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Performance of Fixed Bed Column Study for The Removal of Nickel and Rhodamine B by Low Cost Hydroxyapatite/Alginate Composite Bead Adsorbent

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Abstract: Hydroxyapatite (HAp) /Alginate composite bead was tested in this research to identify its effectiveness on reducing the Nickel (Ni^{2+}) and Rhodamine B (RhB) elements due to these substances are commonly discharged to the river in conjuction to various industrial activity occurred nowadays. The aim of this study is mainly to investigate the HAp/alginate composite media and to determine its performance in the dynamic system. Raw n-HAp powder and Alginate acid were used to develop the adsorbent bead and the method of Ni^{2+} and RhB adsorption is by applying fixed bed column technique. To study the effect of flow rate in percentage removal of Ni^{2+} and RhB, three different flow rate are studied where 5 mL/min, 10 mL/min and 15 mL/min of flow rate were used. The dynamic modelling used in the continuous system are Thomas and Yoon-Nelson model. The best range of percentage removal of Ni^{2+} are between 99.5 % and 40.5 % while for RhB the range of percentage removal are between 99.0 %. and 40.0 % using 5 mL/min of flow rate. The most effective flow rate to be utilized in the adsorption of Ni^{2+} and RhB is by using the lowest flow rate and based on the comparative study conducted in this study iand proved that the Thomas and Yoon-Nelson model are fitted to be use. In further studies other metal ion parameter and dye based substances should be tested using this method and adsorbent.

Keywords: HAp, Alginate, Composite, Fixed bed colum, Thomas model, Yoon-Nelson model

1. Introduction

Fresh water that are obtained from the hydrological cycle is essential for daily human activities that are used for domestic, agriculture and industrial sector and obviously contribute to economic growth.

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With the growth of economy, pollution of river and reservoir becomes inevitable due to the inconsideration and greediness of humankind throwing toxic and chemical waste into the river. With the quality of fresh water has been compromised, it will require a more complex and expensive process to treat a contaminated water [1].

Nickel (Ni) is one of heavy metals that is commonly found naturally in earth crust and core. Going through anthropogenic, Ni present in air, water, sediments and soils in natural. The main source of Ni exposure to human is through dietary consumption from foods such as chocolate, coffee, teas, legumes and nuts, which appear to have naturally higher levels of nickel. [2].

Rhodamine B (RhB) is a type of organic dye that widely used in industry which have water solubility characteristics. Hence it usually used in cotton wool and silk dyeing process [3]. Optical characteristics that RhB possess is the dye have it has a bright reddish violet colour and industrially used as a colorant in fabric and food industries and also as a water tracer colorant [4].

1.1 Hydroxyapatite (HAp)

The main purpose of Hydroxyapatite or commonly known as HAp is to act as an absorbent that have the ability to adsorb various heavy metal ions in water. The raw material to produce HAp are widely available and usually disposed in abundance. Fish scale and seashell are the most common natural raw material used in order to obtain HAp. The benefit getting HAp from natural resources is that the material is safe to be use and by utilizing this low-cost material to change it into a valuable product it will minimize the pollution effect to the environment [5].

1.2 Alginate

One of the substances that has the ability to naturally occurring anionic polymer that usually obtained from brown seaweed and broadly studied and has been applied in many biomedical applications. The reason behind its success to be used in biomedical application is because alginate has low toxicity and low cost of raw material and also its biocompatibility and usually used in form of hydrogel especially in biomedical industry [6].

2. Materials and Methods

2.1 Preparation of HAp/Alginate composite adsorbent

The preparation of the HAp/alginate composite adsorbent bead was referred to a past research by [7]. Firstly, 2.5 g of n-HAp powder is dispersed in 100 mL of deionized water and stirred for 1 hour using mechanical stirrer and going through sonication for 20 minutes. Next, 4 g of Alginic acid were , dissolved into 100 mL of distilled water and stirred mechanically for 2 hours at room temperature. Then, 50 mL of n-HAp solution is added in droplet to the polymer solution for 20 minutes and stirred for 1 hour at ± 40.0 °C. Next, the obtained solution is dropped into a flask containing 50 mL of ferric chloride using syringe and left to rest for 24 hours. Finally, after 24 hour the bead is collected and washed thoroughly with distilled water and dried before applied to the fixed bed reactor [7].

