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Removal of Copper from Wastewater using Low Cost Adsorbents

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***Abstract*-In this study, Experiments were conducted in the laboratory to study the influence of important factors like adsorbent dosage and time of contact under the room temperature conditions (27℃ ±3℃). The experiments were conducted for batch adsorption study using pulp and paper mill sludge and cement kiln dust as low cost adsorbents on industrial wastewater. Based on results for quantification of adsorbent dosage for copper, it was observed that the equilibrium was attained for dosage of 4g/L and 2g/L and for contact time of 20 min and 40 min for pulp and paper mill sludge and cement kiln dust respectively. In equilibrium system the removal efficiency was 65% and 98% for pulp and paper mill sludge and cement kiln dust respectively. Adsorption equilibrium study was investigated by Freundlich, Langmuir and Tempkin isotherms for which ultimate adsorption capacity for pulp and paper mill sludge and cement kiln dust for adsorption of copper and zinc were calculated. The adsorption process was well fitted with the isotherms and best fitted for Langmuir isotherm. The maximum monolayer coverage from Langmuir isotherm was 15.47 mg/g for pulp and paper mill sludge and 50 mg/g for cement kiln dust. The calculations of thermodynamic parameters indicated that the adsorption is spontaneous and exothermic. Kinetic studies were analysed using pseudo first order and second order kinetics, and results showed that the pseudo-second order kinetic model gave a better fits than pseudo-first order kinetic model for adsorption. Comparing both pulp and paper mill sludge and cement kiln dust as adsorbents, the cement kiln dust showed more efficiency than pulp and paper mill sludge.**

Keywords: Isotherm, kinetics, cement kiln dust (CKD), paper mill sludge (PMS).

1.INTRODUCTION

Environmental pollution is currently one of the most important issues facing humanity. It was increased exponentially in the past few years and reached alarming levels in terms of its effects on living creatures. Toxic heavy metals are considered one of the pollutants that have direct effect on man and animals. Rapid growth in human population is one of the major causes of environmental pollution. Increased industrialization and urbanization throughout the world results in consistent release of toxic effluents, several industrial processes generate metal containing wastes. Heavy metals are non-degradable metals. Several industrial wastewater streams may contain heavy metals such as Cr, Cu, Pb, Zn, Ni, etc., including the waste liquids generated by metal finishing or the mineral processing industries. Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water. Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers and groundwater. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metals poisoning could result, for instance, from drinking water contamination. The removal of heavy metals can be accomplished by a variety of techniques. Conventional methods typically involve the use of processes such as coagulation, precipitation, ion-exchange, electro-chemical methods, membrane processes, extraction, adsorption, etc. Among these methods, adsorption is currently considered to be very suitable for wastewater treatment because of its simplicity and cost effectiveness. Some widely used adsorbents for adsorption of heavy metals include activated carbon[3], clay minerals, biomaterials, industrial solid wastes and zeolites. The aim of this investigation was to compare adsorption efficiency of copper from wastewater using two different types of adsorbents, pulp and paper mill sludge and cement kiln dust. The pseudo-first order and pseudo-second order kinetic models were used to describe kinetic of adsorption of Cu and lead onto pulp and paper mill sludge and cement kiln dust.

2. MATERIALS AND METHOD

Adsorption experiment study

Paper Mill Sludge (PMS) and Cement kiln dust (CKD) used in this study was collected from South Indian Paper Mills, Nanjangud, Karnataka, Hidelberg Cements, Ammasandra, Tumkur, Karnataka, India respectively. The wastewater was obtained from an electroplating industry which had copper concentration of 60mg/L. Horiba Jobin Yvon make (JY 200 model) Inductively Coupled Plasma Spectrometer (ICP) is used to determine the heavy metals contents. Argon gas is commonly used in the system and plasma temperature can range available between $6000°K$ to $10000°K$. ICP discharges are of relatively high electron density, at the order of $10^{15}cm^3$.

