

Manganese Removal from Aqueous Solution by Steel Slag: Kinetic and Equilibrium Studies

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ABSTRACT

Batch experiments were conducted to evaluate the ability of steel slag in removing manganese from aqueous solution. Several variables had been setup to evaluate the performance of steel slag to remove manganese from aqueous solution in different experimental condition. The variables include contact time, size, dosage, pH and initial concentration of manganese. The equilibrium contact time was achieved at 10 hours. The small size of adsorbent has the higher removal of manganese from aqueous solution compared to the large size. 1 g of adsorbent of dosage is considered enough to remove heavy metal from aqueous solution. The optimum pH for manganese adsorption onto steel slag was 6. Higher initial concentration leads to the decrease in percentage removal of Mn from solution, but increase in adsorption capacity. The Langmuir isotherm models fit well with data of Mn adsorption on steel slag compared to Freundlich isotherm model. Kinetic test using several models indicate that data obtained fit well with the pseudo second order model. Steel slag are capable to remove to remove high percentage of Mn from aqueous solution (>95%) thus suggesting that steel slag has the potential to be used in real application.

Keywords: Batch Experiment, Adsorption, Steel Slag, Manganese, Isotherm Model, Kinetic Test

I. INTRODUCTION

Water from industry activity has been a source of concern because of its contamination by toxic metals and other substance that require treatment before discharge. Such treatment must be carried out using operations and processes that aim to reduce the contamination concentration to level required by environmental regulation or the authorities. Once discharge to the stream without proper treatment, questions will arise whether this water is safe for potable water usage and aquatic consumption or not safe for both. Manganese is common toxic metal that found in the effluents of many industries, as well as in mine waters, either neutral or in acid mine drainage (Silva et al. 2012). The toxicity of Mn is related to kidney, lung and intestinal damage and its compound may reasonably be anticipated to be carcinogens (Dal Bosco et al. 2006). Generally, it is absorbed by the human body by oral or respiratory via and in high

amounts, can cause irreversible damages to the nervous system and other pathologies as pneumonia, circulatory collapse, edema of the respiratory tract, among others (Crossgrove and Zheng 2004). The most common health problems in workers exposed to high levels of manganese involve the nerve system. These health effects include behavioral changes and other nerve system effects, which include movements that may become slow and clumsy.

Current method for the removal of heavy metals from water industry includes precipitation, ion-exchange, reverse osmosis, solvent extraction, flocculation and membrane separation (Kwon et al. 2010). Oxidation and precipitation is the most common method to remove Mn(II). Such method is based on the Mn (II) oxidation to its insoluble manganese dioxide (Roccaro et al. 2006). Adsorption is one of the most widely applied techniques for pollutant removal from contaminated media (Qiu et al. 2008). Steel slag is

solid waste material which is by product of steel making industry. The reported annual global steel slag production is fifty millions ton and dumping it off is gradually becoming a major environmental issue (Yusuf et al. 2014). For this study, steel slag was chosen as low cost adsorbent. The main objective of this research was to study the ability of steel slag to remove manganese under different experimental conditions. These different experimental approaches include effect of contact time, size of adsorbent, dosage, pH and initial concentration of manganese. The adsorption isotherm and kinetic aspect also have been investigated to provide greater understanding of its performance.. The purpose of this document is to provide you with some guidelines. You are, however, encouraged to consult additional resources that assist you in writing a professional technical paper.

II. METHODS AND MATERIAL

A. Preparation and characterization of adsorbent

Steel slag from this study was provided by Mega Steel Sdn Bhd, one of the leading companies for steel production in Malaysia. The steel slag was washed with distilled water to remove any debris and dried at 105°C for period of 24 hours in oven. The steel slag was then crushed and sieved into the sizes of 0.5mm, 1mm, 1.5 mm and 2 mm. The physical surface characteristics of steel slag (specific surface area and pore size) were determined using BET (Brunauer-Emmette-Teller) and BJH (Barrett-Joyner-Halenda) pore size distribution analysis. Scanning electron microscopy (SEM) along with EDX analyzer was used to obtain the morphological structure of steel slag and also the elemental composition of steel slag before and after adsorption.