2.2 Experimental Setup

The dimension of the column is referred from a study [7] where the cylindrical column with internal diameter of 0.075 m and 0.5 m height are used in the continuous system. Both end of the column will be fitted with a layer of glass wool that will act as a filtration system for the reactor. The flowing mechanism in this continuous system will be supported by pump where the solution will be inserted from the bottom of the cylinder (Figure 1). To study the effect of flow rate to the adsorption performance a difference flow rate will be used throughout the experiment (5 mL/min, 10 mL/min and 15 mL/min.) where a fixed adsorbent's bed height was used at 18 cm.

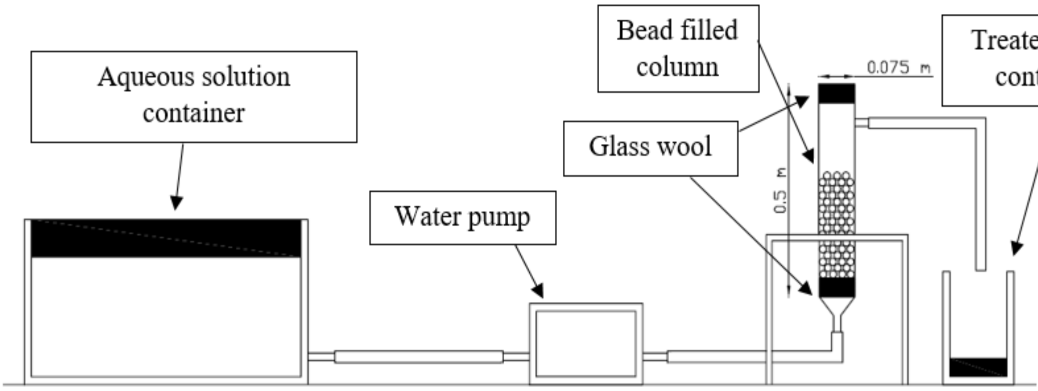

Figure 1: Fixed bed column arrangement

3. Results and Discussion

3.1 Effect of influent flow rate

The amount of flow rate supplied to the reactor have a direct impact on the percentage removal pattern of Ni^{2+} and RhB where a lower flow rate will cause the media be exhausted over a longer period of time where those behavior can be observed in Figure 2 and Figure 3 of percentage removal graph of Ni^{2+} and RhB. Over the time, HAp/alginate composite bead media in the column reached its saturated state where the adsorbing media lost its ability to adsorb the adsorbate. The indicator to identify whether it has reached its adsorbing limit is when the removal percentage value reach uniformity and the value are constant over a period of time. The larger the flow rate flowing through the column the faster the media became saturated with adsorbate.

