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## Adsorption and Kinetic Study on Mg<sup>2+</sup> Removal from Waste Water using Rice Husk based Magnetic Biochar

Mubarak NM<sup>1,2\*</sup>, Shapnathayammal S<sup>1</sup>, Suchithra Thangalazhy-Gopakumar<sup>3</sup>, Sahu JN<sup>4</sup>, Abdullah EC<sup>5</sup>, Jayakumar NS<sup>6</sup> and Sabzoi Nizamuddin<sup>6</sup>

<sup>1</sup>Department of Chemical and Petroleum Engineering, Faculty of Engineering, UCSI University Kuala Lumpur-56000, Malaysia

<sup>2</sup>Department of Chemical Engineering, School of Engineering and Science, Curtin University of Technology, 98009 Sarawak, Malaysia

<sup>3</sup>Department of Chemical Engineering, University of Nottingham, 43500 Semenyih Selangor Darul Ehsan Malaysia

<sup>4</sup>Department of Petroleum and Chemical Engineering, Faculty of Engineering, Institute Technology Brunei, Tungku Gadong, P.O. Box 2909, Brunei Darussalam

<sup>5</sup>Malaysia – Japan International Institute of Technology (MJIT), University Technology Malaysia, Jalan Semarak, 54100 Kuala Lumpur, Malaysia

<sup>6</sup>Department of Chemical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

### Research Article

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#### \*For Correspondence

Mubarak NM, Department of Chemical and Petroleum Engineering, UCSI University Kuala Lumpur-56000, Malaysia. Tel: +60 85 443939 exnt. 3833; Fax: +60 85 443837;

**E-mail:** mubarak.yaseen@gmail.com

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#### ABSTRACT

The adsorption isotherm and kinetic studies on the removal of Mg<sup>2+</sup> metal ion by using rice husk based magnetic bio char have been carried out. The analyses of batch mode experiments were performed to study the experimental parameters of pH, adsorbent dosage, agitation speed and contact time. From the statistical analysis, it was known that the highest removal of Mg<sup>2+</sup> is at pH 4, adsorbent dosage of 0.5 g, agitation speed of 150 rpm and a contact time of 180 minutes. The initial concentration of 0.2 mg/l, the removal efficiency of Mg<sup>2+</sup> using magnetic rice husk was 95% and the maximum adsorption capacity was 39.52 (mg/g) observed. The adsorption isotherms are well described by both Langmuir and Freundlich models and adsorption kinetic obeyed pseudo-second order.

### INTRODUCTION

Nowadays, there are major concerns on the water resources based environmental problems that have been facing by all living organisms. Discharging of pollutants into water resources such as river stream or to the sea is known to be a frequent occurrence in polluted sites. These pollutants mainly consists of heavy metals which are well known to be toxic, carcinogenic and may even pose great threat to living organisms with long term and high dose exposure. Heavy metals are basically elements on ground or water resources with an atomic weight of between 63.5 to 200.6 and a specific gravity of more than 5 or density exceeding 5 g per cubic meter <sup>[1,2]</sup>. Some of the examples of heavy metals are zinc, lead, cadmium, chromium, magnesium, copper and many others. Some of these elements that are in this category are listed more in detail in the **Table 1**. These metals are important to be removed from water resources as the threat to living organism and public health can be minimized. In order to remove these heavy

Heavy Metal	Toxicities	MCL (mg/L)
Arsenic	Skin manifestations, Visceral cancers, Vascular disease	0.050
Cadmium	Kidney damage, Renal disorder, human carcinogen	0.01
Chromium	Headache, diarrhoea, nausea, vomiting, carcinogenic,	0.05
Copper	Liver damage, Wilson disease, insomnia	0.25
Nickel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.20
Zinc	Depression, lethargy, neurological signs and increased thirst	0.80
Lead	Damage the fetal brain, diseases of the kidneys, circulatory system and nervous system	0.006
Mercury	Rheumatoid arthritis, diseases of the kidneys, circulatory system and nervous system	0.00003

**Table 1.** The MCL standards for the most hazardous heavy metals.

metals, a suitable treatment process needs to be introduced which can be satisfied in every possible ways, starting from its removal efficiency to its process cost [3]. Some of the common methods where they use to remove heavy metal around the globe are ion exchange, electrolysis, precipitation, membrane separation, solvent extraction, reverse osmosis (RO) and coagulation-flocculation [4-9]. However, these methods have their own advantages and limitations. These processes also demonstrate some significant disadvantages such as that it undergoes removal which are incomplete, toxic sludge production and high energy requirements.

The sorption technique is proved to be an attractive and an effective method to remove heavy metals. This is because sorption technique stands out from other techniques by having low operating and maintenance cost, consumes less energy, shorter process time, lesser generation of toxic sludge and most importantly high removal efficiency [10]. Some of the common absorbent used for sorption technique are carbon nanotubes, resin, activated carbon, silica gel and recently, Magnetic Biochar [11]. Activated carbons are widely used in absorption processes because of their high ability, reasonable cost and its effectiveness. However, according to studies, activated carbon is still considered to be a high cost absorbent and it gets more expensive as the quality of the activated carbon increases [10]. Thus, this has led to the search of an alternative adsorbent that is cheap and effective.

Biochar is a biocoal or charcoal which is a porous and fine-grained substance that has the same form of potting soil that is mixed with iron solution which is produced under the influence of maximum temperature conditions and oxygen-limited conditions using organic waste. In recent year, biochar has received big demands as a large scale soil modification to improve crop production, the fertility of soil and as nutrient preservation. Biochar, basically, has a high porosity level and wide-ranging surface area of relatively structured carbon matrix. This proves that biochar can act as an absorbent that has similar aspects of an activated carbon which plays a significant role of controlling the pollutants in the environment [11].

