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Kinetic modeling of Batch studies using mixed adsorbent prepared from Activated charcoal and Bone charcoal for the removal of Copper and Cadmium

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ABSTRACT

The present work researches the removal of Cu & Cd ions using mixed adsorbent prepared by blending activated charcoal and bone charcoal in 1:1 ratio in batch studies. The batch adsorption studies have been carried out for 2 hrs considering all the 6 parameters by optimizing each of them. The effect of pH, temperature, initial metal concentration, agitation (high speed rotation) rate, adsorbent dose and contact time were studied with respect to reaction time until the achievement of equilibrium. The maximum removal for Cu (II) is 97.21% and Cd (II) is 78.76% obtained at 2 hrs for pH 6. The % removal for Cu varies from 87.16 to 99.74% at an adsorbent dosage of 5 g, pH 6, initial metal ion concentration of 50 mg/l, with an agitation rate of 180 rpm, and at a temperature of $25^{\circ}C$. Similarly for Cd (II) it varies from 70.23 to 88.4% at 5 g respectively at the same operating conditions. At a temperature of 40oC the % removal for Cu (II) is 99.75% and for Cd (II) it is 88%. The data obtained in the batch study for the optimized parameters are studied through fitting of kinetic models such as Pseudo-first order and Pseudo second order models at different optimized conditions for both Copper and Cadmium along with model equations and Correlation / regression coefficient (R^2) values. Finally it was concluded that the mixed adsorbent prepared by blending activated charcoal and bone charcoal in 1:1 ratio can be taken as a best adsorbent for heavy metal ion removal. These mixed adsorbent studies can be extended to various complex industrial effluents that contains the concentration range of 100-200 ppm and can be applicable to know the interaction between various parameters with respect to % removal in both batch and column studies.

Key words: Batch study, Activated Charcoal, Bone Charcoal, Pseudo-first order model, Pseudo Second order model, Regression Coefficient.

INTRODUCTION

Discharge of industrial waste water containing heavy metals (Cu, Cd, Cr, Zn, Hg, As,Pb) into the environment has become a serious threat to the human and aquatic life. The series of heavy metals that consists of many elements such as chromium, zinc, iron, lead and copper which cause the environmental pollution when they exceed their toxic limit. Heavy metals contamination in air, water and soil is a worldwide issue created by mining and refining operations, metal handling plants and waste incineration. Heavy metals are the centre components of earth's outside layer which are consolidated by metals and metalloids with atomic density greater than 4000 kg/m3. Some of the heavy metal ions are small scale supplements for living creatures, yet at higher concentration range they create serious health effects. The most harmful types of these metals in their ionic species exists in oxidation states like Cd²⁺, Pb²⁺, Hg²⁺, Ag²⁺ and As³⁺ in which they react with the body bio-molecules to form extremely stable bio toxic compounds which are difficult to dissociate. In the very recent years expanding problem about the impact of poisonous metals in nature has brought about more strict ecological and environmental regulations for mechanical

and industrial applications that release the metal bearing effluents. Removal of metal particles from waste water in an effective manner has turned into a vital issue. Although small concentration of heavy metals are needed to all living organisms but at high concentration of these metals can cause several diseases like neurological and psychological effect on human body [1, 2]. In the environment, the heavy metals are generally more persistent and toxic than organic contaminants such as chemicals released from pesticides, fertilizers and petroleum by products, etc. Heavy metal harming can come because of drinking water through tainting (ex. lead channels, mechanical and industrial waste) and passes through the evolved way of life through food chain or high ambient air conditions near emission sources. In natural environments these elements may be sorbed by soil components or sediments and aredissolved in aquatic solution and/ or accumulated by living organisms along with crops, vegetables and fish and then may enter into the food chain. In this manner the sorption of heavy metals on soil segments or residue relates nearly to their portability and bioaccessibility and assumes a basic part in diminishing their danger to individual and creatures [3]. Therefore, the vicinity of particles of substantial metals in waste water even at low concentrations is a huge problem to the biological community and raises numerous dangers for people and aquatic life [4–8].

