Investigation of Kinetics Behaviour of the Eucalyptus, Neem and Mango adsorbents in the removal of Cu ions from aqueous solutions

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Abstract— **The objective of the paper was to study first order and second order kinetic reaction of eucalyptus, neem and mango leaves adsorbent for the removal of Cu ions from aqueous solution. Kinetic studies showed good correlation coefficient for a pseudo-second order kinetic model and suitable to explain experimental data interaparticle transport. The adsorption equilibrium data correlate well with model with regression, R2, range from 0.97-1.00. Kinetic, equilibrium and thermodynamic results revealed that Cu ion removal by the studies adsorbents indicated that removal efficiencies of the tested adsorbents were in the following order neem leaves > mango leaves > eucalyptus leaves. High adsorption capacity of the tested adsorbents makes it preferable and very attractive alternative adsorption material**

Keywords-component; Kinetics; leaves; Cu ions; second order

I. INTRODUCTION

Aqueous effluents emanating from many industries contain heavy metals dissolved in it. If these discharges are emitted without purification, they may have severe impact on environment[1]. Primarily some anthropogenic activities, such as weathering of rocks and volcanic activities play a vital role for enriching the water reservoirs with heavy metals [2,3]. Among heavy metals, copper is considered as one of the most toxic one. The potential source of copper in industrial effluents includes paper and pulp, fertilizer, wood preservatives, refineries, metal cleaning and plating bath etc. The excessive intake of copper may cause renal and hepatic damage, severe mucosal irritation, wide spread capillary damage, gastrointestinal irritation and possibly necrotic changes in kidney and liver.

In the past decades, apart from experimental studies several mathematical models have been proposed to describe adsorption data, which can generally be classified as adsorption reaction models and adsorption diffusion models. Both models are applied to describe the kinetic process of adsorption; however, they are quite different in nature. Adsorption diffusion models are always constructed on the basis of three consecutive steps [4]

1. Diffusion across the liquid film surrounding the adsorbent particles, i.e., external diffusion or film diffusion;
2. Diffusion in the liquid contained in the pores and/or along the pore walls, which is so-called internal diffusion or intra-particle diffusion; and
3. Adsorption and desorption between the adsorbate and active sites, i.e., mass action.

II. THEORETICAL STUDY

A. *Pseudo-first-order equation)*

The pseudo-first order kinetic model assumes that the rate of occupation of sorption sites is proportional to the number of unoccupied sites. The pseudo-first order equation was expressed in equation .1 [5] :

$$\frac{dq_i}{dt} = k_1(q_e - q_t) \quad (1)$$

Where q_e and q_t (mg/g) are the adsorption capacities at equilibrium and time t in min respectively. k_1 (min^{-1}) is the pseudo-first-order rate constant for the kinetic model.

$$\frac{dq_i}{(q_e - q_t)} = dtk_1 \quad (2)$$

Integrating Eq.(1) with the boundary conditions of q_t=0 at t=0 and q_t=q_t at t= t, yields

$$\int_0^{q_t} \frac{dq_i}{(q_e - q_t)} = \int_0^t dtk_1 \quad (3)$$

We get

$$log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (4)$$

To distinguish kinetic equations based on adsorption capacity from solution concentration, Lagergren's first order rate equation has been called pseudo-first-order [6].

B. *Pseudo-second-order rate equation*

In 1995, Ho described a kinetic process of the adsorption of divalent metal ions onto peat [7], in which the chemical bonding among divalent metal ions and polar functional groups on peat, such as aldehydes, ketones, acids, and phenolics are responsible for the cation-exchange capacity of the peat. The pseudo second order is based on the assumption that the rate limiting step may be chemical sorption involving valence forces through sharing or exchange of electrons between heavy metal ions and adsorbent. The pseudo-second order kinetic rate equation was expressed as [8]: The driving force, (qe−qt), is proportional to the available fraction of active sites [9]. Then, it yields