Some of the agricultural wastes or organic wastes derived for biochar as a sorbing organic pollutant are wood or bark, broiler litter, rice husk, pine-wood, corn straw, coconut shell, dairy manure, elephant grass and many more. These agricultural wastes are extensively available as an inexpensive raw material to produce biochar. However, the powdered biochar is proven for being difficult to be separated from an aqueous solution. Therefore, a magnetic medium by chemical co-precipitation is an efficient method for making the sorbent to effectively be separated by magnetic separating technique. Moreover, the joint magnetic medium has the potential of adding the functions of bulk magnetic sorbent [12].

The aim of this study was to produce a cost-effective and high efficiency absorbent to remove the heavy metals. In this study, magnetic biochar is prepared from rice husks to provide a potentially cheap alternative precursor and also to eliminate the waste disposal as well [2]. In this research, the statistical optimization on the removal of  $Mg^{2+}$  from aqueous solution by the usage of Magnetic biochar was carried out. The effect of each process parameter  $pH$ , adsorbent dosage, and agitation speed and contact time on the removal of  $Mg^{2+}$  was investigated using Magnetic Biochar. The equilibrium kinetic and isotherm model equation for the removal of  $Mg^{2+}$  was also investigated.

## MATERIALS AND METHOD

### Preparation of Magnetic Biochar

The dried biomass was crushed and sieved to a particle size of less than 150  $\mu m$ . It was then impregnated at ratios of 0.5 to 1.15 by weight (activating agent/dried biomass), for 4 h at room temperature and dried at 100 °C and stored in desiccator. The pyrolysis of biomass was carried out in a HAMiab-C1500 Microwave Muffle System oven. 20 g of prepared sample was placed inside the quartz tube (35 mm OD, 38 mm ID and 500 mm length). The optimum pyrolysis parameters were, power=800 W, irradiation time=30 min and nitrogen gas flow=0.2 ml/min. After the reaction sample was cooled down to room temperature and final weight taken to determine the yield of the product. The product was washed with distilled water until the pH become neutral. Finally the sample was stored in tightly closed bottles.

### Preparation of $Mg^{2+}$ Stock Solution

Magnesium solution was to be prepared using stock solution from MERCK. Analytical grade is employed to prepare stock solution from a 1000 mg/L of magnesium metal's ions which further dilute with distilled water using volumetric flask to required concentrations. As for this research, the initial concentration of  $Mg^{2+}$  metal ions was set to 0.20 mg/L and the prepared solution was used for batch adsorption experiments.

## Design of Experiment using Design Expert 8.0

The Design Expert 8.0 is basically software designed for optimizing the growth of processes and products. In other words, it was designed to help with the understanding of a multi-factor experiment. In this research, the Design Expert 8.0 was employed to design the batch adsorption experiments by varying the pH, adsorbent dosage, contact time and the agitation speed which are the optimizing conditions. The parameters used for this research are of various variables that consist of dosage of the adsorbent from 0.1 to 0.5 g, pH of the adsorbent from 4 to 8, agitation speed from 120 rpm to 150 rpm and agitation time from 120 minutes to 180 minutes room temperature.

### Batch Adsorption Experiment

A batch adsorption experiment was performed by using 125 ml of 2.0 mg/L of  $Mg^{2+}$  agitated with varying dosages of Magnetic Biochar and other variable parameters according to the design obtained from the Design of Expert (DOE). The initial and final concentration of  $Mg^{2+}$  stock was determined using Atomic Spectrometer (PerkinElmer an Analyst 400). Once the agitation process takes place, the process is then continued with filtration before the testing of the final concentration. The design of experiment of various runs with different parameters is shown in **Table 2**.

Run	pH	Agitation speed (rpm)	Agitation time (hrs)	Adsorbent dosage (g)
1	4	120	3	0.1
2	8	150	2	0.5
3	4	150	2	0.5
4	4	120	3	0.5
5	4	150	3	0.1
6	4	120	2	0.1
7	8	120	2	0.1
8	8	120	3	0.1
9	6	135	2.5	0.3
10	8	150	3	0.5
11	4	150	2	0.1
12	8	120	2	0.5
13	4	150	3	0.5
14	8	120	3	0.5
15	4	120	2	0.5
16	8	150	3	0.1
17	8	150	2	0.1

**Table 2.** Design of experiment using Design Expert software for Magnesium.

The adsorption capacity of magnetic biochar at time  $t$  was determined by using this equation (1) while the adsorption equilibrium of  $Mg^{2+}$  was computed based on equation (2)

$$q_t \text{ (mg/g)} = [(C_0 - C_t)V]/m \text{ (1)}$$

$$q_e \text{ (mg/g)} = [(C_0 - C_e)V]/m \text{ (2)}$$

where  $C_0$  represents the initial concentration of  $Mg^{2+}$  solution (mg/L),  $q_t$  represents the concentration of  $Mg^{2+}$  at time  $t$  (mg/g),  $q_e$  represents the  $Mg^{2+}$  uptake at equilibrium,  $C_e$  represents the equilibrium concentration of  $Mg^{2+}$  (mg/L) respectively;  $V$  represents the volume of  $Mg^{2+}$  stock solution (L) and  $m$  indicates the weight of the adsorbent used (g).