1.1 Available Technologies for the removal of metals from waste water and their limitations

Heavy metals are of special concern because they are non-degradable and thus persistent. Heavy metals have harmful effect on the human body, physiological and other biological systems when they exceed the tolerance levels [9]. Exposure to these metals can cause liver diseases, brain damage, and kidneys failure and even to death ultimately. Besides chronic exposure to these contaminants present even at low concentrations in the environment they also proved to be harmful to the human health. Due to the above reasons the heavy metals must be removed from industrial effluents [10].

Many procedures have been adopted in order to remove heavy metals from aqueous streams, among the most commonly used techniques are coagulation, In-situ reduction process, co-precipitation, evaporation, chemical coagulation/flotation, flocculation, cementation, heavy metal removal from biosurfacants, biosorption, ion exchange, chemical precipitation, chemical oxidation and reduction, ion exchange, filtration, electrochemical treatment, reverse osmosis (membrane technologies), evaporative recovery and solvent extraction. These classical or conventional techniques give rise to several problems such as unpredictable metal ions removal and generation of toxic sludge which are often difficult to de-water (remove the contaminants) and require extreme caution in their disposal. Besides that most of these methods also have some limitations whereby they are economically viable at high or moderate concentrations of metals but not at low concentrations, which means the dilute solutions containing from 1 to 100 mg/l of dissolved metals (s). Heavy metals removed by classical techniques involve expensive methodologies. These are due to high energy and frequent reagent requirements. Some of them are explained in brief with their disadvantages [11].Several technologies exist for the remediation of heavy metals contaminated groundwater and soil and they have some definite outcomes such as:

- Complete or substantial destruction/ degradation of the pollutants
- Extraction of pollutants for further treatment or disposal

• Separation of non-contaminated materials and their recycling from polluted materials which requires further treatment

• Contaminant polluted material restrict exposure to the wider environments.

There is a long series of technologies involved in the removal of heavy metals from various types of industrial waste-water and mine drainage. The conventional heavy metal ion remedial technologies have some major technical shortcomings. Comparing with conventional methodologies, generally the adsorption and bio sorption of heavy metals is a very cheap, eco-friendly and efficient methodology. Bio-remediation processes include the use of biomass. These are not only cheap but also do not produce any secondary chemical sludge which is the main advantage of bio-sorption process. The biosorbents are readily available and they are quite efficient for the remediation of heavy metals below a minimum concentration of 100 mg/l. The way of bonding between the adsorbate and the adsorbent's surface recognizes the sorts of adsorption.

EXPERIMENTAL SECTION

2.1 Adsorption

Adsorption refers to the selective collection and concentration of a particular type of molecules contained in a fluid phase onto a solid surface. The molecules of the adsorbate come from the fluid phase into the interface, where they remain for a period of time. In a reversible process, the molecules go back to the phase from which they came or reversibly passes into another phase while other molecules replace them at the interface. On reaching the solid surface the adsorbed molecules exchange energy with structural atoms of the surface and if sufficient time is given for adsorption, the adsorbed molecules and the surface atoms reach thermal equilibrium. At equilibrium, the number

of molecules arriving at the interface in a given time is equal to the number of molecules leaving the interface to go into the fluid phase [12].

Molecular or atomic interactions occur at interfaces between gas and solid, gas and liquid, liquid and solid, two liquids and sometimes between solid phases. Interaction at an interface causes the transition of a molecule from one phase to another which is called as sorption of the molecule by the given phase. Adsorption of atoms or molecules on to a solid from a fluid phase takes place when the sorbed molecules or atoms concentrated only at the interface. Thus the substances contained in a fluid phase is said to be adsorbed on a solid phase when its concentration in the boundary region is higher than that in the bulk of the fluid phase. The substance which is adsorbed is called adsorbate (metal ions) and the phase of boundary which adsorption occurs is called adsorbent. For adsorption to take place on the surface of an adsorbent it should have the larger surface area accessible to the adsorbate, preferential ability to take up the adsorbate. Large surface areas are available from substances which are both very porous and finely divided. Adsorbents are usually highly porous materials and adsorption takes place primarily on the walls of the pores or specific sites inside the particle. The surface area available for some adsorbents may be as high as 2000 m^2/g . Activated carbon, activated alumina, molecular sieve and silica gel are widely used as adsorbents. When the adsorbent reaches its saturation capacity, the adsorbed material can be removed by the industrial methods such as displacement of adsorbate, desorption of the adsorbate, combustion of the adsorbate decomposition or radioactive decay of the adsorbate. If the combustion of the adsorbate is used in the operation it is called reactivation and when the displacement or desorption of adsorbate is used; the operation is called regeneration.