$$\frac{dq_i}{dt} = k_2(q_e - q_t)^2 \quad (5)$$

The eq. (5) can be rearranged

$$\frac{dq_i}{(q_e-q_t)^2} = dtk_1 \quad (6)$$

Integrating Eq. (6) with the boundary conditions of q_t=0 at t=0 and q_t=q_t at t=t, yields

$$\int_0^{q_t} \frac{dq_i}{(q_e-q_t)^2} = \int_0^t dtk_1 \quad (7)$$

$$\frac{1}{(q_e-q_t)} = \frac{1}{q_e} + k_2 t \quad (8)$$

Put $h = k_2 q_e^2$ (mg/g min) is the initial rate then the equation becomes

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (9)$$

III. EXPERIMENTAL STUDY

In this study, the forest wastes such as eucalyptus, neem and magno leaves were selected as adsorbent for removal of Cu ion. Mature leaves were collected and washed thoroughly under running water to remove dust and any adhering particles. The leaves were then dried under sunlight for a few days and then in oven at 80 ºC until it became crisp. The powdered fiber material was sieved through a mesh size of 105 μm to obtain fine biomass. The finely sieved biomass was treated with 0.3 M HNO_3 solution for 24 h, followed by washing with deionized water until pH of 7.2 was achieved and oven dried at 60°C with constant mixing. The prepared biomass was stored in desiccators. Present study was focused cupper ion was used as the adsorbate. A 100 mg/L Cu stock solution was prepared by dissolving accurately weight amount of copper nitrate trihydrate ($Cu(NO_3)_2.3H_2O$) in double distilled water. Appropriate dilution of the stock solution was carried out in order to obtain the desired concentration of Cu solution used later in the experiment. The solutions were prepared using a standard flask. The range of concentrations used was prepared by serial dilution of the stock solution with deionized water. Batch experiments were carried out at room temperature using a conical flask by shaking a mixture of 0.1 g of prepared leaves powder and 20 mL of Cu solution in a centrifuge tube, at agitation rate of 150 rpm for allowing sufficient time for adsorption equilibrium. All samples were carried out in duplicate under the same conditions and the average results were taken. After agitation, the powder was removed by filtration using filter paper. The concentration of Cu in the filtrates as well as in the control samples were determined by using GBC Avanta Flame atomic Absorption Spectroscopy (AAS) spectrometer.

IV. RESULT AND DISCUSSION

A. *Determine q_e by experimentally*

The equilibrium isotherm was determined by using a range of different concentration of Cu solution (5 mg/L, 10 mg/L, 15 mg/L and 20 mg/L). Mixture of 0.1 g of leaves powder and 20 mL of Cu solution was contacted at agitation speed of 150 rpm for 50 hours, which was sufficient to reach equilibrium. The amount of Cu adsorbed at equilibrium (q_e) was calculated by using the equation (5)

$$q_e = \frac{(c_0 - c_e)}{m} V \quad (10)$$

Where V = volume of solution (L) = 20x10^{-3} L, m = mass of adsorbent (g) = Final wt – initial wt of leaf powder (before and after experiment), C_0 = Initial concentration of metal ions (mg/L) and C_e concentration of metal ions at equilibrium state (mg/L)

The experimental studies are given in previous report. The experimental results are tabulated in Table 1.

Table 1. Determination of q_e values of different leaves and different concentration from experimental results (initial wt. 0.1g and volume 20 ml.

