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Study on the removal of iron and manganese in groundwater by granular activated carbon

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Abstract

One of the problems related to groundwater is the reddish colour caused by the presence of ferrous and manganese. Initially, this colour cannot be seen but after it has been exposed to the air, the oxidation of groundwater will promote the precipitation of ferrous and manganese. Eventually, the groundwater turns into reddish in colour. Batch test had been carried out to determine the potential and the effectiveness of granular activated carbon (GAC) in removal of ferrous and manganese from water. The test was conducted by mixing certain amount of GAC with 200 mL sample solution and shook for 6 h in room temperature to achieve an equilibrium. The two most common adsorption equations, Freundlich and Langmuir adsorption isotherms, were used in the study to verify the adsorption performance. From interpretation of the equations, the Langmuir adsorption isotherm was found to fit the experimental data better than that of the Freundlich adsorption isotherm. This shows that the relatively high ambient temperature allowed only monolayer adsorption to occur between the adsorbate and adsorbent. According to Langmuir adsorption isotherm's assumption, the bonding that was established between the adsorbent and adsorbate are chemically bonded which known as chemisorption. In this study, the adsorption capacity of Fe(II) and Mn(II) were 3.6010 and 2.5451 mg/g, respectively. Therefore, the adsorption capacity for Fe(II) was higher than Mn(II). The main factors that contribute to difference adsorption capacity of Fe(II) and Mn(II) onto GAC are due to ionic radius and electronegativity of metal ions.

Keywords: Ferrous; Manganese; GAC; Adsorption; Langmuir; Freundlich

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1. Introduction

The rapid industrialization in Malaysia in the last ten years has caused serious repercussions such as the pollution of natural resources like groundwater. Since groundwater moves through rocks and subsurface soil, it has a lot of opportunity to dissolve substances as it moves. Even though the ground is an excellent mechanism for filtering out particulate matter, such as leaves, soil, and bugs, dissolved chemicals and gases can still occur in large enough concentrations in groundwater to cause problems. Leaching agricultural or industrial pollutants or substances from leaking underground storage tanks (USTs) are contaminating groundwater [1].

Iron and manganese are common metallic elements found in the earth's crust [2]. Water percolating through soil and rock can dissolve minerals containing iron and manganese and hold them in solution. Occasionally, iron pipes also may be a source of iron in water. Polluted water may cause taste, odour, colour, or turbidity problems. Iron and manganese present in groundwater will cause a severe colour condition. When exposed to air, groundwater with dissolved iron and manganese turn to indissoluble and leave the water with brown-red colour. The problems cause by iron and manganese are aesthetic problems, indirect health concerns and economic problems [1].

Activated carbon is popular in potable water treatment. Activated carbon is effective in removing taste and odour causing compounds, chlorinated compounds, and many metals [3]. Activated carbon is prepared from a char form material such as almond, coconut, and walnut hulls, other woods, and coal. Activated carbon has the strongest physical adsorption forces or the highest volume of adsorbing porosity of any material known to mankind. It is a highly porous material; therefore, it has an extremely high surface area for contaminant adsorption. The equivalent surface area of 1 pound of AC ranges from 60 to 150 acres [4].

The objective of this study was to determine the potential and the effectiveness of granular activated carbon (GAC) in removing iron and manganese from the water. If this study shows favourable result, therefore it can be used as an alternative to remove iron and manganese in groundwater treatment. Batch test was conducted to investigate the adsorption capacity of ferrous and manganese onto the granular activated carbon. Besides, two empirical models, Freundlich and Langmuir adsorption isotherms, were used in this study.

1.1. Theoretical consideration

The Freundlich isotherm was commonly used to describe the adsorption characteristics of the activated carbon in water and wastewater treatment. The empirically derived Freundlich isotherm is defined as:

$$q_e = \mathrm{K_f} C_e^{(1/\mathrm{n})} \quad (1)$$

$\mathrm{k_f}$ and n are the empirical constants. The adsorption isotherm can be expressed in the linear form as:

$$\log q_e = \left(\frac{1}{\mathrm{n}}\right) \log C_e + \log \mathrm{k_f} \quad (2)$$

