



AN EFFICIENT TECHNIQUE FOR REMOVAL OF K^+ AND MnO_4^- IONS THROUGH ADSORPTION IN AQUEOUS SOLUTION BY USING ACTIVATED CHARCOAL

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Abstract Potassium Permanganate ($KMnO_4$) is an oxidizing agent widely used throughout the water industry. It has an effect on the development of a disinfection strategy by serving as an alternative to pre-chlorination or other oxidants at locations in a treatment plant where chemical oxidation is desired for control of color, taste, odor and algae. Potassium Permanganate when exposed in extreme quantity can react with human tissue and causes similar effect as that of acid, it can also cause severe eye irritation on contact and possible burns, may cause chemical conjunctivitis and corneal damage. The objective of this study is to evaluate the ability of activated charcoal to retain Potassium Permanganate ions (K^+ and MnO_4^-) through adsorption in an aqueous solution. On the laboratory scale length of unused bed and equilibrium concentration was found out keeping in mind various parameters like effect of temperature, effect of concentration of adsorbate and flow rate of adsorbate for the removal of $KMnO_4$ ions from water. The isotherm data was verified with the Langmuir adsorption isotherm as well as Freundlich adsorption isotherm equations.

Keywords Activated Charcoal, Adsorption Isotherms, Langmuir and Freundlich adsorption Isotherm, Length of Unused Bed, Potassium Permanganate

Introduction

In adsorption, the solid is usually held in fixed bed, and fluid is passed continuously through the bed until the solid is nearly saturated. The flow is then switched to a second bed, and the saturated bed is replaced or regenerated. Here in this work we are decolorizing a solution of potassium permanganate in water with the help of activated carbon by passing it through packed bed. Applications of adsorption for chemical processing air pollution control and water treatment are well known. Applications in wastewater treatment and water pollution control are generally not as well recognized, nor as well understood. The process has been demonstrated to be widely effective for removing dissolved organic substances from wastewaters, but it should not be viewed as a catholicon for waste treatment, nor should its application be made in an empirical fashion. The purpose of this paper is to develop the details of this application, highlighting advantages over other wastewater purification process [1].

Potassium permanganate ($KMnO_4$) is used primarily to control taste and odours, remove colour, control biological growth in treatment plants, and remove iron and manganese. It is highly reactive under conditions found in the water industry. It will oxidize a wide variety of inorganic and organic substances. Potassium permanganate (oxidation no. of Mn is +7) is reduced to manganese dioxide (MnO_2) [here oxidation number of Mn is +4] which precipitates out of solution. Potassium permanganate is a strong oxidizer and should be carefully handled when preparing the feed solution. No by-products are generated during making the solution. However, this dark purple/black crystalline solid can cause serious eye injury, is a skin and inhalation irritant, and can be fatal if swallowed [2].



Adsorption

The phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or solid resulting in the higher concentration of the molecules on the surface is called adsorption [3]. Adsorption of a substance on a solid surface occurs because of an 'affinity' of the surface for the particular substance. It is natural that the surface will have varying affinity for different substances. Similar to surface tension, adsorption is a consequence of surface energy. Adsorption processes, especially those employing activated carbon, represent a fundamental technology for water purification and industrial wastewater treatment. Bioactive adsorption systems using activated carbon are extensively used because they are efficient and cost-effective in degrading a broad spectrum of organic contaminants, and are capable of meeting higher effluent and water reuse standards [4]. Pressure (or concentration) and temperature are the two most important variables that determine the amount of solute adsorbed per unit mass of the adsorbent at equilibrium. Adsorption is favored at a higher pressure and a lower temperature. Adsorption usually takes place in two forms one is physisorption (characteristics of weak van der Waals forces) and the other form is chemisorption (characteristics of covalent bonding).

Experimental Section

A. Adsorbent

Granular Activated Charcoal was taken as adsorbent which was filled in the Packed Bed for adsorption process. It is normally made by thermal decomposition of carbonaceous materials followed by activation with steam or carbon dioxide at elevated temperature (700-1100 °C).