2.1 *Adsorbent*

Experiments were conducted using paper mill sludge (PMS) and cement kiln dust (CKD) as adsorbents for the removal of heavy metal from wastewater collected from an electroplating industry. Paper mill sludge (PMS) was dehydrated at 110℃ for about 24 hours, then grind into fine powder and then sieved with 425 micrometre sieve size. Cement kiln dust (CKD) was also dehydrated at 110℃ and then sieved with 425 micrometre sieve size. X-ray fluorescent analysis was used to characterize the chemical composition of CKD.

3.RESULTS AND DISCUSSION

3.1 *Scanning Electron Microscope*

The surface morphology of the adsorbents before and after metal ion adsorption was observed using SEM analysis. There are significant changes to the surface morphology of the adsorbents, as well as the formation of discrete aggregates on their surfaces following metal ion adsorption. The SEM images of the adsorbents before and after metal uptake was noted and the adsorbents displayed a dense and porous surface texture. Interaction of the adsorbents with Copper has resulted in the formation of flake-like deposits on its surface.

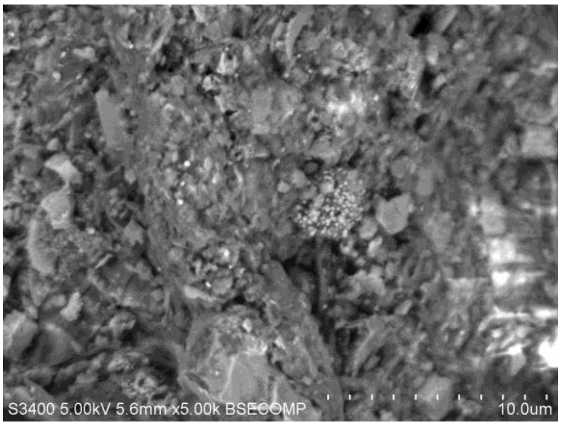

Fig1: Pulp and Paper Mill Sludge before Adsorption

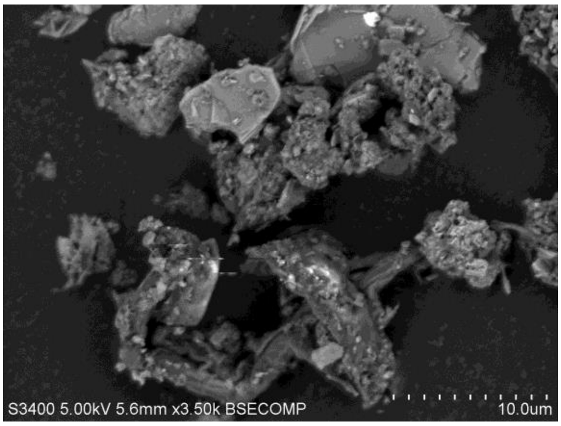

Fig2: Pulp and Paper Mill Sludge after Adsorption

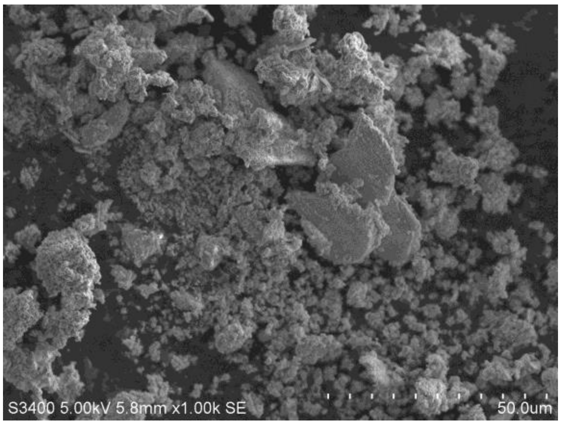

Fig3: Cement Kiln Dust before Adsorption

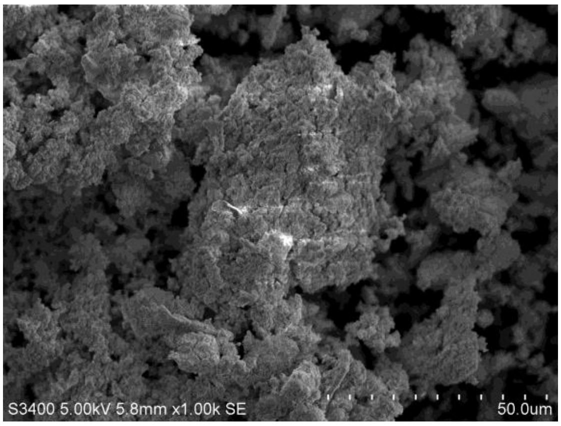

Fig4: Cement Kiln Dust after Adsorption

3.2. *Batch adsorption studies*