### Characterization of Magnetic Biochar

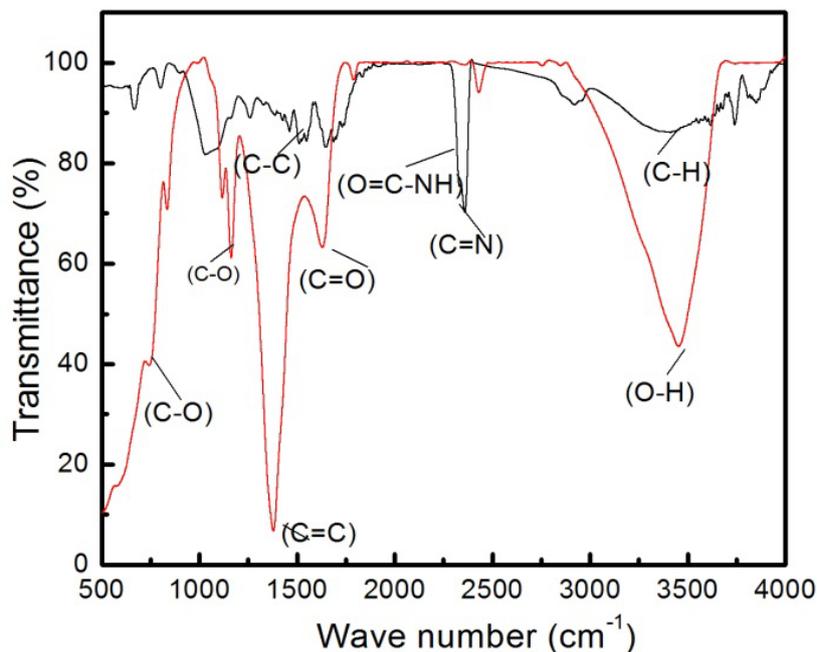
The physical structure and morphology of the Magnetic Biochar had been examined by the Field Emission Scanning Electron Microscope (FESEM) technique. The Fourier Transform Infrared (FTIR) spectroscope was used to study the surface chemistry of Magnetic Biochar. Elemental analysis (carbon, hydrogen, nitrogen, and sulphur values) was studied through using Elemental Analyzer, (Model: TRUSPEC CHNS MICRO). Oxygen content was calculated by the formula,  $100 - (C\% + H\% + S\% + N\% + \text{ash}\%)$

## RESULTS AND DISCUSSION

### Characterization of FTIR image on Magnetic Biochar

Fourier Transform Infrared (FTIR) spectroscope ((Bruker, IFS66v/S) was used to analyse the magnetic biochar for determination of the surface functional groups. Besides porosity, adsorption behaviour of magnetic biochar is also influenced by the chemical reactivity of the surface especially in the form of chemisorbed oxygen in various forms of functional groups. The surface oxides have acidic as well as basic properties. The magnetic biochar before and after adsorption of heavy metal was successfully investi-

gated using Fourier Transform Infrared spectroscopy (FTIR) (Bruker, IFS66v/S). **Figure 1** shows the FTIR spectra before adsorption (a) and after adsorption (b). The band located at 3714-341  $\text{cm}^{-1}$  is related to the N-H groups, while the band 2361 is grouped as C=C stretch of alkynes Vibration of C=N is ascribed at intensity 1995  $\text{cm}^{-1}$ . The transmittance at 1652-1498  $\text{cm}^{-1}$  is similar to the

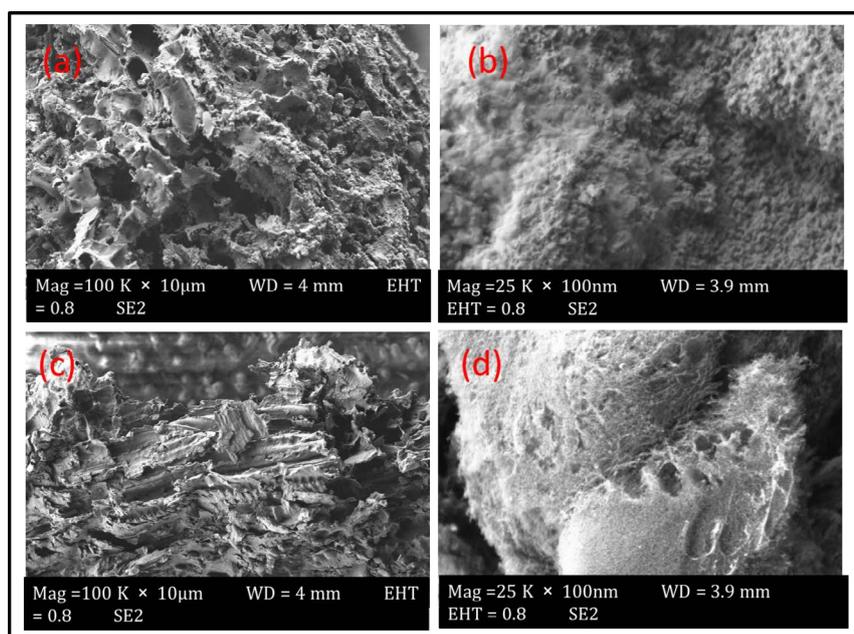


**Figure 1.** FTIR Spectra on a) magnetic biochar before adsorption and b) magnetic biochar after adsorption.

O-H (hydroxyl) group, and  $\text{CH}_2$  and C-O-C (ether, ester and phenol) functionalities are shown with intensive peaks at 1425 and 1276  $\text{cm}^{-1}$ . The transmittance at 1652-1497  $\text{cm}^{-1}$  is similar to the O-H (hydroxyl) group, and absorption peak of 1557  $\text{cm}^{-1}$  recommends the occurrence of aromatic with C-C stretch (ester and phenol) whereas the peak observed at 1071  $\text{cm}^{-1}$  represents the presence of either group. On the other hand, the peak observed at 668  $\text{cm}^{-1}$  reveals alkynes with C-H blends is present. These result good agreement with previous researchers [13,14].