All the adsorption processes are exothermic. The heat of adsorption may be defined as the decrease in the heat content of the system. Adsorption on solid surfaces may be classified on the basis of the magnitude of the energy of adsorption. van der Waals or physical adsorption refers to a process in which energy changes are very small. When the energy changes are greater the process is called chemisorption or chemical adsorption. In case of physical adsorption, the adsorbate merely condenses in a thin film on the surface of the adsorbent. The forces which retain the adsorbate in this state are purely physical and are called as vanderwaals forces (weak). They are very weak molecular attractions and physically adsorbed substances are loosely bound. In chemical adsorption the adsorbate is much more strongly bound when compared to physical adsorption and the intermolecular forces of attraction are very strong. The heats of adsorption are in the same order of the magnitude as of the corresponding chemical reactions. The actual Chemical Combination occursbetween the adsorbed molecule and the active centre on the surface of the adsorbent. Chemisorption plays an important role in Adsorption and Catalysis. In the physical adsorption the removal of adsorption is usually instantaneous while chemical adsorption generally requires activation energy and in some cases it may be instantaneous [13].

Adsorption may occur in two different ways according to the interactions of the adsorbent and adsorbate which are named as physical adsorption (physisorption or van der Waals) and chemical adsorption (chemisorption). The adsorption processes with nonspecific interactions are generally referred as physisorption. In chemisorption processes, electrons are shared or transferred between two phases. Since chemical bonds occur between the adsorbate and the surface of the adsorbent, new chemical compound is formed. As a result of this, interactions are very strong at the chemisorption processes with respect to the physisorption processes. Also only monolayer is observed in chemisorption and it is slower than the physisorption processes. In addition, if the solid or the gas is polar in nature, there will be also electrostatic (columbic) forces comprising dipole-dipole, dipole induced dipole interactions.

Due to the specific interactions between adsorbate and adsorbent, the heat of adsorption of chemisorption is higher than physisorption and is observed in the short range. However, there are different heat of adsorption ranges for physical and chemical adsorption processes 10 to 40 kJ/mol and 40 to 800 kJ/mol, respectively. Adsorption of vapour on to a solid surface is a spontaneous in nature, so the overall free energy change for the process is negative. On the other hand, during the adsorption process, the adsorbing molecules lose a degree of freedom and their entropy decreases. From the thermodynamic relationship given in Equation it is obvious that for ΔG to be negative, ΔH should be negative. So, adsorption process generally becomes exothermic.

$$\Delta \mathbf{G} = \Delta \mathbf{H} - \mathbf{T} \Delta \mathbf{S} \tag{1}$$

However, an endothermic trend can also be observed in some cases. For instance, due to the lateral protein-protein interactions and conformational changes in the adsorbed protein, adsorption becomes endothermic [14].

2.1.1 Physisorption

The fundamental interacting force of physisorption is caused by weak van der Waalsforce. Even though the interaction energy is very weak (10 to 100 m eV) and physisorption plays an important role in adsorption system. Van der Waals forces originate from the interactions/metal binding tendencies between induced and permanent or transient electric dipoles. In contrast with chemisorption, in which the electronic structure of bonding atoms or molecules is changed and covalent or ionic bonds are formed where as physisorption can only be observed in the environment of low temperature (thermal energy at room temperature which is equal to 26 m eV) and the absence of the relatively strong chemisorption. In practice, the type of a particular adsorption as physisorption or chemisorption depends principally on the binding energy of the adsorbent to the substrate or adsorbate [15]. The strength by which adsorbate molecules are attached/ bonded with the adsorbents determines the nature of adsorption. Normally the release of energy is in the range of 8 to 25 kJ/mole due to adsorption which is defined as physisorption and a much larger energy is required for the formation of chemical bonds which leads to chemisorption.

