Kinetics of Iron (II) Biosorption onto the Waste Leaves of *Myrica esculata* (Kafal)

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Abstract

Water pollution due to heavy metals is the major challenging environmental issue. Heavy metals released into environment through various anthropogenic and natural activities. Beyond the limit, heavy metals are harmful to all living organisms and some of them are very harmful even at very low concentrations. Various methods cited in the literature are used for the removal of heavy metals from water or waste water. Among these, biosorption is an efficient, low cost, eco-friendly and very economical process. The readily available and good biosorbents can increase the reliability of the biosorption process. In the present study, the waste leaves of Myrica esculata were used for the removal of iron (II) from synthetically prepared waste water. Experimental data indicates that these leaves are efficient biosorbents for the removal of iron (II) ions. The applying kinetic parameters such as pseudo first order, pseudo second order, infra particle diffusion and Elovich model favors suitability of biosorption of iron (II) onto the leaves of Myrica esculata.

Keywords: Heavy metals, Conventional methods, Biosorption, Iron, Kinetics

Introduction

Heavy metals introduced into water or waste water is now become a matter of environmental concern [1]. Most of them are harmful even at very low concentrations and some heavy metals are essential for the proper growth and development of organisms under the concerned limits. Beyond the limit, they are definitely harmful and their concentrations in aquatic bodies has increased due to some anthropogenic activities i.e. mining, tannery, jewelry, chemical, metallurgical, electrical and electronics large scale industries in industrial nations, and also arts and crafts in developing countries [2,3]. Heavy metals are significant environmental pollutants, and their toxicity is a problem of increasing significance for ecological, nutritional and environmental reasons [3,4]. Heavy metals include lead (Pb), cadmium (Cd), nickel (Ni), cobalt (Co), iron (Fe), zinc (Zn), chromium (Cr), arsenic (As), silver (Ag) and the platinum group of elements. Through food chains, they are deposited in the cells and tissues of human and causing poisonous effects [5-7]. Various methods cited in the literature used for the removal of metal contaminants from water or waste water are ion exchange [8], chemical precipitation [9], preconcentration [10], reverse osmosis [11], membrane filtration [12], adsorption biological treatment [13-15] and phytoremediation [16-18]. Among these biosorption is relatively new, efficient and economical method and can be used in large scale. The reliability and efficiency of the process is actually depending on the choice of biosorbents. The cheap and easily biological materials cited in the literature are rice husk [19], coconut shell [20], plant barks [21,22], leaves [23,24], sawdust [25], sugarcane bagasse [26], peat moss [27] and algal and fungal biomass [28,29].

Iron is essential for the growth and development of the living organisms under the limit (0.3mg/L) [30,31]. Iron is an essential part of the haemoglobin that transport oxygen in the body. Hemoglobin, the oxygen-carrying protein found in red blood cells. Iron is also present in enzymes needed for various biochemical reactions. Iron overload can increase the risk of diabetes, heart attack and cancer, particularly in older people, stomach pain, nausea, vomiting, bloody vomiting, metabolic acidosis and death may occur from liver failure [32,33]. Iron is present in water in its soluble ferrous form (Fe^{++}) and the iron contaminated water may cause taste, odor, color, or turbidity problems [30,34]. Kafal is an angiospermic plant (family Myricaceae) and is commonly found in the northern hills of Kumaun and Garhwal of India and western Nepal. The waste leaves were collected in the month of April at the region of Kumaun hills, India.

