models along with Chi-square (λ^2) test between the experimental and predicted q_e value to identify the best fit isotherm. Fig.7 shows the comparison plot between Experimental and predicted value for adsorption of Fe(II) ion onto ACT for both Langmuir and Freundlich isotherms. The maximum adsorption capacity was found to be 4.03 mg/g. The experimental data for the removal of Fe (II) ion by ACT fits adequately to both Langmuir and Freundlich isotherm, giving correlation coefficient (R^2) values of 0.97 and 0.96 respectively, thus suggesting the better fit of Fe (II) adsorption onto ACT by both the isotherm models [8].

Table 2 : Non - linearized Isotherm coefficients for the adsorption of Fe(II)ion onto ACT.

Langmuir Isotherm	q_m (mg/g)	b	R^2	χ^2
	4.03	0.97	0.96	0.05
Freundlich Isotherm	K_F	$1/n$	R^2	χ^2
	0.7556	0.3229	0.97	0.003

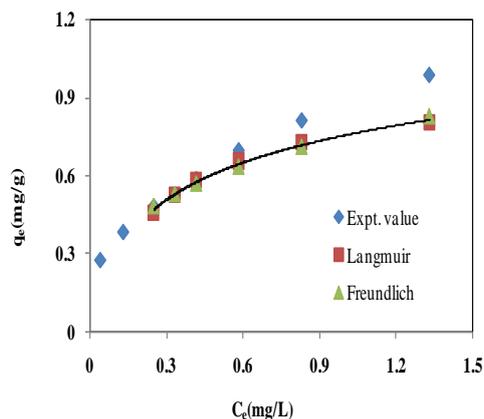


Fig.7: Comparison plot of Experimental and Predicted value of Isotherm models for Fe (II) ion removal by ACT.

Conclusion

The experimental data were evaluated with the existing kinetic models and isotherms. The finding reveals that the experimental data agrees well with the Elovich kinetic model with the correlation coefficient (R^2) of 0.99 and chi square of 0.001 thus, confirming chemical adsorption behaviour of Fe (II) ion onto ACT. The isotherm data fitted best with both the Langmuir and Freundlich isotherms with R^2 values of 0.96 and 0.97 respectively through the formation of both homogenous and heterogenous surface. The maximum adsorption capacity obtained was 4.03 mg Fe(II)/g ACT.

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Authors Profile



Reenarani Wairokpam has completed her Bachelor of Engineering (B.E) in Civil Engineering from Manipur Institute of Technology, Manipur and M.Tech in Water Resource from Kaziranga University, Jorhat on the dissertation topic Comparison of numerical methods of unsteady flow. She is a research scholar at National Institute of Technology, Manipur. Her research work is regarding removal and treatment of heavy metals from both groundwater and wastewater. She has published one Conference paper titled "Assessment and Removal of Iron from Groundwater by *Alocasia indica*" in International Conference on Water, Energy and Environmental Sustainability (WEES 2020) held on 13th – 15th January 2020 at National Institute of Technology, Durgapur. She has attended workshop on New Technologies for Development held at Asian Institute of Technology, Bangkok, Thailand from 2nd -14th September, 2016. She has also participated in the workshop on National Information System for Climate and Environment Studies (NICES) and its activities conducted at Interdisciplinary Climatic Research Centre, Cotton University, Guwahati, Assam on 29th January, 2018 with the collaboration of National Remote Sensing Centre (NRSC) ISRO, Department of Space, Government of India, Hyderabad, North Eastern Space Application Centre (NESAC), Department of Space, Government of India, Umiam, Shillong and Interdisciplinary Climatic Research Centre (ICRC), Cotton University, Government of Assam, Guwahati.



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