B. Adsorbate

Potassium permanganate is used as adsorbate. It is a salt consisting of K^+ and MnO_4^- ions. It is a strong oxidizing agent and dissolves in water to give intensely pink solutions. (Molar mass = 158.03 g/mol, equivalent mass = 31.6 g/mol).

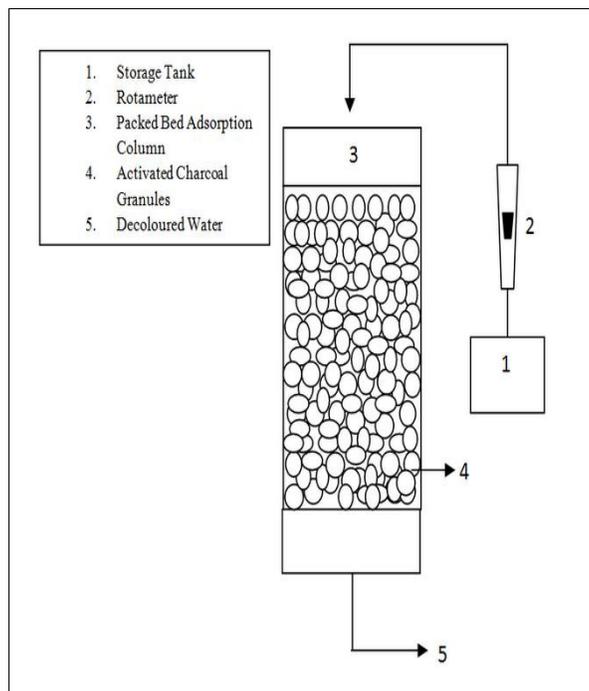


Figure 1: Schematic of experimental setup

Preparation of Adsorbate Solution

Pure crystals of $KMnO_4$ are taken and properly stirred in water so that $KMnO_4$ gets properly mixed with water leaving no crystals and gives an intensely pink solution which will be fed to the packed bed.



Analytical Study

For finding the concentration of the solution that we get from the Packed Bed Column after adsorption we need to plot a graph between concentration and absorbance which will give us a relation (in terms of linear equation) between these two parameters which will help us to know the concentration if we know the absorbance. To plot the graph we should have solutions of known concentration of KMnO_4 whose absorbance can be found out by using UV VIS Spectrophotometer (SL-159).

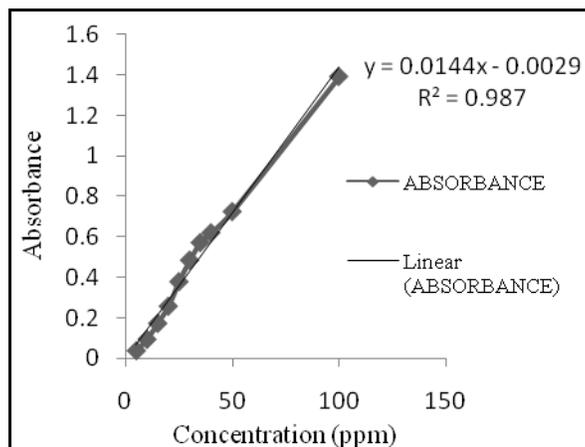


Figure 2: Calibration Curve plotted between absorbance of K^+ and MnO_4^- ions and their concentration in the aqueous solution at room temperature that is 27°C

Results and Discussion

The effect of change in absorbance with the change in concentration of KMnO_4 in the aqueous solution can be seen (Figure1). The relation is close to linear curve which gives us an equation from which we can find the concentration of the unknown samples if we have their absorbance value, which is found out by using UV VIS Spectrophotometer (SL-159).