Batch adsorption studies were conducted on a solution of heavy metal ion mainly Cu. Using PMS and CKD as adsorbents with different dosages and time of contact. The results are plotted in figures ****.The figures show the influence of dosages and contact time on the removal efficiency of heavy metals. The results of batch adsorption studies are important to develop a model which represents accurately the results which could be used for design purposes. Several models are listed in the literature. Generally the actual amount of Cu adsorption increased with an increase in the dosage and contact time and after the optimum time it was found to be constant.

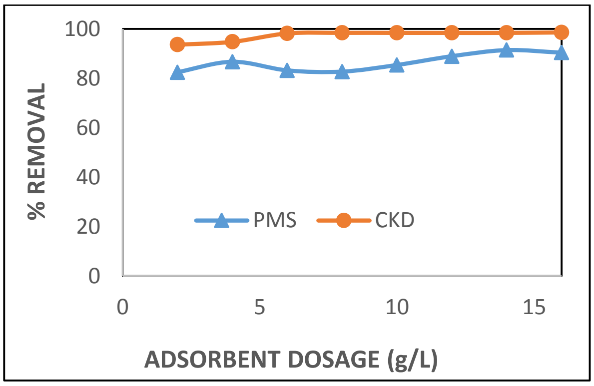

Fig5: Effect of adsorbent dosage on copper

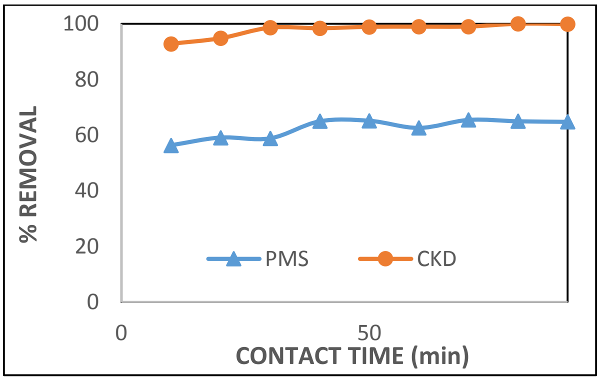

Fig6: Effect of contact time on CKD

3.3 *Adsorption isotherms*

3.3.1 *Freundlich Isotherm*

Freundlich adsorption isotherm is obeyed by the adsorptions where the adsorption form a monomolecular layer on the surface of the adsorbent.

The general form of Freundlich isotherm is,

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

The linear form of Freundlich isotherm can be represented as:

$$log q_{e=} log K_f + \frac{1}{n} log C_e \qquad (2)$$

Where, $q_e = \left(\frac{x}{m}\right)$ is the weight of the adsorbate by m gm of the adsorbent, thus $\left(\frac{x}{m}\right)$ represent the amount of adsorbate adsorbents per gm (unit mass) K and n= constants at a particular temperature for a particular adsorbent and adsorbate,1/n=magnitude of the exponent that gives an indication of the favorability of adsorption .The value of n> 1 represent favorable adsorption conditions.