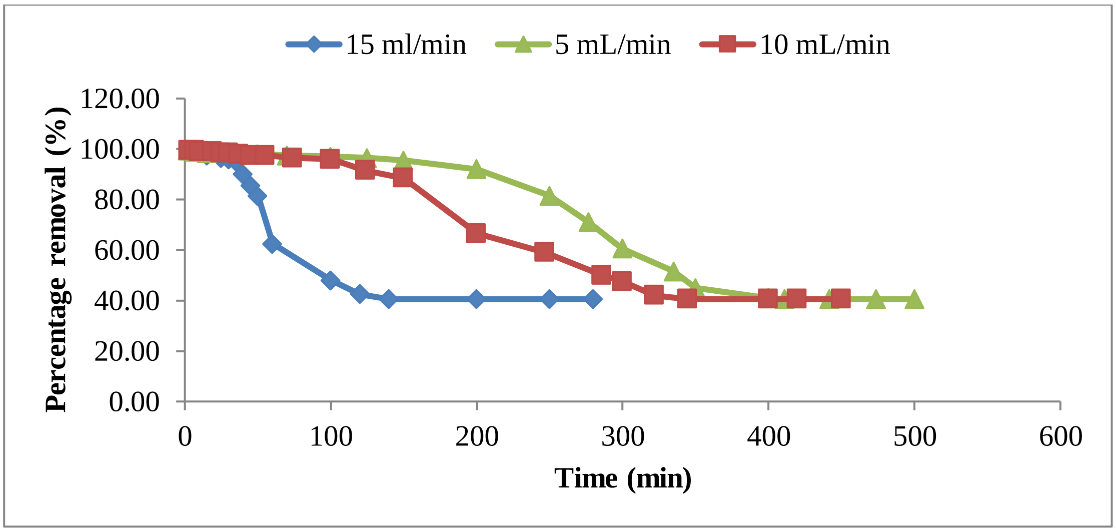

Figure 2: Percentage removal of Ni^{2+}

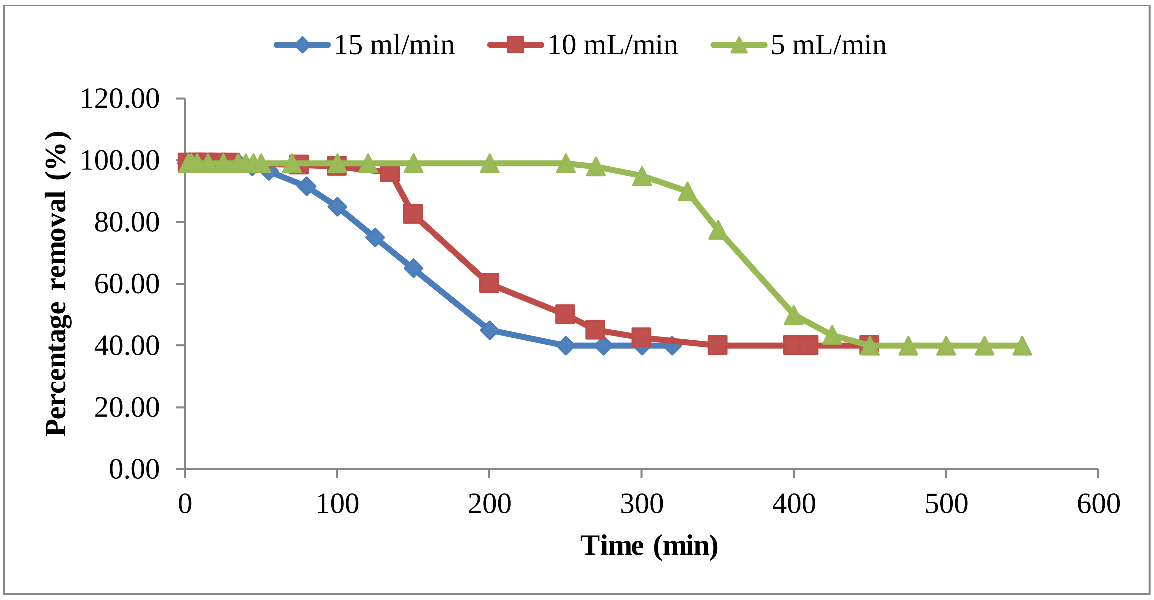

Figure 3: Percentage removal of RhB

3.2 Dynamic modelling of continuous system

The data retrieved from the experiment conducted by [7] are used to determine the dynamic model parameters for the adsorption of Ni^{2+} and RhB by applying Thomas model which are already studied by [7] and additional kinetic modelling of Yoon-Nelson model that are commonly used in fixed bed column study.

3.2.1 Thomas model

In the previous study by [7], Thomas model was used to identify the efficiency of Ni^{2+} and RhB adsorption to the HAp/Alginate composite bead. The assumption of this model made is where the negligible axial dispersion of adsorbate within the adsorbent bed inside the column since the adsorption obeys the second order reversible kinetics [8].