Physisorption is due to the absence of chemical bonds and the molecule retains its gas phase electronic structure, although some disturbances are still possible. The binding energy depends on the polarizability and on the number of atoms involved of the atoms and varies between few milli eV light gases and several eV for heavy metals and large organic molecules).

2.1.2 Chemisorption

Chemisorption is a kind of adsorption which involves a chemical reaction between the adsorbent surface and the adsorbate. New chemical bonds are generated at the adsorbent surface. The strong interaction between the adsorbate and the substrate (adsorbate) surface creates new types of electronic bonds [16,17]. In comparison with Physisorption, Chemisorption leaves the chemical species of the adsorbate on surface to interact. It is conventionally accepted that the energetic threshold limit separating the binding energy of physisorption from that of chemisorption is equivalent to 0.5 eV per adsorbed species. Due to specificity, the nature of chemisorption can greatly differ, depending up on the chemical identity and the surface structure of the adsorbent [30]. In Chemisorption, there is stronger perturbation of the molecular electronic structure with formation of chemical bonds along with the substrate molecules and the energies typically are of several eV.

2.2 Model equation for batch studies

In order to research the system of adsorption and potential rate controlling steps, for example, transport and chemical reaction phenomena, dynamic models are utilized to test the obtained data. The kinetic models incorporate the pseudo-first order mathematical statement and pseudo-second order equation.

2.2.1 Pseudo First order equation

Considering the reversible binding of metal ions with the adsorption on active sites present on biomass/ adsorbent surface, the rate of adsorption is directly proportional to the number of vacant sites [18, 19]. The pseudo-first order equation is represented by Equation 2 which is expressed in non-linear form as

$$\frac{\mathrm{d}q_{\mathrm{t}}}{\mathrm{d}\mathrm{t}} = \mathbf{k}_{1} \left(\mathbf{q}_{\mathrm{e}} \cdot \mathbf{q}_{\mathrm{t}} \right) \tag{2}$$

Where q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg/g) and k_1 is the rate constant of pseudo first order equation (min⁻¹). Integrating the above equation and applying the boundary conditions from t = 0 to t = t, and $q_t = 0$ to $q_t = q_t$, the integrated form becomes

$$\log (q_e - q_t) = \log (q_e) - \frac{K_1 t}{2.303} (3)$$

Eq. 3 is applicable to experimental results but generally differs from a true first order equation in two ways: (i) The parameter $k_1(q_e-q_t)$ does not represent the number of available sites and (ii) the parameter $log(q_e)$ is an adjustable parameter and often it is found not equal to the intercept of a plot between $log(q_e-q_t)$ vs t, whereas in a true first order $log(q_e)$ should be equal to the intercept for the plot of $log(q_e-q_t)$ against t. In order to fit the equation to experimental data, the equilibrium adsorption capacity q_e must be known. In many cases q_e is unknown and as chemisorption tends to become un-measurably slow, the amount sorbed is still significantly smaller than that of the equilibrium uptake capacity [34]. In most cases in the literature, pseudo first-order equation of Lagergren does not well fit for the whole range of contact time and is generally applicable over the initial 20 to 30 minutes of the adsorption process.

2.2.2 Pseudo Second order equation

In this model it is assumed that adsorption/ binding of metal ion/ adsorbate on the adsorbent surface is mediated by chemical forces rather than physical forces of attraction. Non-linear form of the model is given as

$$\frac{dq_t}{dt} = \mathbf{k}_2 \left(\mathbf{q}_e \cdot \mathbf{q}_t\right)^2 (4)$$

Upon integration with boundary conditions from $q_t = 0$ at t = 0, $q = q_t$ at t = t, the above equation (Eq. 4) reduces to $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} (5)$

Where q_e and q_t are the adsorption capacities at equilibrium and at time t, respectively (mg/g) and k_2 is the rate constant of pseudo second order equation (g/mg.min). A plot of t/qt vs t for the equation holds a straight line relationship and the parameters q_e and k_2 can be determined from the slope and intercept.