B. Chemical and reagent

All the chemical and reagents used in this work were analytical grade (Sigma-Aldrich, Bendosen). Stock solution of Mn with concentration of 1000 mg/L was prepared by dissolving an appropriate amount of $MnSO_4 \cdot H_2O$ (manganese (II) sulfate-1-hydrate) with deionized water (Milipore Corp, USA). The stock solution further diluted with deionized water to obtain desired concentration of Mn used in this study. 0.1 M NaOH and 0.1 M HNO_3 were used to adjust the desired pH throughout the experiments.

C. Batch experiments

Several batch experiments with variation of variables were conducted in this study to assess the performance of Mn adsorption into steel slag. Orbital shaker with agitation speed of 200 rpm were used throughout whole experiment to ensure homogenous mixing. The experiments were carried out at maintained temperature between 24-25°C. During the experiment, all the solutions were tightly cap-covered to prevent any circumstances that might occur such as contamination and spillage. The effect of equilibrium contact time, size, dosage, pH and initial concentration of were studied in this experiment. The first experiment was to analyze the effect of adsorbent equilibrium contact time. 1 g of adsorbent with size of 1mm was added into 30 mL of Mn solution at concentration of 30 mg/L with a required interval time of 24h.

Second experiment aim to determine the effect of adsorbent size of adsorbent. Various size of adsorbent 0.5mm, 1mm, 1.5mm, 2.0mm were added into 30 mL Mn solution at concentration of 30mg/L. Third experiment was to look into the effect of adsorbent dosage. 0.1, 0.5, 0.8, 1.0, 1.2, 1.8 and 2.0g of adsorbent were added into 30 mL Mn solution at concentration of 30 mg/L. Fourth experiment was to assess the performance of adsorbent at various pH conditions. Using 0.1 M NaOH and 0.1 M HNO_3 , the pH of Mn solutions were adjusted from 3.0 to 8.0. Fifth experiment was to study the effect of initial Mn solution. 5, 10, 30, 50 and 100 mg/L of Mn solution were used in this experiment. All solution samples were filtered using 0.45µm nylon membrane filter and kept at 4°C before analysis. The Mn concentration was analyzed using atomic absorption spectrophotometer (AAS). The whole batch experiments were conducted in duplicate to ensure the findings were precise and consistent.

D. Removal efficiency and adsorption capacity

Removal efficiency of adsorbent is calculated at time (qt) and also at equilibrium (qe).

The calculation of removal efficiency is calculated as:

Removal percentage (%):

$$\frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$\frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

The amount of adsorbate adsorbed per unit mass of adsorbent, is calculated as:

$$\frac{C_0 - C_t}{m} \times V \quad (3)$$

$$\frac{C_0 - C_e}{m} \times V \quad (4)$$

C_0 and C_e are the initial and final Mn concentrations at equilibrium time (mg/L). C_t represent Mn concentration of contact time (mg/L). V represent the volume of working solution (L) and m (g) is the mass of the adsorbent used.

E. Adsorption Isotherms

Langmuir and Freundlich isotherm models were used in this study to analyze equilibrium data obtain from the removal of Mn. The assumptions made in derivation of the Langmuir model are the adsorbed layer is made up of single layer of molecules with adsorption can only occur at a finite (fixed) number of definite localized sites, that are identical and equivalent, with no lateral interaction (Vijayaraghavan *et al.* 2006). The Langmuir equation is given as follow:

$$\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{C_e}{q_m} \quad (5)$$

b and q_m are Langmuir constants, which relate to the rate of adsorption (L/mg) and adsorption capacity (mg/g). Langmuir constant (b and q_m) can be determined from the slope and intercept from linear graph of C_e/q_e versus C_e . The effect of Langmuir isotherm whether favorable or not can be determined by the following equation:

$$R_L = \frac{1}{1 + b C_0} \quad (6)$$

Where b is Langmuir constant and C_0 represents initial concentration of Mn. The R_L value indicates whether the isotherm is suitable for the adsorbent. When $R_L = 1$, it indicates a linear relationship. The $R_L > 1$ value shows that the type of isotherm is not favorable, when $0 < R_L < 1$, the isotherm is likely to be favorable and when $R_L = 0$ it shows an irreversible relationship.