To design the column itself saturation loading capacity of an adsorbent need to be discover in the first place where this model will provide the information on the evaluation of saturation loading capacity of the adsorbent. [8]. The Thomas model equation are illustrated below:

$$\ln\left(\frac{C_o}{C_t} - 1\right) = \frac{k_{th} q_o m_c}{Q} - k_T C_o t \qquad \text{Eq. 1}$$

Which k_{th} is the Thomas rate constant, q_o represent the saturation loading capacity of adsorbent, Q is the flow rate used and m is the mass of the adsorbent in the column, C_o is for the solution influent's concentration whereby C_t is for the effluent's concentration. In order to find out the value of k_T and q_o a graph of ln[(Co/C)-1] against time need to be plotted. In Table 1, it shows that the parameter obtained from linear plot for RhB and Ni^{2+} for Thomas model.

Table 1: Thomas model parameter obtained from linear plot for RhB and Ni^{2+}

Parameter	C_0 (mg/L)	Q (mL/min)	k_{th} (mL/min/mg)	q_o (mg/g)	R^2
RhB	200	5	0.0000535	0.75	0.87
	200	10	0.0000695	0.5	0.90
	200	15	0.000073	0.37	0.85
Ni^{2+}	200	5	0.0000615	0.58	0.96
	200	10	0.0000675	0.5	0.92
	200	15	0.000086	0.27	0.70

The range of determined coefficient, R^2 of the Thomas model are between 0.85 and 0.90 for RhB and for Ni^{2+} the R^2 range between 0.7 and 0.96. Both coefficient value are high which indicate it fits to be used in Thomas model

From table for RhB and Ni^{2+} the value of k_{th} increase when the influent flow rate increase whereas the value of q_o increase when the value of influent flow rate decrease. This is due to the correlation of mass transfer with flow rate where mass are transferred higher with greater flow rate [9].

For RhB, when the flow rate was set at 5 mL/min the k_{th} value is 0.0000535 mL/min/mg and the value of q_o 0.75 mg/g. when the flow rate was increased to 10 mL/min the k_{th} value also increased to 0.0000695 mL/min/mg and q_o was drop to 0.50 mg/g. Then, final adjustment of flow rate was done to 15 mL/min and an increment of k_{th} value to 0.00007 mL/min/mg and the value of q_o continue to decline to 0.37 mg/g. Moving on to Ni^{2+}, initially, when the value of flow rate was set at 5 mL/min the value of k_{th} is 0.0000615 mL/min/mg and the q_o value was shown at 0.58 mg/g. Next, when an increment of flow rate was made to 10 mL/min there is an increasing trend of k_{th} value to 0.0000675 mL/min/mg and on contrary the value of q_o shows a decreasing trend to 0.50 mg/g. Then, when the flow rate was adjusted to 15 mL/min the k_{th} value keep showing an increasing trend to 0.0000860 mL/min/mg and also q_o value continue to show a decreasing trend to 0.27 mg/g.

3.2.2 Yoon-Nelson model

Yoon-Nelson model is a simple model that are designed for a single component system developed by Yoon and Nelson [10]. Yoon-Nelson model doesn't require any detail data on the characteristics of the absorbent, the physical properties of the adsorption bed and the type of adsorbent. Thus, Yoon-Nelson model are much less complicated than any other model [11].