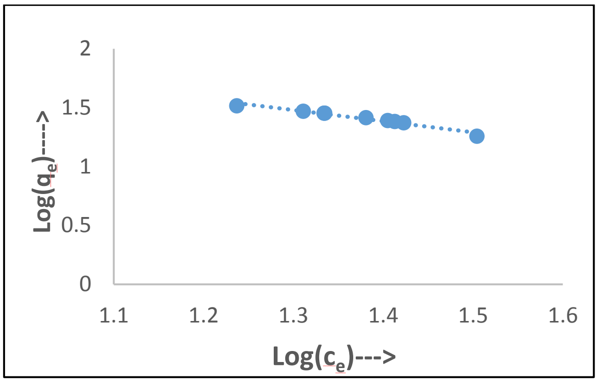

Fig7: Freundlich isotherm for PMS

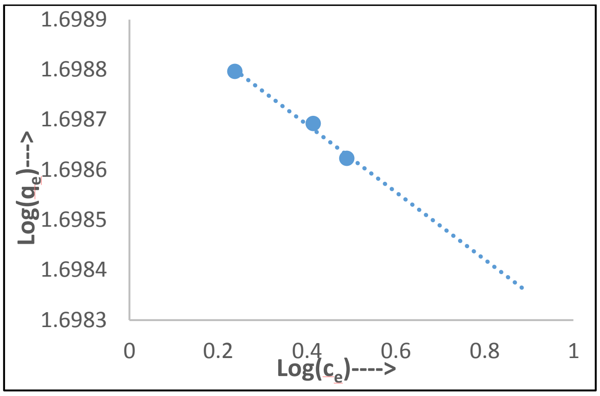

Fig8: Freundlich isotherm for CKD

3.3.2 *Langmuir Isotherm*

The Langmuir adsorption model is valid for single layer adsorption. The Langmuir isotherm is represented by,

$$q_{e=} \frac{q_m b C_e}{(1+bC_e)} \qquad (3)$$

Where $q_{e=}$ amount adsorption per unit weight of adsorbent,b= Langmuir's constant related to the enthalpy of the process, $q_{m=}$ adsorption capacity to form the single layer,C_e= equilibrium concentration of adsorbate in solution after adsorption in mg/L. The linear form of Langmuir isotherm can be represented by the equation,

$$\left(\frac{C_e}{q_e}\right) = \left(\frac{1}{q_m b}\right) + \left(\frac{1}{q_m}\right) C_e \qquad (4)$$

The essential feature of the Langmuir isotherm can be expressed in terms of Separation factor(R_L) which is dimensionless constant also referred to equilibrium parameter.R_L can be calculated by using the equation,

$$R_{L=} \frac{1}{(1+bC_0)} \qquad (5)$$

Where C_o is the initial adsorbate concentration (mg/L), b can be obtained from Langmuir plot of $\frac{C_e}{q_e}$ v/s C_e. The separation factor R_L indicates the isotherm shapes as:

$R_{L>1}$	Unfavorable
$R_{L=1}$	Linear
$0< R_L < 1$	Favourable
$R_{L=}$ 0	Irreversible

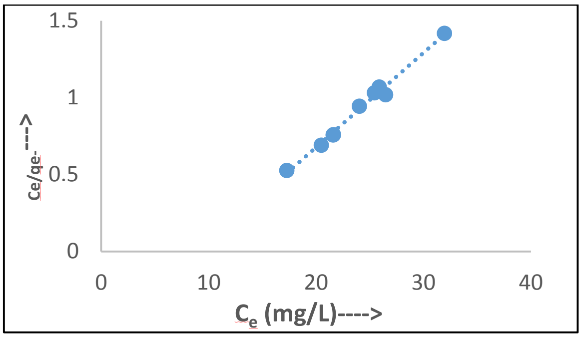

Fig9: Langmuir isotherm for PMS

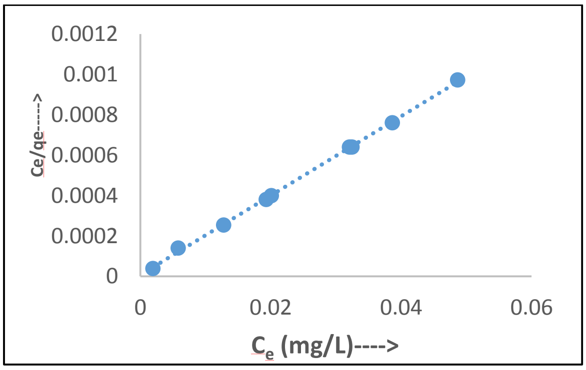

Fig10: Langmuir isotherm for CKD

3.3.3 *Tempkin Isotherm*

Tempkin adsorption isotherm equation assume that heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interaction, and adsorption is characterized by a uniform distribution of the binding energies, up to certain maximum binding energy.