The Freundlich isotherm can be applied for non-ideal adsorption on heterogeneous surface and multilayer adsorption (Foo and Hameed 2014). The Freundlich equation is given as follow:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (7)$$

k and n are Freundlich constant which can be obtained from the slope and intercept from linear graph of $\log q_e$ versus $\log C_e$.

F. Kinetics test

Lagergren's pseudo first order, pseudo second order and intra particle diffusion model were selected in this in this study to describe the kinetic adsorption of manganese onto steel slag as adsorbent. The Lagergren's pseudo first order equation (Ho, 2004) can be expressed as

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (8)$$

Where q_e and q_t are adsorbate concentration at equilibrium and also at time (minute) while k_1 (min^{-1}) is the rate constant of this model. k_1 and q_e can be determined from the slope and also the intercept from the graph of $\log(q_e - q_t)$ versus t (minutes). The pseudo second order equation (Ho and McKay, 1998) can be expressed as

$$\frac{dq}{dt} = k_2 (q_e - q_t)^2 \quad (9)$$

This equation was integrated and can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (10)$$

Where k_2 (g/mg min) is the rate constant of this model. q_e and k_2 (g/mg min) can be determined from the slope and intercept of t/q_t versus t (minutes). Webber and Morris had proposed in intra particle diffusion model in 1962. The intra particle diffusion model can be written as,

$$q_t = k_i t^{1/2} + C \quad (11)$$

Where k_i is the intra particle diffusion rate constant ($\text{mg/g min}^{1/2}$). For the intercept C , McKay *et al.* stated that the intercepts are proportional to the extent of the boundary layer thickness that is, the larger the intercept, the greater the boundary layer effect. The k_i can be determined from the slope of q_t (mg/g) versus $t^{1/2}$ ($\text{min}^{0.5}$) graph.

III. RESULTS AND DISCUSSION

A. Characterization of steel slag

The specific surface area and pore size distribution of steel slag were derived from BET analysis and BJH pore size distribution analysis method. The results were obtained from N_2 adsorption/desorption isotherm

at 77 K. The result from multi point BET analysis and BJH pore size distribution analysis were tabulated in table 1:

TABLE I
Surface data of steel slag

Parameters	Value
BET surface area, m ² /g	30.268
Pore volume, cc/g	0.028
Pore Radius, Å	15.364

Scanning Electron Microscopy (SEM) revealed the surface image of steel as shown in figure 1. The images illustrates that there are pores that exist in surface of steel slag thus confirm its porosity. Particle size, pore diameter, specific surface area of considered as a main factors that affecting the adsorption capacity of adsorbent (Wang *et al.* 2010). EDX analysis also conducted to determine the major element that present in steel slag before and after adsorption (Table 2). The presence of high amount of aluminosilicate compound (aluminium, silicon, oxygen) in the presence of calcium oxide could facilitate in the provision of sufficient negatively charged sites for cation exchange reactions to take place with heavy metal present in aqueous solution (Aziz *et al.* 2014). Moreover, the present of aluminosilicate is responsible for the removal of metal ions from aqueous solution (Das *et al.* 2006). From the result, Mn is present after the adsorption occurs. Some other metals present before adsorption also gain some loss after adsorption give suggestion that ion exchange is potential mechanism responsible for the adsorption of Mn onto the steel slag.