Material and Methods

The collected waste leaves were washed 2-3 times by double distilled water for removing water soluble impurities on the surface of the leaves. After that leaves were dried for 5-6 days in laboratory and heated at 70^0C for next three hours in hot air oven under controlled conditions. After grinding and sieved in particle size 63 microns the powder of leaves was preserved in sealed bottles. The synthetic waste water containing Fe (II) was prepared from the salt ferrous sulphate ($FeSO_4.7H_2O$, AR grade) in double distilled water. The pH of this solution was adjusted to 3 because acidity favors the solubility of iron (II) ion in water. A 100 ml solution containing requisite concentration of Fe (II) ion was treated with a 1g of adsorbent in a 250 ml of conical flask at a constant shake 170 rpm. The solution was then filtered and adsorbent filtered out. The concentration of metal ions before and after adsorption was determined by atomic absorption spectrophotometer (Model: AAS Vario 6, Analytik Jena, Germany).

Results and Discussion

The kinetic study of biosorption of iron (II) ion uptake by the biosorbent prepared from Kafal leaves is an essential study for the optimized batch conditions and suitability of biosorption on to biosorbent. It is also necessary to identify the types of biosorption mechanism in an applicable batch operation. Therefore, the experimental data of adsorption have been tested with four usual kinetic models such as pseudo first order kinetic model, pseudo second order kinetic model, elovich kinetic model and intra particle diffusion.

Pseudo first order kinetic model: The pseudo-first order or Lagergren equation is usually represented as below:

$$ln\,(q-q') = ln\,q - k.t$$

Where q and œ′ are the adsorption capacity at equilibrium and at time t, respectively, in mg/g, and k is the pseudo-first order rate constant in min^{-1}. Lagergren pseudo first-order kinetics is not proved to be effective in representing the experimental kinetic data for the biosorption process. In some cases, it provides excellent fit with the experimental kinetic data; it failed to predict the amount of adsorbate theoretically thereby deviating from the theory [35,36].

By plotting the value of ln (q - œ′) versus t, the value of the rate constant k and q are obtained from the slope and intercept and are given in Table 1. In this pattern, the value of rate constant is lower than the metal uptake at equilibrium and the value of regression (R^2=0.961) indicate that the biosorption is occurring onto one site per ion (Table 1).

***Pseudo second order kinetic model*:**

In this model, the rate-limiting step is the surface adsorption that involves chemisorption, where the removal from a solution is due to physicochemical interactions between the two phases [37]. The pseudo second-order model is found to well explain the kinetics of the most of sorption processes and very well for the entire range of sorption time periods. The pseudo second-order model was found to show a better fit towards the biosorption of heavy metals from the aqueous solutions. The pseudo second order kinetic [38] model for iron (II) adsorption is given as below:

$$\frac{t}{q} = \frac{1}{k'} \times q' + q \qquad \textbf{(4)}$$

Where k′ is the second order rate constant in g/mol/min and q and q′ are the amount of metal ion adsorbate at equilibrium and at time t in mg/g respectively. The regression value (R^2=0.971) is indicating that the iron (II) biosorption is following the pseudo second order kinetics more than pseudo first order kinetics and the rate limiting step is not a physical interaction. In this pattern the value of second order rate constant (k′) is more than metal uptake at equilibrium (q).