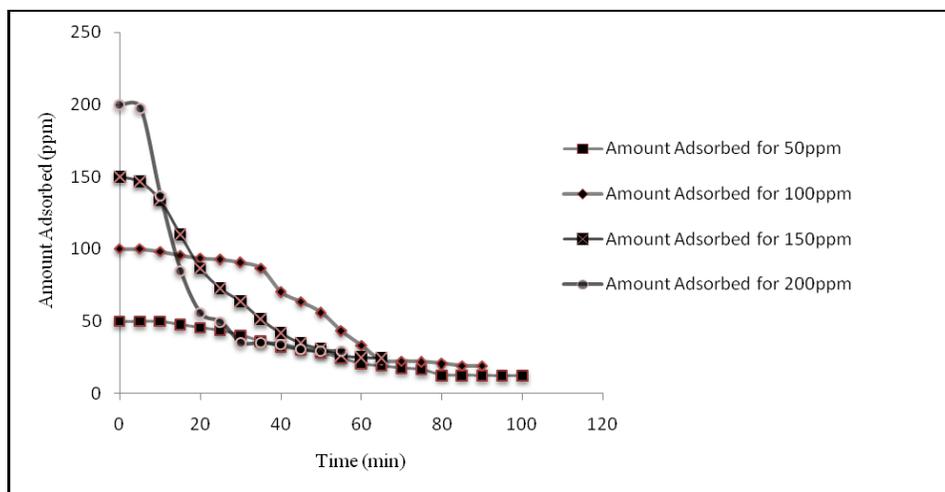


Figure 3: Graph showing the effect of change in dosing of K^+ and MnO_4^- in the aqueous solution on the amount adsorbed by activated charcoal with respect to change in time (min) at Standard temperature *i.e.* $(27 \pm 5)^\circ\text{C}$



A. Length of Unused Bed

$$\text{LUB} = L [1 - (t_b / t_a)] \quad (1)$$

Where:

L is the length of bed which is 500 mm

t_a is the stoichiometric time (average time)

t_b is the break through time obtained from graph.

Table 1: Length of Unused Bed based on sample concentration

Sample Concentration	Equilibrium Time (t_b)	Length of Unused Bed
50 ppm	20 min	277.78 mm
100 ppm	40 min	312.5 mm
150 ppm	30 min	333.34 mm
200 ppm	27.5 min	390.9 mm

From (Table 1) we can conclude that Length of Unused Bed varies with the concentration of K^+ and MnO_4^- ions in water in direct proportion, which means that if we increase the concentration of K^+ and MnO_4^- ions it will result in less use of adsorbent in the packed bed which will decrease the breakthrough time.

B. Adsorption Model

In this study we used Langmuir and Freundlich adsorption models to quantify the adsorption of $KMnO_4$ from aqueous solution onto the activated charcoal. Langmuir developed the simplest theoretical model for monolayer adsorption. This model was originally developed to represent chemisorptions on a set of distinct localized adsorption sites.

The basic assumptions on which the model is based are, molecules are adsorbed at a fixed numbers of well-defined localized sites and each site can hold one adsorbate molecule. There is no interaction between molecules adsorbed on neighboring sites. The adsorption involves the attachment of only one layer of molecules to the surface, i.e. monolayer adsorption.

$$\frac{c}{\Gamma} = \frac{c}{\Gamma_{\max}} + \frac{1}{K\Gamma_{\max}} \quad (2)$$

Where, K is Langmuir equilibrium constant, Γ_{\max} is maximum amount adsorbed, c is aqueous concentration Γ is the amount adsorbed.

From (Figure 4) we get a plot between $\frac{c}{\Gamma}$ and c which is a linear graph with intercept of $\frac{1}{K\Gamma_{\max}}$ and slope is $\frac{1}{\Gamma_{\max}}$. A straight line (Figure 4) shows us the validity and applicability of Langmuir isotherm model with our experiment.