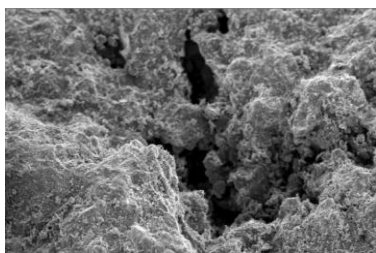


Figure 1: SEM images of steel slag

TABLE II

Element present in steel slag before and after adsorption

Element	Before (%)	After (%)
N	8.09	5.23
O	33.32	26.97
Mg	3.10	1.77
Al	3.66	1.22
Si	12.53	5.61
Ca	22.09	11.63
Fe	17.21	36.91
Mn	-	10.67
Total	100	100

B. Effect of contact time

The effect of contact time was assessed to determine the optimum time for Mn adsorption onto steel slag. The time was set at 24 hour and reading was taken for every 2 hour. Figure 4 shows the effect of contact time and adsorption capacity of steel slag. For the first two hours, the removal percentage shows rapid increase and then slowly increases until it reached optimum time at 10 hours. Higher removal percentage at the beginning of experiment is caused by the large surface area of steel slag that available for the sorption of the metals (Yusuf *et al.* 2013). Therefore, there are available abundant free binding sites are that lead to the higher removal at early experiment (Aziz *et al.* 2014).

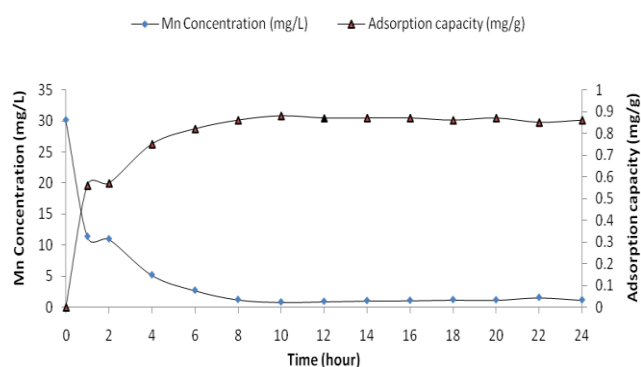


Figure 2: Effect of contact time on adsorption of Mn onto steel slag (Initial Mn concentration: 30 mg/L, dosage: 1 g, size: 1 mm, initial pH: 5.7)

After 10 hours, the removal percentage shows no significance difference of removal. The graph starts to

slightly decrease an increase in inconsistent way but still shows high removal rate (> 95%). The removal percentage within 24 hour contact time can be referred from figure 2. The concentration of Mn was lowered from 30 mg/L to 0.78 mg/L after 10 hours contact time, achieving 97.4% removal of Mn from solution. The equilibrium time was noted at 10 hours which is considered as optimum time enough to remove Mn from solution. Therefore, the contact time was set at 10 hours for the next experiment.

C. Effect of size

Generally, small sizes have the large surface area. Figure 3 shows the concentrations of Mn reduce from 30 mg/L to 0.35 mg/L when the size of adsorbent is 0.5 mm. Figure 6 shows the increasing of removal percentage from 84.3 % to 98.8% when the sizes of adsorbent tend to decrease from 0.5 to 30 mm. Larger particle size has a longer diffusion path, while smaller particle has a shorter diffusion path, allowing adsorbate to penetrate quickly and deeply into the adsorbent particles, resulting to higher rate of adsorption (Yusuf *et al.* 2013). Smaller particles sizes reduce internal diffusional and mass transfer limitation to penetration of the adsorbate inside the adsorbent.

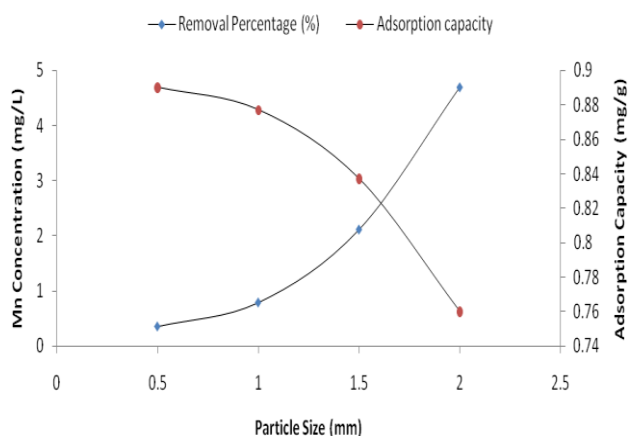


Figure 3: Effect of particle size (Initial Mn concentration: 30 mg/L, contact time: 10 hours, dosage: 1 g, initial pH: 5.7)