2.3 Optimized Parameters of the batch study

The optimized parameters of the batch study are obtained with respect to higher % removal on y-axis vs reaction time on x-axis and are tabulated as follows in Table 1

Parameters	Optimized value		
pH	6		
Temperature	40°C		
Metal Ion concentration	100 ppm		
Adsorbent dosage	5 g		
Agitation rate	180 rpm		
Contact time	120 min		

Table 1 Optimized parameters of the batch study

RESULTS AND DISCUSSION

3.1 Kinetic Modeling of Batch studies

The Kinetic models include the Pseudo- first order equation and Pseudo-second order equation. The Pseudo First order and Second order modeling has been carried out for both the metals at the optimized conditions of each parameter in the batch study (pH 6, T = 40 °C, Initial Metal ion Concentration of 100 ppm and adsorbent dosage of 5g).

3.1.1 Pseudo First order equation

In order to fit the equation to experimental data, the equilibrium adsorption capacity q_e must be known as discussed in Section 2.2.1; In many cases q_e is unknown and as chemisorption tends to become measurably slow, but the amount adsorbed is still significantly smaller than that of the equilibrium uptake capacity [34]. In most cases in the literature, the Pseudo First-order equation of Lagergren does not well fit for the whole range of contact time and is generally applicable over the initial 20 to 30 minutes of the adsorption process. A plot of log (q_e - q_t) against time was plotted for the obtained data at the optimized parameters for pH = 6, T = 40 °C and initial metal ion concentration of 100 ppm for both the metal ions to find the Correlation Coefficient or Coefficient of Regression (R^2) which holds a straight line relationship and the parameters q_e and k_1 can be determined from the intercept and slope respectively. The slope and intercept values are shown in Table 3 and 4 for both the metals (Cu and Cd respectively) at the optimized conditions.

It can be concluded that the Coefficient of Regression (R^2) values are close to 1 in case of Cu (II) at adsorbent dosage of 5 g and Temperature of 40°C which indicates that the adsorption systems follow the pseudo first order equation for copper when compared to cadmium as shown in Table 2 and 3. The tabular column also gives the data about the first order rate constant k_1 in min⁻¹ and q_e in mg/g obtained theoretically from the slope and intercept respectively from the Figs 1 to 8. It can be concluded that the data fits well for Cu (II) than Cd (II) because of closely higher R^2 values of 1 in case of copper.



Figure 1: Pseudo first order equation at pH = 6 for Cd (II)





PFOE conditions	Model Equation	$k_1 (min^{-1})$	\mathbf{R}^2	q _e (mg/g)
pH 6	y = -0.0146x + 0.078	0.0336	0.8192	1.2
$T = 40^{\circ}C$	y = -0.0147x + 0.51	0.0338	0.886	3.23
MIC= 100 ppm	y = -0.0113x -0.19	0.026	0.6064	0.646
Adsorbent dosage 5 g	y = -0.0138x - 1.21	0.0318	0.97	0.06

Table 3: Pseudo First order model equation for Cd (II) at optimized conditions

PFOE conditions	Model Equation	k_1 (min ⁻¹)	\mathbf{R}^2	q _e (mg/g)
рН б	y = -0.0074x + 0.0278	0.017	0.863	1.9
$T = 40^{\circ}C$	y = -0.019x + 0.578	0.044	0.835	3.8
MIC= 100 ppm	y = -0.0184x + 0.76	0.042	0.895	5.73
Adsorbent dosage 5 g	y = -0.0286x - 0.679	0.066	0.82	0.21



Figure 3: Pseudo first order equation for Cd (II) at MIC of 100 ppm





Figure 6: Pseudo first order equation at T= 40 $^\circ C$ for Cu (II)



Figure 7: Pseudo first order equation at 100 ppm for Cu (II)



Figure 8: Pseudo first order equation at 5 g of adsorbent dosage for Cu (II)

3.2 Pseudo Second order equation

In this model, it is assumed that adsorption/binding of metal particle/adsorbate on the adsorbent surface is mediated by chemical forces instead of physical forces. Non-linear type of the model is described earlier in Sec. 2.2.2