The constants in the Freundlich isotherm can be determined by plotting log q_e vs. log C_e. The Langmuir adsorption isotherm was developed by assuming that a fix number of accessible sites are available on the adsorbent surface, all of which have the same energy, adsorption is reversible, and there is no transmigration of adsorbate in the plane of the surface [5]. From these rational considerations, the Langmuir adsoprtion isotherm is defined as:

$$q_e = \frac{\mathrm{ab}C_e}{1 + \mathrm{b}C_e} \tag{3}$$

After rearranged, The Langmuir adsorption isotherm can be expressed in the linear form as:

$$\frac{1}{q_e} = \frac{1}{\mathrm{ab}} \cdot \frac{1}{C_e} + \frac{1}{\mathrm{a}} \tag{4}$$

By plotting a graph $(1/q_e)$ vs. $1/C_e$, a straight line will be obtained. From the graph the empirical constant can be obtained where the slope is 1/ab and the linear line will intercept the vertical axis is 1/a.

2. Material and methodology

Materials that were used in this study were granular activated carbon (GAC), ferrous solution (Fe(II)) and manganese solution (Mn(II)). The GAC was supplied by Kekwa Indah Sdn Bhd in Nilai, Negeri Sembilan, Malaysia which is a local manufacturer of GAC. The GAC was produced from coconut shell. Solution of Fe(II) and Mn(II) were prepared from ferrous sulfate heptahydrate, $FeSO_4.7H_2O$ and manganese sulfate, $MnSO_4.H_2O$ respectively.

The GAC used in the experiment was crushed by using a stainless steel blender to reduce the carbon size. The crushed carbon was sieved by using two sieves with the size of 850 and 1000 μm respectively. The carbon which retained between these two sieves was used in the study. GAC was washed with 1 N HCl several times and rinsed repeatedly with deionized water to remove oil and impurities before the GAC can be used in the experiment [6]. After washing, GAC was then heated in an oven at 110°C for 24 h [7] before stored in a sealed bottle for later use.

The batch test was carried out to determine the adsorption capacity of Fe(II) and Mn(II) onto GAC. The test was conducted by mixing certain amount of processed GAC with 200 ml of aqueous solution in a beaker and shook at 150 rpm in room temperature until equilibrium is reached. This test was conducted using various dosages of GAC, between 0.1 and 0.6 g and 0.2–0.9 g for Fe(II) and Mn(II) respectively. Preliminary experiment that was conducted showed that equilibrium was attaining after 6 h. After the equilibrium was achieved, the aqueous solution was collected and analyzed by the Atomic Absorption Spectrometer (AAS) for the residual concentration remained.

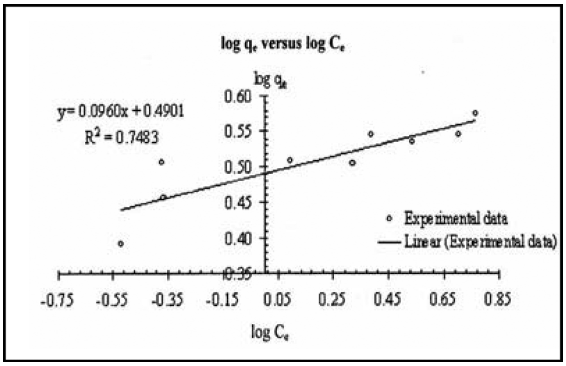

Fig. 1. Plots of log q_e vs. log C_e for Fe(II). ○, Experimental data; ------, Linear (Experimental data).

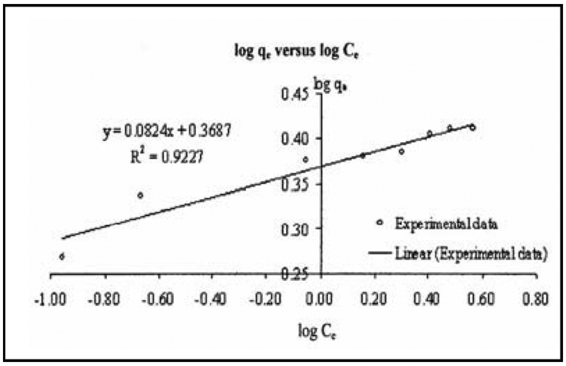

Fig. 2. Plots of log q_e vs. log C_e for Mn(II). ○, Experimental data; ------, Linear (Experimental data).