D. Effect of adsorbent dosage

Adsorbent dosage does have a great influence towards the rate of adsorption. Figure 4 show the percentage removal of manganese using different adsorbent dosage ranging from 0.1 g until 2.0 g. There is rapid

removal percentage when using adsorbent used ranging from 0.1 until 1.0 g. The percentage removal was increased from 12.37% to 97.37%. After exceed that range, the percentage removal of manganese start to become constant. The initial rapid removal might be due to the increase in adsorbent surface and therefore results in more active site for Mn adsorption (Kumar and Kirthika 2009). Increase in availability of surface active sites resulting from the increased dose of adsorbent, especially at higher doses (Emmanuel and Rao 2008). After 1.0g, the removal percentage starts to become constant or no significant increase due to saturation level attained during adsorption process (Ragheb 2012). Therefore the dosage of 1 g was chosen for the next experiment. The equilibrium achieves between Mn concentration and solution also results in this constant removal percentage. Based on figure 4 also, the adsorption capacity of the adsorbent decrease when the adsorbent dosage start to increase. Many factors can contribute to this adsorbent concentration effect. The most important factor is that adsorption sites remain unsaturated during the adsorption of the adsorption reaction. This decrease in adsorption capacity with the increase in adsorbent dosage is mainly because of non-saturation of the adsorption sites during the adsorption process (Han *et al.* 2006)

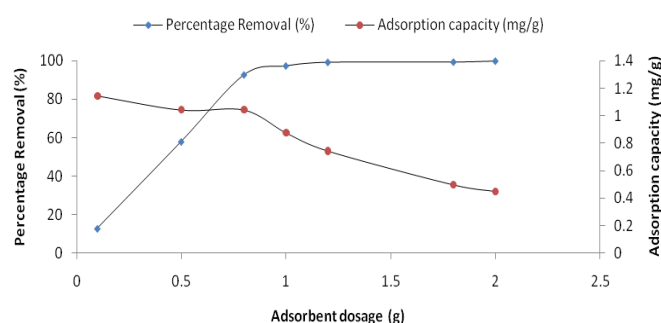


Figure 4: Effect of dosage (Initial Mn concentration: 30 mg/L, contact time: 10 hours, size: 1 mm, initial pH: 5.7)

E. Effect of pH

The pH of the metal ion solution is an important parameter for adsorption of heavy metal. The adsorption of heavy metal depends on the pH of aqueous solution (Omri and Benzina 2012). This is because hydrogen ion competing with positively charged metal ion on the site of adsorbent (Lohani *et al.*

2008). To examine the effect of pH on Mn removal efficiency, the pH was varied from 3.0 to 8.0 and changed manually using 0.1 M HNO₃ and 0.1 M NaOH. As shown in Figure 5, the percentage removal of manganese at pH conditions 3.0-8.0 is relatively high which exceeds 93% of percentage removal. The graph also shows that at low pH condition (pH 3), the removal of heavy metal is low compared to others pH condition. After pH 3, the removal percentage slowly increase until it reached constant range between ranges of initial pH (5.7) until pH of 8. The best results were obtained at pH 6. It was observed that the value of pH solution after 10 hours contact time increase between range of 8-9. This may due from the result of CaOH formation from CaO that present in steel slag. Similar result was obtained from the study by Aziz et al. that using POFA as adsorbent to remove selected heavy metal. The POFA also contain CaO which results in hydroxide ion (-OH) liberation thus increase the solution pH during adsorption process. The absence of adsorption at lower pH is apparently due to higher concentration of hydrogen ion present in the reaction solutions, which can compete with metal ion for the adsorption sites. With an increase in pH, the competing effect of hydrogen ions decreased and the positively charged of metal ion hook up the free binding sites. Hence, the metal ion uptake was increased on the surfaces of the adsorbent with the increase in pH (Duan and Su 2014). When the pH is reduced to an acidic condition, the hydrogen ions also increase thus increase the competition between metal ions to be adsorbed on binding sites of adsorbent (Kour et al. 2012).