### Characterization of FESEM on Magnetic Biochar

The Field Emission Scanning Electron Microscopy (FESEM) is basically a technique used to capture 3 dimensional images at a high resolution and it was used to observe the surface physical morphology at different magnification scales of the magnetic biochar as shown in **Figure 2**. Through these images, it was learnt that porosity is created during the chemical activation by  $\text{N}_2$  gas as the oxidant agent diffusion through the carbon is involved in the impurities removal and consumption of carbon. The micro



**Figure 2.** (a-b) FESEM images before adsorption (c-d) FESEM image after adsorption at different magnification scale.

porosity on the surface favours the opening, which creates large pores on the surface and a porous structure. This causes the well-structure magnetic biochar favours high adsorption capacity for the adsorption of  $Mg^{2+}$  metal ions. The properties of magnetic biochar are shown in the **Table 3**.

### Statistical analysis for the removal of magnesium, $Mg^{2+}$

Batch experiments were conducted using the Design Expert software which is employed to design the batch adsorption experiments by varying the pH, adsorbent dosage, contact time and the agitation speed which are the optimizing conditions. **Table 4** illustrates the results from analysis of variance using magnetic biochar as an adsorbent in the removal of  $Mg^{2+}$ . The fisher *F*-test value and the p value which is the lower probability are important values from the analysis for model validation. Normally, the fisher *F*-test value indicates the mean square of the regressed model to compare the mean square of the residuals of errors while the p value (lower probability) is important to show the higher significance for regression model.

The model *F*-test value is significant as the value obtained from the analysis of variance is 20.23. The Curvature *F*-test value obtained is 2.97, which implies that the model is significant curvature as measured by the difference between the average of the centre point and the average of the factorial point in the design model. The correlation coefficient value  $R^2$  is 0.9964 whereas the adjusted determination coefficient,  $R^2_{adj}$  is 0.9472, which implies that the model is significant. From the ANOVA obtained, the model designed was significant with the sum of square value of 1370858. The regression model for magnesium residual (mg/L) in terms of coded factors is given by the following equation:

Removal% in coded factors

$$\text{Removal\% of } Mg^{2+} = 78.59 - 8.05A + 3.09B + 1.31C + 1.46 - 1.18AB - 0.75AC - 0.85AD + 0.74BC - 0.86BD + 0.96CD - 0.75ABC - 0.93ACD - 0.74$$

Based on the equations developed from coded factors, a represent for  $p^H$ , B is the dosage and C is the contact time of adsorbent the single factor coefficient is represents effect on the particular factor while two factor coefficients represent the interaction among the two factors involved. The positive sign in the equation is describes the synergistic effect and negative sign is represent antagonistic effect.

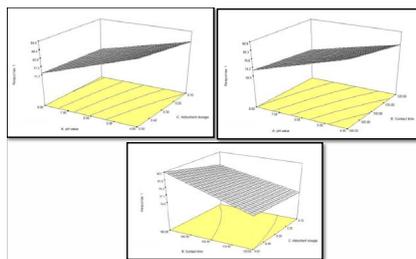
The 3-dimensional plot for the removal of  $Mg^{2+}$  from aqueous solution using Magnetic Biochar is demonstrated in **Figure 3(a-c)**. These plots were done to determine the relationship between the percentage removals of heavy metal  $Mg^{2+}$  ion with the optimizing conditions. The interaction of  $p^H$  and adsorbent dosage were plotted on **Figure 3(a)**. Based on the plot, the removal of  $Mg^{2+}$  ions are increased as the dosage increase but reduced when the  $p^H$  increases. In another word removal efficiency is directly proportional to adsorbent dosage and inverse proportional to  $p^H$  value. Meanwhile  $p^H$  is also an important parameter as it exhibit high removal at lower  $p^H$  for the biochar. **Figure 3(b)** shows the interaction between contact time and  $p^H$  value. An optimum removal percentage was obtained at a long contact time and a lower  $p^H$  value. The last analysis was done that denotes the contact time

Properties	Magnetic Biochar
Bet surface ( $m^2/g$ )	765
Particle size ( $\mu m$ )	<150
Carbon content	55
$p^H$	7
Bulk density ( $g/cm^3$ )	1.24

**Table 3.** Characterization of Magnetic Biochar.

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Status
Model	1370.86	14	97.92	20.23107	<0.0001	Significant
A	1036.84	1	1036.84	214.22	0.043	
B	152.52	1	152.52	31.51	0.11	
C	27.56	1	27.56	5.69	0.25	
D	34.2	1	34.22	7.07	0.22	
AB	22.09	1	22.09	4.56	0.27	
AC	9	1	9	1.86	0.40	
AD	11.56	1	11.56	2.38	0.36	
Curvature	2.96	1			0.0005	significant
Pure Error	0.95	9				
Cor Total	1448.375	16				