C_0 (mg/L)	C_e (mg/L)	Final weight, g	m= w_f-w_i	q_e mg/g
Eucalyptus leaves				
5	0.499	0.2096	0.1096	0.8209
10	2.446	0.1924	0.0924	1.6344
15	5.346	0.1788	0.0788	2.4516
20	9.803	0.1621	0.0621	3.2848
Neem leaves				
5	0.082	0.2162	0.1162	0.8467
10	1.750	0.1997	0.0997	1.6552
15	3.747	0.1881	0.0881	2.5548
20	7.609	0.1744	0.0744	3.3324
Mango leaves				
5	0.740	0.2044	0.1044	0.8164
10	2.758	0.1887	0.0887	1.6332
15	5.205	0.1800	0.0800	2.4489
20	9.120	0.1666	0.0666	3.2662

B. *Determine Pseudo-first-order*

To determine the value of reaction constant k_1Pseudo-first-order rate equation using experimental values and computed and ploted Fig. 1 (a), Fig. 1(b) and Fig. 1(c) for eucalyptus leaves, neem leaves and mango leaves respectively. Figures showed the linear plots of log(qe-qt) against t at initial Cu ions concentration of 5 mg/L, 10 mg/L, 15 mg/L and 20 mg/L respectively. The k1 values were determined from the slope and intercept of the linear plots in figures.

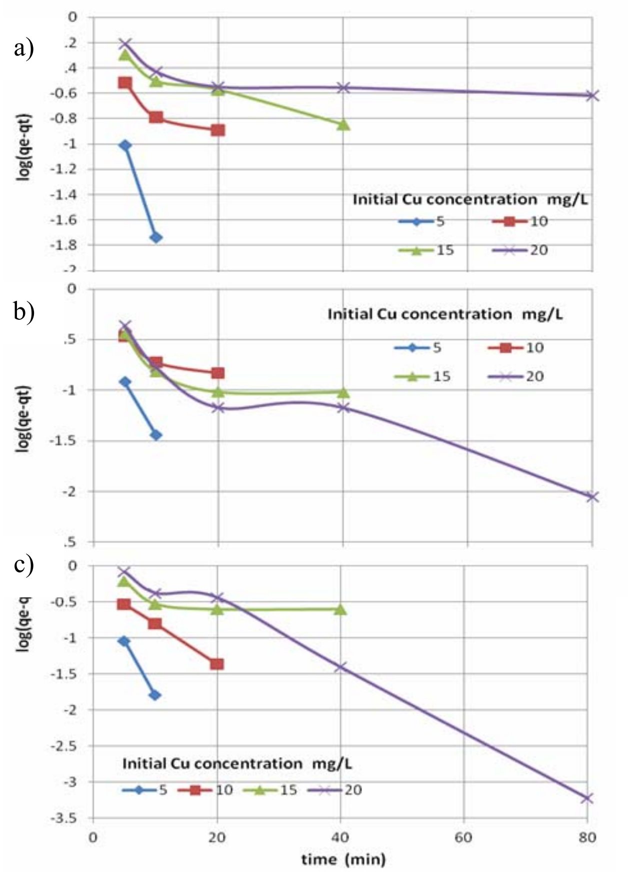

Fig. 1: Pseudo-first order plot for the sorption of Cu ions onto a) eucalyptus, b) neem leaves and c) mango leaves

C. Determine Pseudo-second-order

The pseudo-second order linear plots of t/q_t against contact time (t) at different initial Cu ions concentration for eucalyptus leaves, neem leaves and mango trees respectively. All graphs drown data obtained from experimental studies which was explained previous secition. The values of q_e , h and k_2 were calculated from the slope and intercept of the plots respectively. Fig. 2 (a), (b) and (c) give the values of k_2, experimental and calculated values of q_e as well as R^2 values for the pseudo-second order plots. It was observed that all linear plots with different initial concentration in figures showed R^2 values of nearly 1. This indicated that the kinetics data fitted perfectly well with the pseudo-second order model. In addition to the high values of R^2, the calculated qe values also agreed well with the experimental data obtained from the pseudo-second order kinetics. From figures it was observed that the values of h decrease from 4.6296 mg/mg min to 1.1884 mg/mg min when the initial concentration of Cu ions increased from 5 mg/L to 20 mg/L for eucalyptus leaves. For neem leaves show h values initially decrease 5mg/l to 10 mg/l and it increased upto 20 mg/l. For mango leaves showed different nature the h values decreased upto 15 mg/l and then it increased. This was because the higher the initial concentration of Cu ions, the higher the chances of collision with the binding sites of adsorbent and hence, leads to a higher initial sorption rate and it decreased. Apart from that, it was obvious that the values of k^2 was higher than the corresponding values of k1. This was because the pseudo-second order kinetic model assumed that the sorption rate is proportional to the square of number of unoccupied sites [10]. The values of k_2 decreased from with increasing initial Cu ions concentration. This occurred because at higher concentration of metal ions, the competition for surface active sites was high and consequently lower sorption rates are obtained [11]. The pseudo-second order kinetic model was also reported to fit well with the kinetics data from studies of a number of authors, including the adsorption of Cd ions onto pomelo peel [12], adsorption of Cu(II) ions onto Tectona grandis leaves [13], adsorption of Pb(II) ions onto pumpkin seed shell activated carbon [14], adsorption of Ni(II) ions onto potato peel [15], and adsorption of Cr(VI) ions onto cooked tea dust [16].