The general form of Tempkin equation is given by,

$$\boldsymbol{\theta = \frac{RT}{\Delta Q} logK_oC_e} \qquad (6)$$

Where, $\theta = \left(\frac{q_e}{q_m}\right) =$ Fractional coverage ,R=universal gas constant (KJ/mol/K), T=Temperature (K), $\Delta Q=$ variation adsorption energy(KJ/mol), K_o =Tempkin equilibrium constant (L/mg)the linear form of Tempkin adsorption isotherm can be represented by,

$$\boldsymbol{q_e = \frac{RT}{b} lnK_T + \frac{RT}{b} lnC_e} \qquad (7)$$

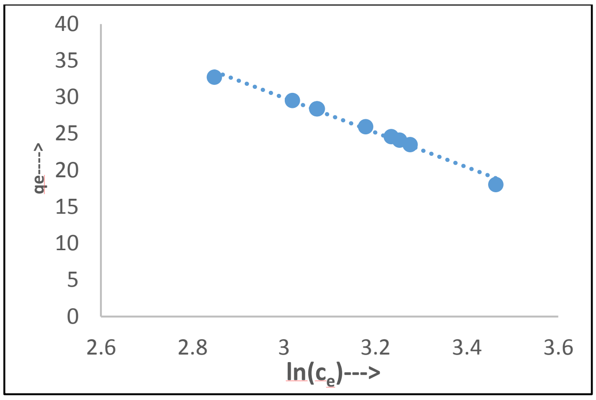

Fig11: Tempkin isotherm for PMS

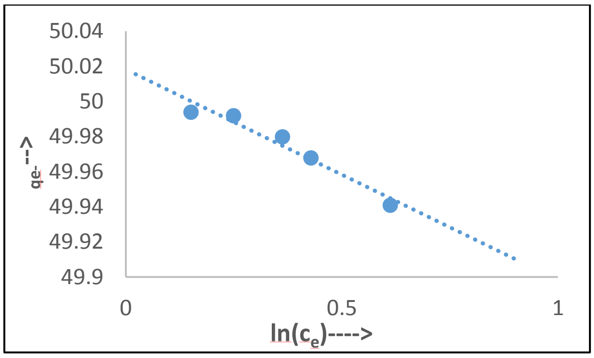

Fig12: Tempkin isotherm for CKD

3.4 Kinetic parameters

3.4.1 *Pseudo First Order Reaction*

The general form pseudo first order equation is given by,

$$\left(\frac{dq}{dt}\right) = K_1(q_e - q_t) \qquad (8)$$

The linear form is given by,

$$\log(q_e - q_t) = \log q_e - (K_1 * \frac{t}{2.303}) \qquad (9)$$

Where, qe and qt represents the amount adsorbate adsorbed (mg/g) at any time t and at equilibrium time , respectively and K_1 represents the adsorption rate constants.