The assumption made in the Yoon-Nelson model are the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent [11] [12]. In order to predict adsorption under variety conditions and to obtain the process variable the Yoon-Nelson model are not so effective [12].The Yoon-Nelson equation are shown in the equation 2 below:

$$\ln\left(\frac{C_t}{C_O - C_t}\right) = k_{YN}t - t_{0.5}k_{YN} \qquad \text{Eq.2}$$

Where k_{YN} is the Yoon-Nelson rate constant, $t_{0.5}$ is the time taken for the 50% adsorbate to break through the column, C_o and C_t is the initial and final concentration of solution respectively. In order to find out the value of k_{YN} and $t_{0.5}$ a graph of ln[C/(Co-C)] against time need to be plotted. In Table 2, it shows the parameter obtained from linear plot for RhB and Ni^{2+} for Yoon-Nelson model

Table 2: Yoon-Nelson model parameter obtained from linear plot for RhB and Ni^{2+}

Parameter	C_0 (mg/L)	Q (mL/min)	k_{YN} (mL/min/mg)	$t_{0.5}$ (min)	R^2
RhB	200	5	0.0107	495.6	0.87
	200	10	0.0139	331.8	0.90
	200	15	0.019	240.6	0.91
Ni^{2+}	200	5	0.0123	387.0	0.96
	200	10	0.0136	327.4	0.91
	200	15	0.0151	205.6	0.68

The value of determined coefficient, R^2 for Yoon-Nelson model at RhB experiment are ranged between 0.87 and0.91 while for Ni^{2+} ranged between 0.68 and 0.96 and this shows that Yoon-Nelson model are suitable to be used as the dynamic model for this experiment.

In Yoon-nelson model, for both RhB and Ni^{2+} when the value of flow rate increase the reaction at the k_{yn} also showing an increase trend. Inversely, when an increment of flow rate has been made the value of $t_{0.5}$ showing a decrease trends and These behaviours happens due to the saturation of the hap alginate bead occur more rapidly as the influent flow rate are increased.

Looking into RhB, when the flow rate was set at 5 mL/min the k_{YN} value is 0.0107 mL/min/mg and the value of $t_{0.5}$ is 495.6 minute. When the flow rate was increased to 10 mL/min the k_{YN} value also increased to 0.0139 mL/min/mg and $t_{0.5}$ was reduced to 331.8 minute. Then, final adjustment of flow rate was done to 15 mL/min and an increment of k_{YN} value to 0.019 mL/min/mg and the value of $t_{0.5}$ continue to decline to 240.6 minute Moving on to Ni^{2+}, initially, when the value of flow rate was set at 5 mL/min the value of k_{YN} is 0.0123 mL/min/mg and the $t_{0.5}$ value was shown at 387.0 minute. Next, when an increment of flow rate was made to 10 mL/min there is an increasing trend of k_{YN} value to 0.0136 mL/min/mg and on contrary the value of $t_{0.5}$ shows a decreasing trend to 327.4 mg/g. Then, when the flow rate was adjusted to 15 mL/min the k_{YN} value keep showing an increasing trend to 0.0151 mL/min/mg and also $t_{0.5}$ value continue to show a decreasing trend to 205.6 minute.

3.2.3 Comparison of kinetic model

The kinetic modelling in the continuous system are important to determine the suitability of the data to be fitted on the various model that can be applied to. In this research Thomas model and Yoon-Nelson model are chose to check its appropriateness to be applied on the data obtained by [7]. Thus, a comparison has been made with other past study in Table 3 and Table 4 that has been successful to remove Ni^{2+} or RhB using other adsorbent media that are applied to the Thomas model and Yoon-Nelson mode.

Based on the Table 3 and Table 4 are the indicator to check whether the Thomas model and Yoon-Nelson model are appropriate to be used on the data is by analysing the value of regression line, R^2 and comparing it to other past research using other adsorbent media.