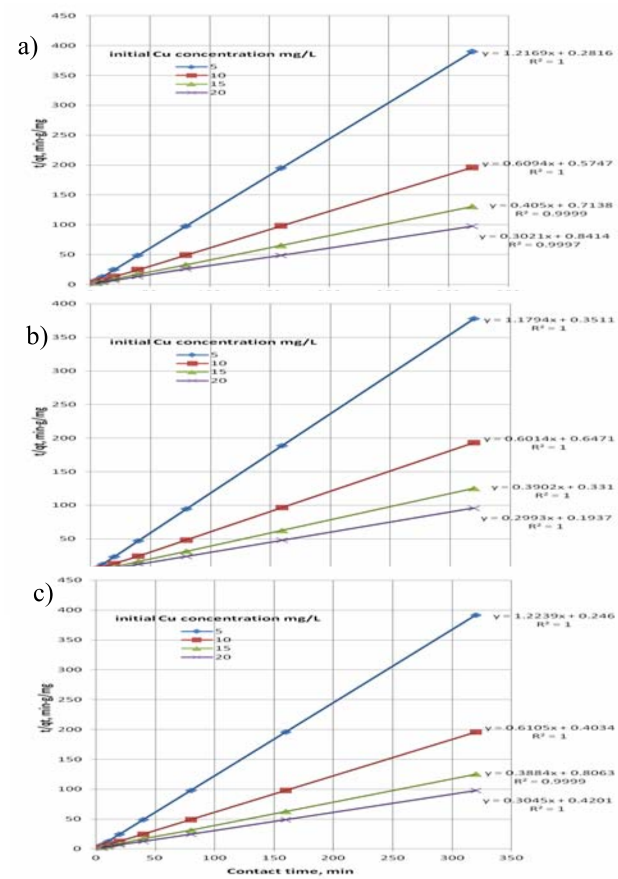

Fig. 2: Pseudo-second order plot for the sorption of Cu ions onto a) eucalyptus, b) neem leaves and c) mango leaves

IV CONCLUSION

. This part of the work is highlighted the use of highly efficient low cost and abundant materials for removal of Cu ions from aqueous solution. The quick removal and high capacity of eucalyptus, neem and mango indicated that they could be better alternative for removal of cu from waste water by sorption process. Kinetic experimental data revealed that fitted well with the pseudo-second order model and the sorption profiles derived based on the pseudo-second order kinetic model showed good agreement with experimental curves. Kinetic, equilibrium and themodynamic results revealed that Cu ion removal by the studies adsorbents indicated that removal efficiencies of the tested adsorbents were in the following order neem leaves > mango leaves > eucalyptus leaves. Based on the experimental condition and kinetic model it is found that the removal of Cu ion form their aqueous solution could attain nearly 100 %. This shows a new trend for using forest wastes for cleaning wastewater, which is another method for the benefit of environmental pollution control.

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