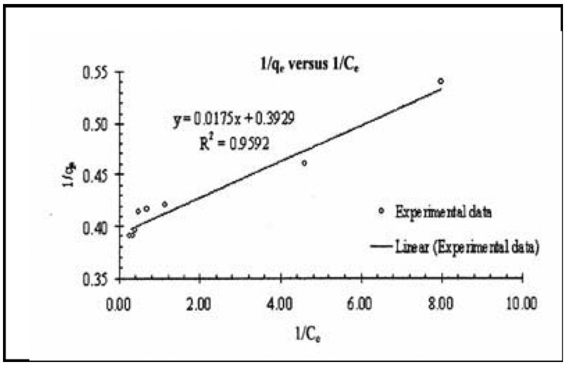

Fig. 4. Plots of $(1/q_e)$ vs. $(1/C_e)$ for Mn(II). ○, Experimental data; ------, Linear (experimental data).

3. Results and discussion

Experimental data obtained were fitted into Freundlich and Langmuir adsorption isotherm. Figs. 1 and 2 show the linearized Freundlich equation fitted with the experimental data obtained for Fe(II) and Mn(II). The slope of the straight line represents (1/n), while log k_f is the interception of the line on the y-axis.

The graphs $(1/q_e)$ vs. $(1/C_e)$ were plotted for Fe(II) and Mn(II) in order to determine the Langmuir constant are shown in Figs. 3 and 4.

From the linearization of both equations with the experimental data, it was found that the Langmuir adsorption isotherm fitted the experimental data better than that of the Freundlich adsorption isotherm. The correlation coefficient, (R^2) obtained for the Langmuir equation was in the range of 0.79–0.96 while the correlation coefficient obtained for the Freundlich equation was in the range of 0.74–0.92. The Freundlich and Langmuir adsorption isotherm were fitted with the experimental data for Fe(II) and Mn(II) and are shown in Figs. 5 and 6. The data obtained

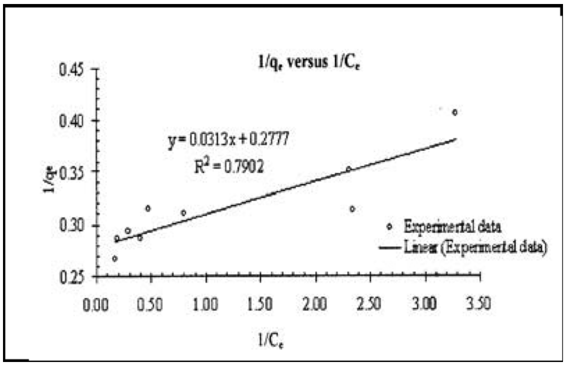

Fig. 3. Plots of $(1/q_e)$ vs. $(1/C_e)$ for Fe(II). ○, Experimental data; ------, Linear (experimental data).

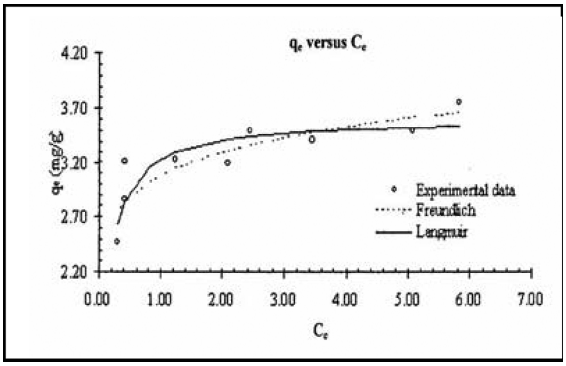

Fig. 5. Fitting of Langmuir and Freundlich isotherm for Fe(II). ○, Experimental data; ------, Langmuir; . . . . . . , Freundlich.

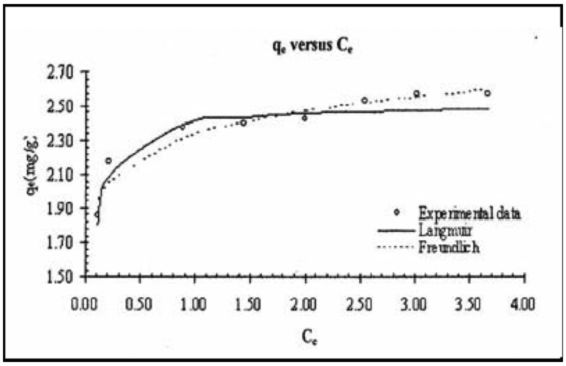

Fig. 6. Fitting of Langmuir and Freundlich isotherm for Mn(II). ○, Experimental data; ------, Langmuir; . . . . . . , Freundlich.

from the batch test is summarized in Tables 1 and 2.