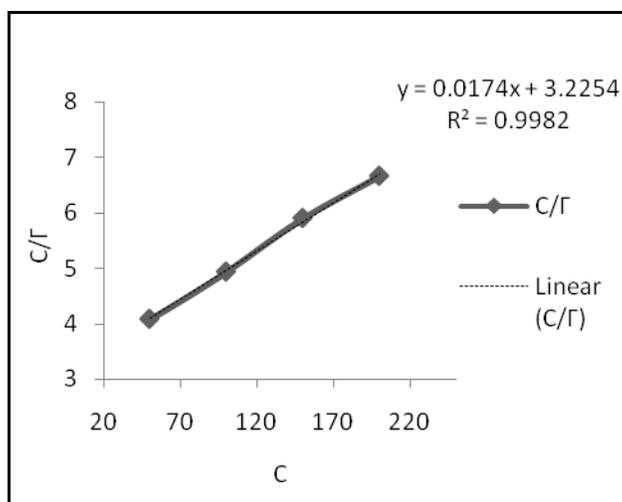


Figure 4: Langmuir Adsorption Isotherm at $(27 \pm 5) ^\circ\text{C}$

In 1909, Freundlich gave an empirical expression which assumes that the amount adsorbed at equilibrium has a power law dependence on partial pressure (or concentration) of the solute.

$$\frac{x}{m} = K c^{1/n} \quad (3)$$

This expression can be written as:

$$\ln C^* = \ln K + (1/n) \ln C \quad (4)$$

Where x is the mass of adsorbate, m is the mass of adsorbent, c is equilibrium concentration of adsorbate in solution, K and n are constants for a given adsorbate and adsorbent at a particular temperature. (n should be in range of 1 to 5),

$$x/m = C^* \quad (5)$$

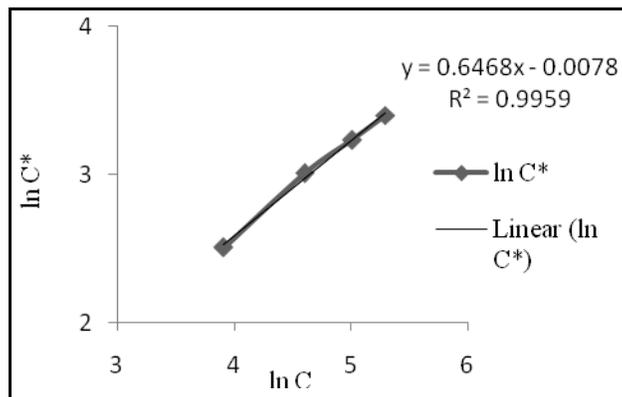


Figure 5: Freundlich Adsorption Isotherm at $(27^\circ\text{C} \pm 5) ^\circ\text{C}$



From (Figure 5) we obtained a plot between $\ln C^*$ and $\ln C$ which is a linear graph with intercept of $\ln K$ and slope is $\frac{1}{n}$. A straight line between $\ln C^*$ and $\ln C$ shows us the validity and applicability of Freundlich isotherm model with our experiment.

Table 2: Constant Values from Langmuir and Freundlich Isotherms

Experimental Langmuir Isotherm Constants		Experimental Freundlich Isotherm Constants	
l_{max}	57.47	N	1.546
K	0.00539	K	0.9922

Conclusion

The results acquired in the study are explicitly experiment based where in adsorption in packed bed is done to de-color the colored water using a specific adsorbent (in this case activated carbon), as the dye is adsorbed onto the activated carbon, we can see the liquid turning clear, this provides a visual example of adsorption, which aids the mathematical analysis and helps in calculating the length of unused bed which is nothing but the amount of activated charcoal that remains unused during the adsorption process and according to our calculations, with the increase in concentration of $KMnO_4$ in water, the length of unused bed increases and the breakthrough time decreases. Langmuir and Freundlich isotherms both successfully fit to our experimental data and each of the isotherms generate acceptable constant values which validate our experimental study, proving it to be an efficient and economic way for removal of K^+ and MnO_4^- from water and also the adsorbent used (Activated Carbon) can be regenerated after every run which makes it reusable till many such repetitions. The whole set-up being economical can be replicated at a bigger level in various chemical industries which would help them to treat the effluents (containing various toxic ions) that are squandered away in water bodies, which is detrimental if the health of living beings is considered, as intake in excess concentration of such ions could provoke many health issues in humans or animals and also can lead to a degraded environmental conditions.

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