**Table 4.** Analysis of variance (ANOVA) for the removal of  $Mg^{2+}$  using Magnetic Biochar.



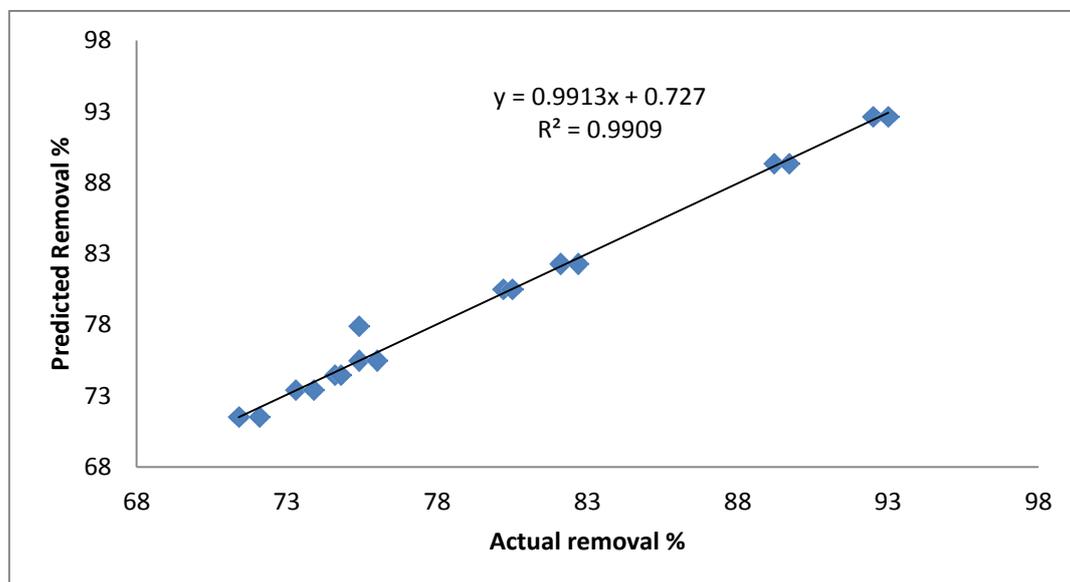
**Figure 3.** A 3-D interaction plot of the removal of  $Mg^{2+}$  using magnetic biochar, (a) Interaction of pH and adsorbent dosage (b) Interaction of contact time and solution pH, (c) Interaction of contact time and adsorbent dosage. and the adsorbent dosage where the highest removal percentage was obtained at a longer contact time and a high adsorbent dosage. Based on these **Figure 3(c)**, it can be concluded that as the contact time and adsorbent dosage increases, the removal percentage increases as well but at a lower  $p^H$  value.

**Figure 4** shows the theoretical values versus the experimental values for magnesium residual. These predicted percentage removal values and the actual values were obtained from the Design Expert software. It is clearly shown that the theoretical values obtained were quite close to the experimental values, indicating that the model developed was successful in bridging the correlation between the process variables to magnesium residual. The quality of the model developed was evaluated based on the correlation coefficient value as the correlation coefficient was above 0.95 from the plot. The model equation presented high  $R^2$  statistics of 0.9965 showing that 99.65% of the variations in magnesium residual can be explained by the independent variables such as adsorbent dosage, contact time, agitation speed and  $p^H$  value. The R-value obtained was relatively high, indicating that there was a good agreement between the experimental and the theoretical values from the models. The model also shows that  $R^2$  is in reasonable agreement with the adjusted  $R^2$  value of 0.9472. According to these criteria, the best model can be identified. The statistical analysis gave several comparative solutions for optimum conditions of best magnesium adsorption by magnetic biochar. The optimum condition selected by the software as the first choice was at an adsorbent dosage of 0.5 g, contact time of 3 hours, agitation speed of 150 rpm and a  $p^H$  value of 4. These optimum conditions were used for the adsorption isotherms and kinetics study for the determination of particle limiting adsorption capacity ( $q_m$ ) as well as for bench scale model operation.

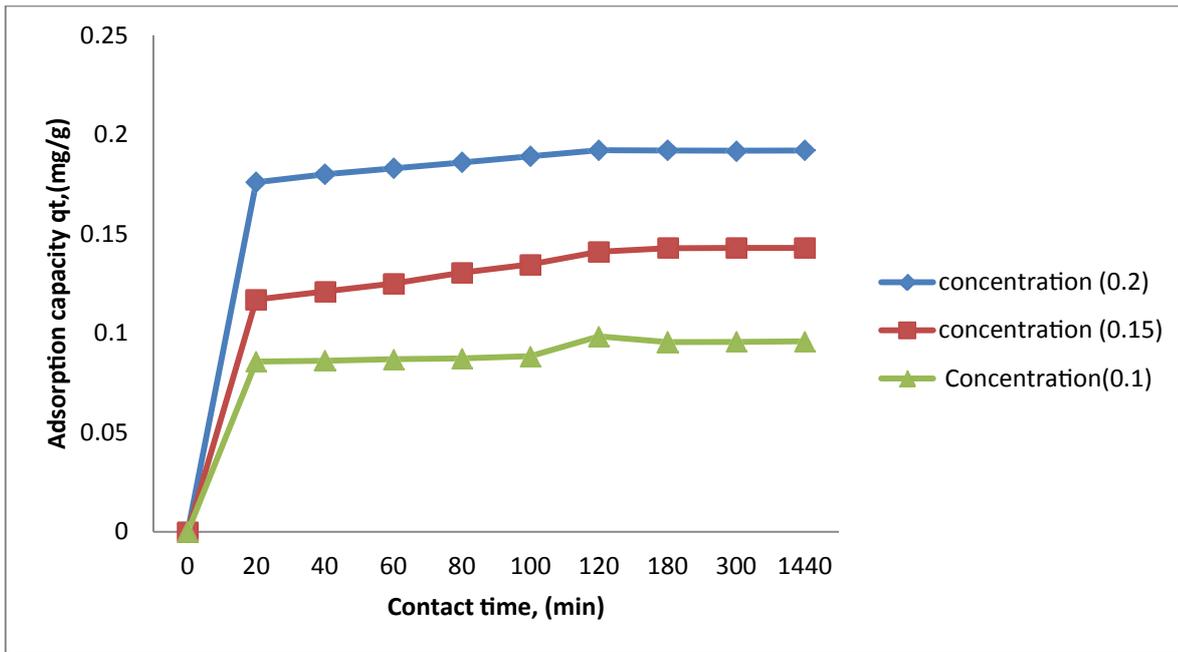
#### Adsorption kinetic and adsorption isotherm studies