The adsorption capacity of GAC with respect to the adsorption by using Langmuir adsorption isotherm (due to the fitness of this equation with the experimental data) is discussed. The Langmuir equation is an isotherm which is valid for monolayer sorption onto a surface with a finite number of identical sites. In Langmuir adsorption equation, the constant a is the adsorption capacity of adsorbate adsorbed onto GAC to form a monolayer. In this study, adsorption capacity of Fe(II) and Mn(II) were 3.6010 and 2.5451 mg/g respectively. Besides, the empirical constant b in the equation is a constant related to the affinity of the binding sites. The values of b obtained from the batch test for Fe(II) and Mn(II) were 8.8722 and 22.4521 L/mg respectively.

The Langmuir isotherm can fit the experimental data better due to the relatively high ambient temperature that allowed only monolayer adsorption to occur. The van der Waals force that forms multilayer adsorption was overcome by the adsorbate due to the high ambient temperature [8]. With relatively high room temperature of about 30°C where the adsorption process occurs, the chemisorption was more dominant as compared to the physisorption. The relatively high room temperature cause the chemical bond to occurs between the metal ions. Furthermore desorption will also occur between adsorbate and activated carbon at high temperature which physically bonded by the van der Waals force. Adsorbate which are physically adsorbed onto activated carbon receive sufficient energy from such high temperature to overcome the van der Waals force. Thus, the Freundlich adsorption equation did not fit well compared to the Langmuir adsorption equation.

Activated carbon has higher adsorption capacity for Fe(II) as compared to Mn(II). This may relate to adsorbates characteristics in terms of electronegativity and ionic radius. The electronegativity of Fe(II) is higher than the Mn(II) which are 1.8 and 1.5 respectively. In fact, electronegativity is a measure of strength for element to attract electron. In this case, it would measure the strength of Fe(II) and Mn(II) attach to negative charge at activated carbon surface. According to [9], higher electronegativities corresponded to the

Table 1
Freundlich adsorption equation for Fe(II) and Mn(II)

Element	Equation	k_f	1/n	R^2
Fe(II)	$q_e = 3.09\ C_e^{0.096}$	3.0910	0.0960	0.7483
Mn(II)	$q_e = 2.34\ C_e^{0.0824}$	2.3372	0.0824	0.9227

Table 2
Langmuir adsorption equation for Fe(II) and Mn(II)

Element	Equation	a	b	R^2
Fe(II)	$q_e = \frac{31.9C_e}{1+8.9C_e}$	3.6010	8.8722	0.7902
Mn(II)	$q_e = \frac{57.1C_e}{1+22.5C_e}$	2.5451	22.4521	0.9592

higher adsorption levels of metal ions onto the GAC.

Another factor that contributes to different GAC adsorption capacity on metal ion is ionic radius. Fe(II) has relatively smaller ionic radius than that of the Mn(II) since Fe(II) has the higher attractive charge in nucleus on the electron orbital as compared to Mn(II) [8]. The smaller ionic radius of Fe(II) makes it easier to penetrate into the micropores of the GAC.

There were four major functional groups on the surface of activated carbon which are carboxyl, carbonyl, hydroxyl, and lactonized carboxyl [10]. All these four functional groups were promoted to attract cation to it and ion exchange would occur. Therefore, the Fe(II) and Mn(II) which have positive charge would react and attach onto GAC surface's functional groups with chemically bonded. However, the actual chemical reaction between the metal ion and functional groups on the activated carbon surface was complex and difficult to understand.

4. Conclusion

In this study, results showed that the adsorption of Fe(II) and Mn(II) that performed by GAC was very encouraging. The classical Langmuir and Freundlich adsorption isotherm were applied to evaluate the experimental data and it was found that the experimental data could better fit the Langmuir isotherm. The relatively high ambient temperature could affect the bonding between adsorbate and adsorbent. GAC has higher adsorption capacity for Fe(II) as compared to Mn(II). This may relate to adsorbates' characteristics in terms of electronegativity, ionic radius and the amount of functional groups on the activated carbon surface that interact with both Fe(II) and Mn(II).

Notation

R^2 Correlation coefficient
q_e Amount of dye adsorbed per gram of activated carbon
C_e Equilibrium concentration
k_f Adsorption capacity for Freundlich adsorption isotherm
N Freundlich empirical constant
a Adsorption capacity for Langmuir adsorption isotherm
b Langmuir constant

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