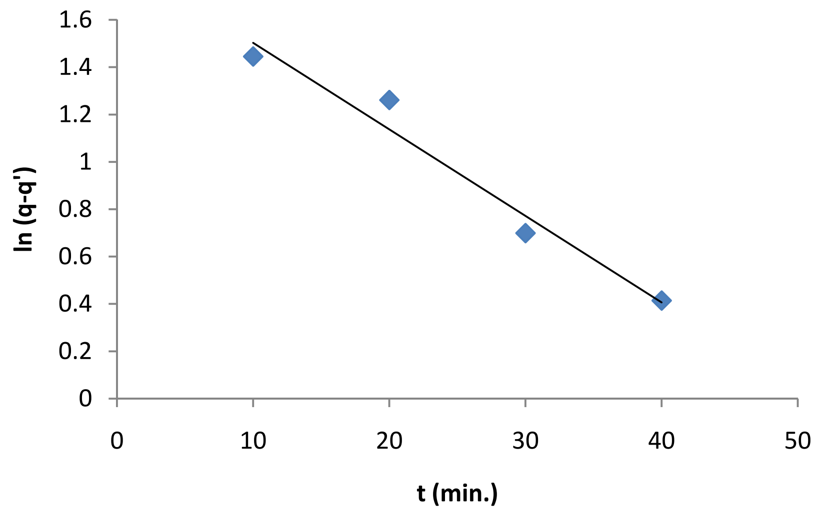

Fig. 1 Pseudo First Order Kinetic Model

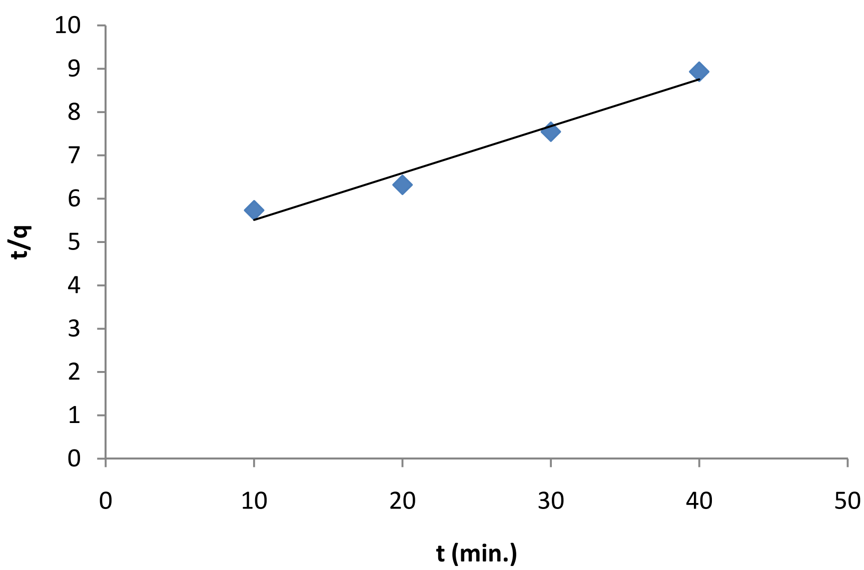

Fig. 2 Pseudo Second Order Kinetic Model

***Intra particle diffusion*:**

The intra particle diffusion model describes adsorption processes, where the rate of adsorption depends on the speed at which adsorbate diffuses towards adsorbent. Intra-particle diffusion model used here refers to the theory proposed by Weber and Morris [39] and it controls the batch process for most of the contact time. It explains a better adsorption mechanism which is related to an improved bonding between iron and Kafal leaves. The initial rate of intra-particle diffusion can be obtained by linearization of the curve according to equation.

$$q= k_d t^{1/2} + I$$

Where k_d and I are intra particle diffusion and obtained from slop and intercept of the plot q vs $t^{1/2}$. The value of I is as $I \neq 0$ indicate that the intra particle diffusion is not rate limiting step and the value of R^2 is calculated 0.964 which indicates the better applicability of the Weber and Morris equation.