In order to determine the optimize conditions of  $Mg^{2+}$ , an analytical study was done on magnetic biochar through kinetics and isotherm studies. As the  $p^H$  value of 4 showed the highest removal efficiency, it was selected to conduct this kinetic study. The parameters that were kept constant are the adsorbent dosage, volume of solution and agitation speed. An interval of 20 minutes, for the first two hours, the samples were taken to analyse. Then, it was followed by the 3<sup>rd</sup> hour and the 5<sup>th</sup> hour and

finally at the end of 24 hours was recorded. From the **Figure 5**, it can be seen that adsorption increases until it reaches 120 minutes. After that, the concentration was constant. This indicated that the magnetic biochar reached equilibrium at 120 minutes. Further increase in the contact time leads to liner trend was observed.



**Figure 4.** Relation between the Predicted and Actual value of the removal of  $Mg^{2+}$  using magnetic biochar.



**Figure 5.** Adsorption capacity ( $q_t$ ) versus contact time at different concentration values.

Langmuir and Freundlich equations are important in adsorption isotherm and kinetics studies. Both models were applied in the present research. Langmuir equation is used to relate the solid phase adsorbate concentration ( $q_e$ ) and the equilibrium solution concentration ( $C_e$ ) of  $Mg^{2+}$  from the batch adsorption as shown in equation (3).

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (3)$$

Where  $C_e$  (g/L) and  $q_e$  are the unadsorbed  $Mg^{2+}$  concentration in solution at equilibrium and the amount of adsorbed  $Mg^{2+}$  concentration per unit weight of the adsorbent,  $K_L$  is the equilibrium constant or Langmuir constant related to affinity of binding sites (L/mg) and  $q_m$  represents a particle limiting adsorption capacity when the surface is fully covered with  $Mg^{2+}$  and support for the adsorption performance comparison.  $K_L$  and  $q_m$  from the slope and intercept lines of  $C_e/q_e$  versus  $C_e$  graph.

**Figure 6** represents the adsorption isotherm for linearized Langmuir model with Magnetic biochar. Based on the plotted graph it can observe that the isotherm data fits for Langmuir equation as it obtained correlative coefficient  $R^2$  was 0.9971. The  $K_L$  and  $q_m$  values were calculated using the slope and intercept of the graph which then compared to the Langmuir equation described earlier. The  $K_L$  and  $q_m$  values for biochar obtained 4.77 L/mg and 39.52 mg/g.

The model further analyzed using Freundlich isotherm. The equation for this isotherm was derived into linear form in order to calculate the  $K_F$  and  $n$  value which are the Freundlich constant and constant value which describes the importance of a relationship between the adsorbate and adsorbent. The  $K_F$  and  $n$  values were calculated from slope and intercept of the linear plot of  $\ln q_e$  versus  $\ln C_e$ . Meanwhile the correlation factor,  $R^2$  were obtained 0.998 which shows both models are favourable for Freundlich isotherm. **Table 5** shows the calculated values for Langmuir and Freundlich meanwhile **Figure 6 and 7** shows the linearized Langmuir and Freundlich models.

The Langmuir and Freundlich equations were developed in order to relate the unadsorbed metal ions  $Mg^{2+}$  with equilibrium adsorption capacity to the as shown the equations below.