Table 3: Comparison of HAp/alginate composite bead with other adsorbent on the Thomas model

Adsorbate	RhB		Ni^{2+}		Reference
	$t_{0.5}$ (mg/g)	R^2 -	$t_{0.5}$ (mg/g)	R^2 -	
HAp/Alginate composite bead	495.6	0.87	387.0	0.96	Present study
Brown algae (*Cystoseira indica*)	-	-	18.98	0.98	[15]
Polyaniline coated *Prosopis Julifora* activated carbon	845.60	0.94	-	-	[16]

The highest possible value on R^2 is 1 and based on the result of the present study the value of regression line in Thomas model for RhB in this study is 0.87. To be compared with a study by Auta [14] for the removal of RhB by using Oil palm empty fruit bunch activated carbon the regression line obtained was 0.96 which is close to the regression line obtained in this study. Auta [14] concluded in his study that the regression line in his data for the removal of RhB by using oil palm empty fruit bunch activated carbon are fitted to be used in Thomas model. In comparison with the sets of data retrieved from this study the regression line are also fitted to be used in Thomas model.

The regression line obtained for nickel in this study are 0.96. A comparison with the past research conducted [14] for the removal of nickel using modified water thyme (*hydrilla verticillata)* as an adsorbent has been done. The regression line obtained by [14] in his study are 0.98 and it is confirmed by [14] that his sets of data are suitable to be used in Thomas model. Looking into the result from this study the regression line for nickel are close to the value of regression line obtained by [14] thus for nickel removal in this study Thomas model are appropriate to be applied.

Table 4: Comparison of HAp/alginate composite bead with other adsorbent on the Yoon-Nelson model

Adsorbate	RhB		Ni^{2+}		Reference
	qo (mg/g)	R^2 -	qo (mg/g)	R^2 -	
HAp/Alginate composite bead	0.75	0.87	0.58	0.96	Present study
Modified water thyme (*hydrilla verticillata)*	-	-	81.24	0.998	[13]
Oil palm empty fruit bunch activated carbon	118.62	0.96	-	-	[14]

For the additional kinetic modelling in this study which is Yoon-Nelson model the value of regression line for the removal of RhB in this study is 0.87. In comparison with a study [16] to remove rhodamine B by using polyaniline coated *Prosopis Julifora* activated carbon as an adsorbent media the value of the regression line from his study are 0.94 and concluded that the regression line obtained from his research are suitable to be used in Yoon-Nelson model. To be compared with this study's regression line for the removal of RhB is 0.87 which is not far from the value obtained by [16] thus the data for RhB removal in this study are fit to be used in Yoon-Nelson model.

To analyse the suitability of nickel removal in Yoon-Nelson model a comparative study has been made with a study by [15] for the removal of nickel using Brown algae (*Cystoseira indica*). From a past study by [15] stated that in his study the value of regression line obtained from the removal of nickel which is 0.98 are fitted in the Yoon-Nelson model. In this study the regression line obtained are 0.96 which is close to the value obtained by [15] in his study. From that the nickel removal regression line in this study are suitable to be applied in Yoon-Nelson model.

4. Conclusion

The range of percentage removal for Ni^{2+} and Rhodamine B by using the Hap alginate composite media is 99.0 % to 40.5 % and 99.0 % to 40.0 % respectively. The effect flow rate to the exhaustion of media are obviously known where a larger flow rate will caused the adsorbent to exhaust quickly in the reactor. These statement are valid where based on the result of the experiment for both Ni^{2+} and RhB the largest flow rate used which is 15 mL/min exhaust earliest throughout the experiment.

In term of percentage removal, all flow rate used during the same experiment show almost the same range of percentage removal, only the difference between them is the exhaustion period of the media. Thus, to categorize which flow rate would be the most efficient to be applied in the fixed bed column adsorption method is to analyse period to reach its exhaustion period. The most efficient flow rate for Ni^{2+} and RhB would be 5 mL/min followed by 10 mL/min and 15 mL/min is the least efficient thus, to be conclude that the application of Hap/Alginate composite bead are suitable for the removal of Ni^{2+} and RhB based on the high value of percentage removal shown during the experiment.

In term of the kinetic modelling that are used in this study it is certain that both Thomas model and Yoon-Nelson model are fitted to be used on the data when comparing the present result with some previous research using different adsorbent media that obtain a great fitment by using Thomas model and Yoon-Nelson model when the regression value, R^2 of this research are closing to the R^2 value of the past research.

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