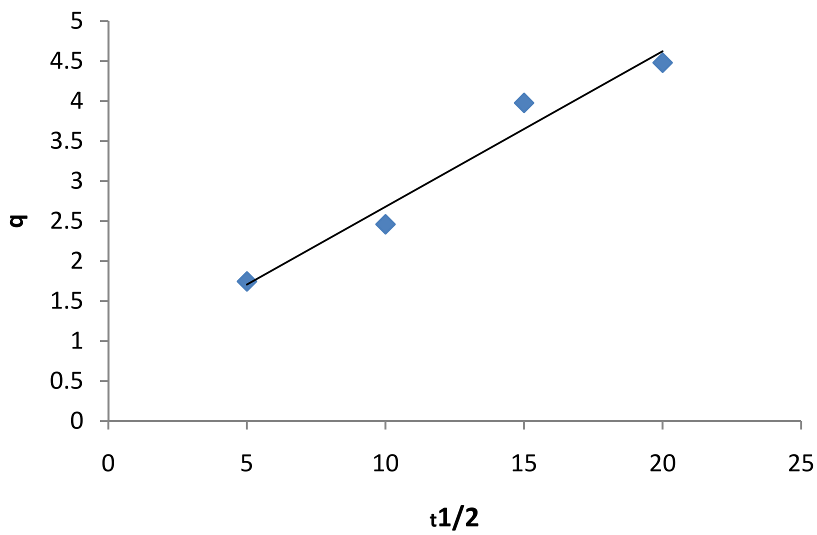

FIG. 3 INTRA PARTICLE DIFFUSION

***Elovich model*:**

The Elovich equation was first developed to describe the kinetics of chemisorptions of adsorbate onto adsorbent and its activation energy [40]. Elovich equation also describes second order kinetic assuming that the actual solid surfaces are energetically heterogeneous, but the equation cannot explain any definite mechanism for adsorbate–adsorbent interaction [40]. This is mathematically expressed by following equation:

$$q= a + b \ln t$$

Where a and b are the initial adsorption rate (mg/g/min) and desorption constant. These are obtained from the intercept and slop of the plot q versus ln t (Fig.3). The value of regression R^2 is obtained 0.931 which is found lesser than the pseudo first and second kinetic model and the values of a and b are found 2.054 and 3.196 respectively (Table 1). Biosorption kinetics of iron (II) examined using Elovich model indicates that the dynamics data fitted for the Kafal leaves.

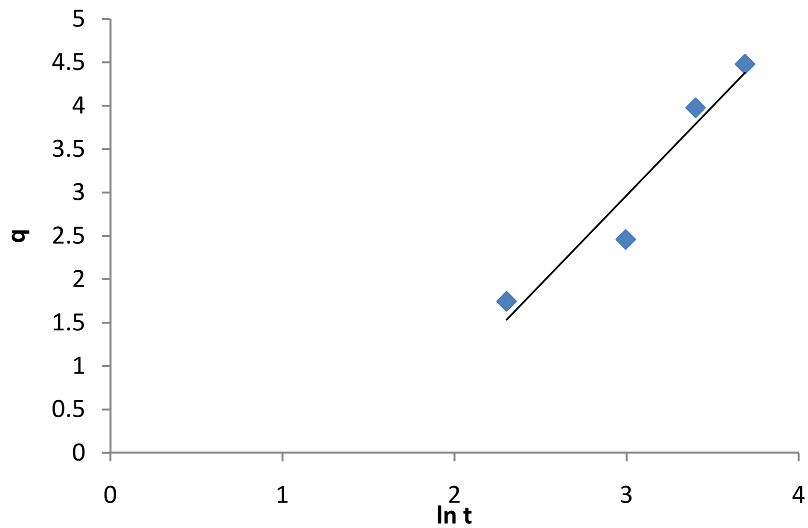

Fig. 4 Elovich Model

Table1. Adsorption Kinetic Constants for Adsorption of Fe (Ii) Ion Onto Kafal Leaves

Heavy metal	Kinetic models	Parameters	Values
Copper	Pseudo first order	k	0.036
		q	6.475
		R^2	0.965
	Pseudo second order	k′	9.259
		q	4.428
		R^2	0.971
	Elovich kinetic model	a	2.054
		b	3.196
		R^2	0.931
	Intra particle diffusion	k_d	0.194
		I	0.733
		R^2	0.964

Conclusion

The present study represents the suitability of iron biosorption on to Kafal leaves. The performance of biosorption is actually depending on the choice and availability of biosorbents. A readily available and good biosorbents can increase the efficiency and economy of the biosorption. The leaves of *Myrica esculata* are potential biosorbents for the removal of iron (II) from the industrial waste water.

In the present study, the high correlation for all the kinetic parameters indicate that the suitability of iron sorption under batch operations on to the leaf powder.

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