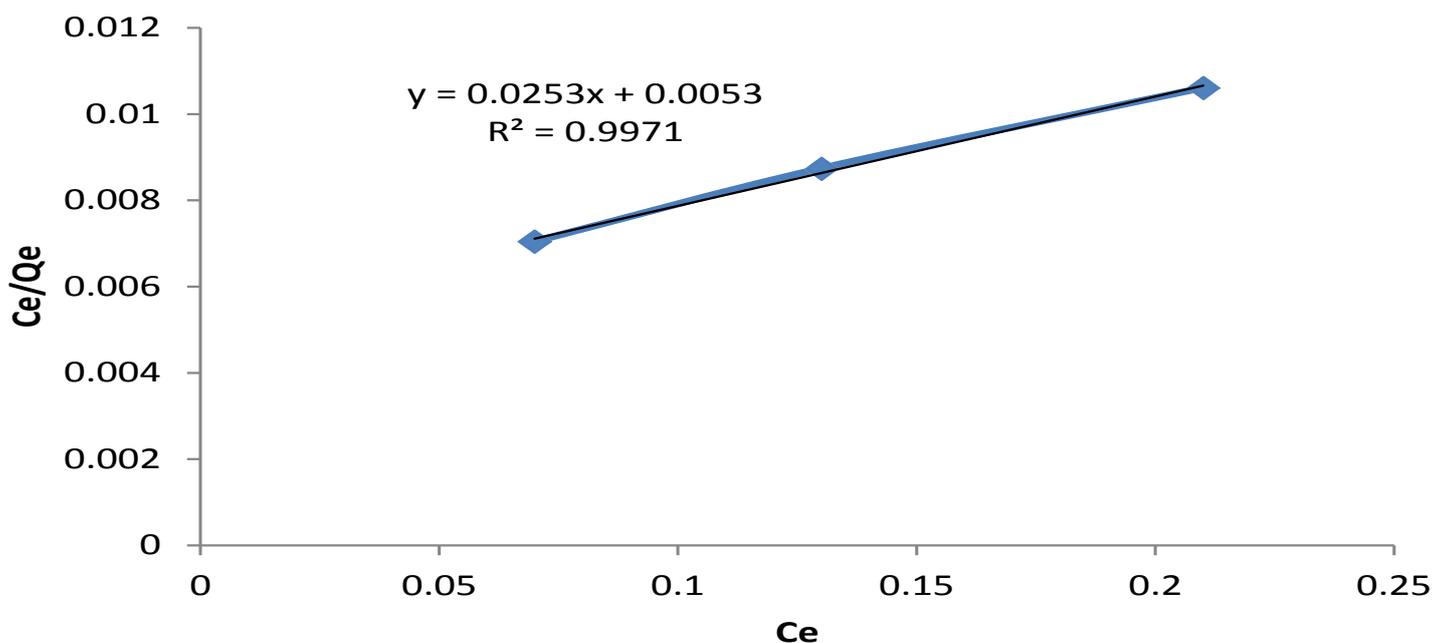
Developed Langmuir equation:

$$q_e = \frac{188.5C_e}{1+39.52C_e} \quad (4)$$

Developed Freundlich equation:

$$q_e = 29.92C_e^{0.865} \quad (5)$$

There are several kinetic models that are available to study the mechanisms of adsorption process. The two kinetic models that were tested to fit the experimental data were pseudo-first order and the pseudo-second order equation [15,16]. This study was conducted by between magnetic biochar and three different  $p^H$  values of  $p^H$  4, 6.5, and 8. This is said to be a successful kinetics



**Figure 6.** Langmuir Adsorption Isotherm of Mg<sup>2+</sup>.

Adsorbent	Langmuir Isotherm			Freundlich Isotherm		
	q <sub>m</sub> (mg/g)	K <sub>L</sub> (L/mg)	R <sup>2</sup> <sub>1</sub>	K <sub>F</sub> (L/mg)	n	R <sup>2</sup> <sub>2</sub>
Magnetic Biochar	39.52	4.77	0.9971	29.92	1.311	0.9982

**Table 5:** Langmuir and Freundlich constants.

description of the fixation reaction of dyes on the adsorbent. The pseudo-first order equation is given by:

$$\text{Log}(q_e - q_t) = \text{Log } q_e - \left( \frac{K_1}{2.303} \right) t \quad (6)$$

Where q<sub>e</sub> and q<sub>t</sub> are the adsorption capacity at equilibrium and at time t respectively in mg/g while K<sub>1</sub> is the rate constant of pseudo first order adsorption in min<sup>-1</sup>. From a plot of  $\text{Log}(q_e - q_t)$  versus t, q<sub>e</sub> and K<sub>1</sub> can be determined from its slope and intercept.

The pseudo-second order equation is given by:

$$\frac{t}{q_t} = \frac{1}{K \cdot q_e^2} + \frac{t}{q_e} \quad (7)$$

Where q<sub>e</sub> and q<sub>t</sub> are the adsorption capacity at equilibrium and at time t respectively in mg/g while K<sub>1</sub> is the rate constant of pseudo first order adsorption in g/mg.h.

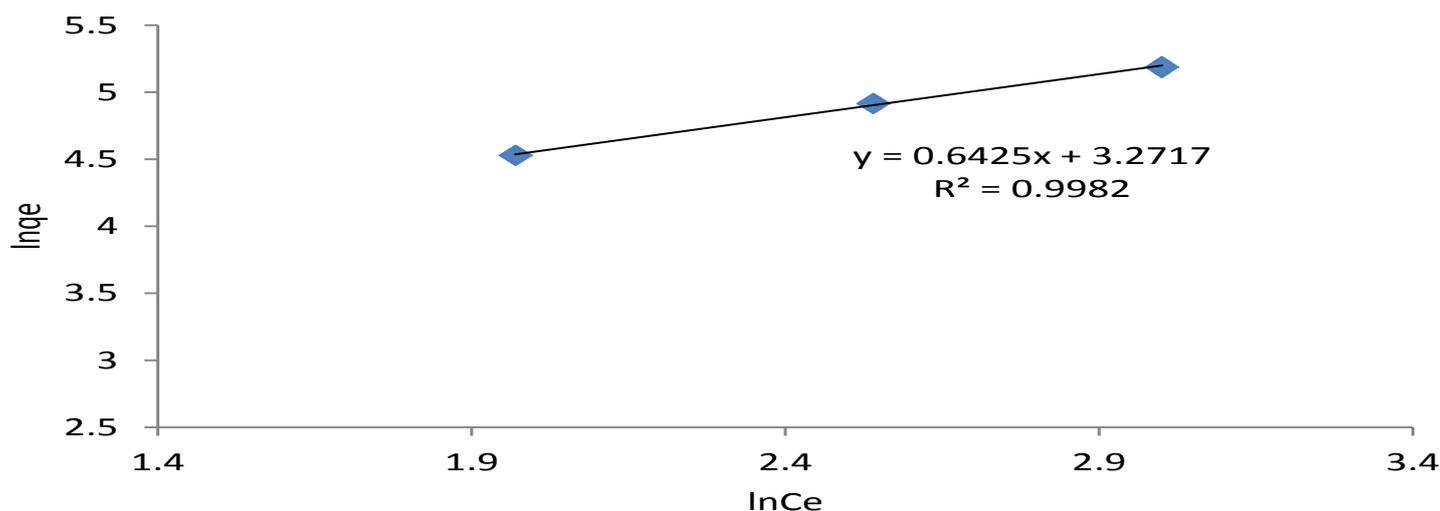
The kinetic constants are obtained by linear regression which as shown in **Figure 7** for pseudo-second order model and are listed in **Table 6**. For the pseudo-first-order kinetic model, the graph of  $\text{Log}(q_e - q_t)$  versus t was plotted. The plot showed that it did not produce a straight line, thus did not yield in proper convergence. Therefore, this clearly proves that the experiment do not follow the pseudo-first-order kinetic model. Meanwhile for the pseudo-second-order adsorption, the graph of (t/q<sub>e</sub>) versus time was plotted and all data were clearly converged. The plot fitted well in a straight line with a high R<sup>2</sup> correlation coefficient value of more than 0.95.