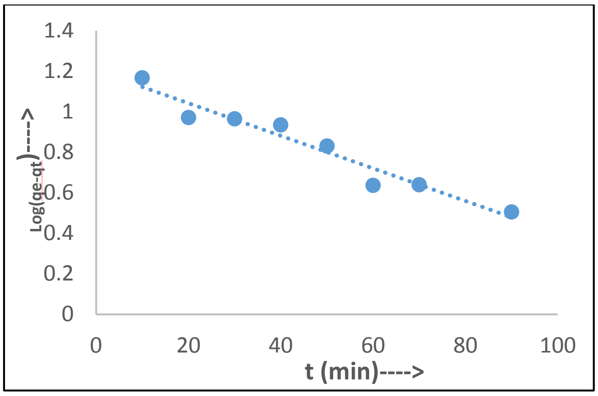

Fig13: Pseudo first order kinetics for PMS

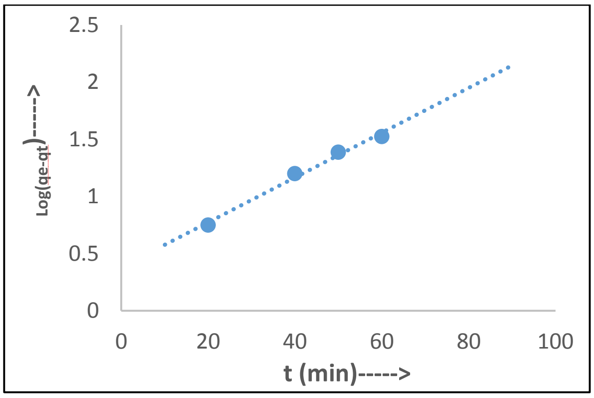

Fig14: Pseudo first order kinetics for CKD

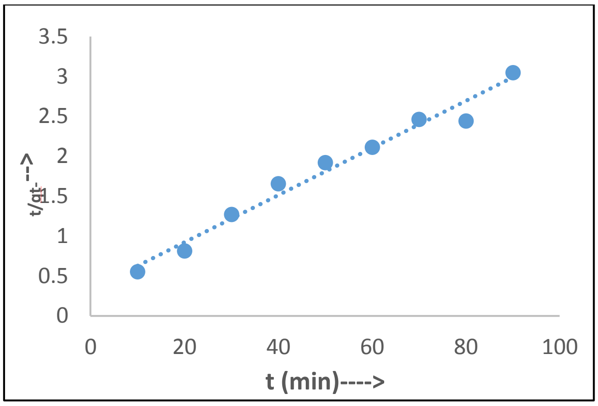

Fig15: Pseudo second order kinetics for PMS

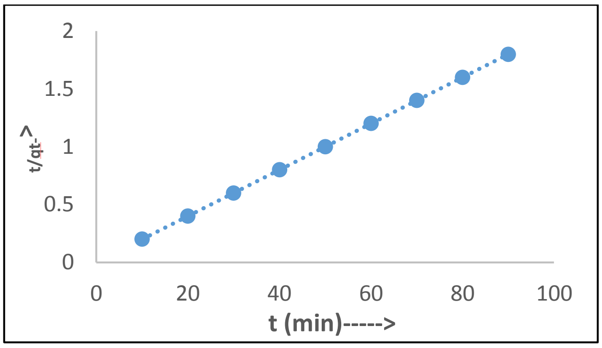

Fig16: Pseudo second order kinetics for CKD

3.4.2 *Pseudo second order kinetics*

The general form of pseudo-second order equation is given by,

$$\left(\frac{dq}{dt}\right) = K_2(q_e - q_t)^2 \qquad (10)$$

The linear from of the above equation is given by,

$$\left(\frac{t}{qt}\right) = \left(\frac{1}{K_2 {q_e}_2}\right) + \left(\frac{1}{q_e}\right) t \qquad (11)$$

Where, K_2 is the pseudo second order rate constant(g/mg-min)

CONCLUSION

The adsorption equilibrium parameters have been estimated for copper using two types of adsorbents mainly PMS and CKD for different dosages and contact time. The maximum removal efficiency was 65% and 98% for pulp and paper mill sludge and cement kiln dust respectively. The values of RL were found to be in the range of 0 to 1 clearly indicating that the adsorption process is favourable for PMS and CKD. The freundlich adsorption constant, 1/n should be between 0.1 to 1 for better adsorption. The Langmuir isotherm was the best fit isotherm, the maximum monolayer coverage from Langmuir isotherm was 15.47 mg/g for pulp and paper mill sludge and 50 mg/g for cement kiln dust. The equilibrium rate constant (k_2) of second order kinetics was found to be 0.003 and 1.333 for paper mill sludge and cement kiln dust. In Tempkin adsorption isotherm, the value of variation of adsorption energy ΔQ for copper was found to be 8.761 J/mol and 17.32 J/mol for paper mill sludge and cement kiln dust respectively.

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