A plot of $t/q_t vs t$ at different optimized conditions of pH 6, T = 40 °C and Initial Metal Ion concentration of 100 ppm for both the metal ions to find the Correlation Coefficient or Coefficient of Regression (R²) that determines the best fit equation relationship and the parameters q_e and k_2 can be determined from the slope and intercept. The slope and intercept values are shown in table 4 and 5 for both the metals Cd and Cu at the optimized conditions

It can be concluded that the Coefficient of Regression (\mathbb{R}^2) values are close to 1 in case of Cu (II) and Cd (II) at adsorbent dosage of 5g and temperature of 40 °C, pH 6 and initial metal ion concentration of 100 ppm which indicates that the adsorption system follows thepseudo second order equation for both cadmium and copper (as shown in Tables 5 and 6 respectively). Second order rate constant k_2 in (gmg⁻¹min⁻¹) and adsorption capacity q_ein



mg/g which are obtained theoretically from the slope and intercept of the plots (Figs. 9 to 16) are also shown in Tables 4 and 5.

Figure 9: Pseudo Second order equation at pH 6 for Cd (II)







Figure 11: Pseudo Second order equation at IMC of 100 ppm for Cd (II)





Table 4: Pseudo second order equation at different adsorbent conditions for Cd (II)

PSOE conditions	Model Equation	$k_2 (g mg^{-1} min^{-1})$	\mathbf{R}^2	q _e (mg/g)
pH 6	y = 0.1342 x + 1.2341	0.0146	0.97	7.45
$T = 40^{\circ}C$	y = 0.1111 x + 0.6903	0.018	0.995	9
MIC= 100 ppm	y = 0.0606 x + 0.2571	0.0143	0.999	16.5
Adsorbent dosage 5 g	y = 1.0808 x + 1.7903	0.652	0.999	0.925

Table 5: Pseudo second order equation at different adsorbent conditions for Cu (II)

PSOE conditions	Model Equation	k ₂ (g mg ⁻¹ min ⁻¹)	\mathbf{R}^2	q _e (mg/g)
pH 6	y = 0.103 x + 0.218	0.0486	0.999	9.7
$T = 40^{\circ}C$	y = 0.098 x + 0.5086	0.019	0.998	10.2
MIC= 100 ppm	y = 0.055 x + 0.099	0.03	0.999	18.18
Adsorbent dosage 5 g	y = 1.001 x + 0.9317	1.075	0.999	1.01



Figure 13: Pseudo Second order equation for Cu (II) at pH 6



Figure 14: Pseudo Second order equation for Cu (II) at pH T= 40 $^\circ C$



Figure 15: Pseudo Second order equation at 100 ppm for Cu (II)



Figure 16: Pseudo Second order equation at 5 g for Cu (II)

CONCLUSION

The conclusions from the batch study give the highest % removal of metal ions with respect to time at optimized parameters.

pH 6 Adsorbent dosage of 5g IMC of 50 ppm Temperature of 40°C Contact time of 120 min Agitation rate of 180rpm

• Pseudo First order equation (PFOE) fits for Cd (II) and Cd (II) with higher R² values close to 1

• Pseudo Second order equation (PSOE) fits for Cu (II) and Cd (II) with higher R² values close to 1

It was concluded that the Coefficient of Regression R^2 values are close to 1 indicating that the adsorption system fits equally well to the pseudo first order equation for both the metals Cu (II) and Cd (II). In case of second order system the Coefficient of Regression R^2 values are very close to 1 indicating that the adsorption systems follows the second order kinetics for the Cu (II) and Cd (II) metal. In comparison of both the models, the Pseudo second order kinetics follows a better fit for both Cu (II) and Cd (II) with higher R^2 values that are very close to 1. It has been shown that mixed adsorbent appears to be technically feasible with high efficiency and removing capability of metal ions. Therefore adsorption can be recommended to use for the removal of other heavy metal ions from complex industrial effluents.

Future scope of research

• The adsorption studies can be extended to various industrial effluents containing complex heavy metals.

• The studies can also extended to the heavy metals other than Cu(II) and Cd(II) and to find the various optimized parameters for other heavy metals.

• Development of improved/modified Mathematical models

• Factorial Design methodology can be studied to know the interaction between the parameters with the % removal of metal ions

• Application of Response Surface methodology models to find the interaction of heavy metals and the selected adsorbent.

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