It can be concluded that the experimental values are closer to the equilibrium adsorption for pseudo-second-order model. As the pH value increases, the values of k<sub>2</sub> and q<sub>e</sub> decreases and the calculated q<sub>e</sub> gave a consistent data with the experimental data. This indicates that the adsorption of Mg<sup>2+</sup> using the adsorbent obeyed the pseudo-second-order kinetic model.

## CONCLUSION

The usage of agricultural wastes can be utilized well and be used as beneficial product in industries. Statistical analysis revealed that the highest removal of Mg<sup>2+</sup> is at pH 4, adsorbent dosage of 0.5 g, agitation speed of 150 rpm and a contact time of 180 minutes.

The maximum adsorption was 39.52 (mg/g) measured to be of 95%. The analysis revealed that the highest removal Mg<sup>2+</sup>



**Figure 7.** Freundlich adsorption isotherm of  $Mg^{2+}$ .

Adsorbent pH	$q_e$ (mg/g)	$K_2$ (min.g/mg)	$R^2$
4	0.0997	2.56	0.984
6.5	0.165	0.08	0.936
8	0.067	0.0954	0.942

**Table 6.** Pseudo-second-order kinetic parameter.

efficiency of 95% removal. It consists of the adsorbent dosage of 0.5 g, agitation speed of 150 rpm, contact time of 3 hours and pH value of 4. From the results obtained, it can be concluded that the experiment followed the Langmuir and Freundlich isotherm. In overall, using agricultural waste such as rice husk based raw material can help in the abundance of agricultural waste to create a more potential application.

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## REFERENCES

1. Srivastava NK and Majumder CB. Novel biofiltration methods for the treatment of heavy metals from industrial wastewater. *J. Hazard. Mater.* 2008;151:1-8.
2. Gupta VK, et al. Low-cost adsorbents: Growing approach to wastewater Treatment—A review. *Critical Reviews in Environmental Science and Technology.* 2009;39:783-842.
3. Kurniawan TA, et al. Physico-chemical treatment techniques for wastewater laden with heavy metals. *Chemical Engineering Journal.* 2006;118:83-98.
4. Barakat MA. New trends in removing heavy metals from industrial wastewater. *Arabian Journal of Chemistry.* 2011;4:361-377.
5. Dabrowski A, et al. Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method. *Chemosphere.* 2004;56:91-106.
6. Lin SH and Juang RS. Heavy metal removal from water by sorption using surfactant-modified montmorillonite. *Journal of Hazardous Materials.* 2002;92:315-326.
7. Qin JJ, et al. A feasibility study on the treatment and recycling of a wastewater from metal plating. *J. Membr. Sci.* 2002;208:213-221.
8. Qdais HA and Moussa H. Removal of heavy metals from wastewater by membrane processes: A comparative study. *Desalination.* 2004;164:105-110.
9. Lesmana SO, et al. Studies on potential applications of biomass for the separation of heavy metals from water and wastewater. *Biochem. Eng. J.* 2009;44:19-41.

10. Hameed MSA. Continuous removal and recovery of lead by alginate beads, free and alginate-immobilized chlorella vulgaris. *African Journal of Biotechnology*. 2006;5:1819-1823.
11. Chen WY, et al. Recovery and recycle of metals from wastewater with a magnetite-based adsorption process. *Research Journal of the Water Pollution Control Federation*. 1991;63:958-964.
12. Bansal M, et al. A comparative study for the removal of hexavalent chromium from aqueous solution by agriculture wastes' carbons. *J.Hazard. Mater*. 2009;171:83–92.
13. Mubarak NM, et al. Synthesis of palm oil empty fruit bunch magnetic pyrolytic char impregnating with FeCl<sub>3</sub> by microwave heating technique. *Biomass and Bio energy*. 2014;61:265-275.
14. Mubarak NM, et al. Adsorption and kinetic study on Sn<sup>2+</sup> removal using modified carbon nanotube and magnetic biochar. *International journal of nano science*. 2013;12:1350044.
15. Ho YS and McKay G. Pseudo-second order model for sorption processes. *Process Biochemistry*. 1999;34:451-465.
16. E. Bulut M, et al. Adsorption of malachite green onto bentonite: equilibrium and kinetic studies and process design, *Micropor. Mesopor. Mater*. 2008;115:234–246.