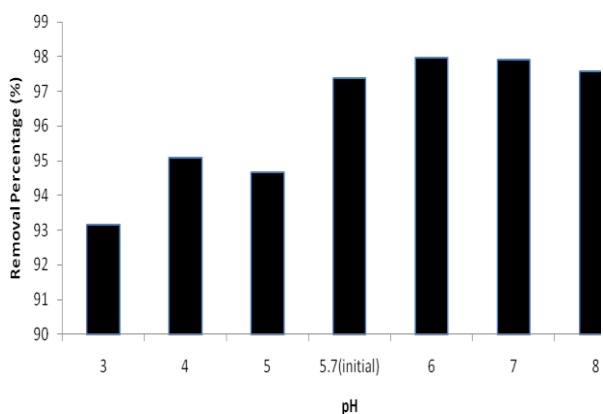


Figure 5: Effect of different pH (Initial Mn concentration: 30 mg/L, contact time: 10 hours, size: 1 mm, dosage: 1g)

F. Effect of initial concentration

The next experiment was to assess the effect of different initial concentrations towards removal efficiencies and also adsorption capacity. The figure 6 shows the removal percentages and adsorption capacity of Mn onto steel slag. The Mn removal decrease when initial concentration of Mn increase, while the adsorption capacity of Mn onto steel slag increases with the increase of initial Mn concentration. The metal ions are dependent on initial concentration. At low initial concentration the surface area and the availability of adsorption binding sites are relatively high and the metal ions is easily adsorbed and removed. Meanwhile, the total available active sites are limit in higher initial concentration thus results in decrease of metal ions uptake (Wang et al. 2010). From the results, the highest initial concentration, 100 mg/L had the lowest removal percentage which is 38.82%. The adsorption capacity increase with the increase of initial concentration due to the driving force that initiated by initial concentration to reduce the mass transfer resistance, thus results in higher adsorption capacity (Almasi et al.2012). The data obtained from this experiment will be use to determine the Mn adsorption isotherms in the next experiment.

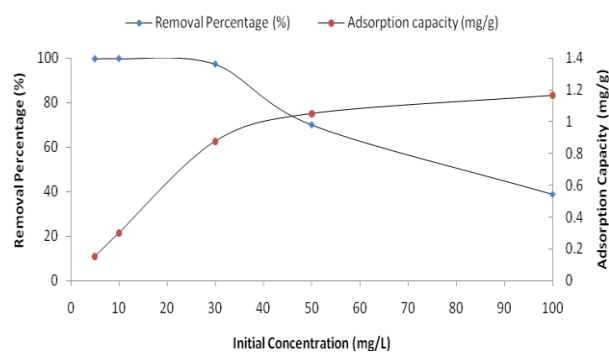


Figure 6: Effect of different initial concentrations (contact time: 10 hours, pH: 6 size: 1 mm, dosage: 1g)

G. Adsorption Isotherm

The equilibrium data were analyzed using Langmuir and Freundlich isotherm model, two isotherm models that generally use to describe adsorption isotherm of adsorbent. Other than that, adsorption isotherm can be described as a model that illustrates the distribution of the adsorbate species among adsorbent and liquid (Lu, Liu, and Rao 2008). Adsorption data for Mn removal

have been correlated with this isotherm model and figure 7 and 8 represent this relation. Table 3 represent the Langmuir and Freundlich constant that obtain from the slope and intercept of both graphs. Based on the figure 10, Langmuir model shows coefficient of determination ($R^2= 0.9993$) for steel slag while Freundlich model in figure 11 shows ($R^2= 0.9395$). Langmuir model fits the data well compared to the Freundlich model. This may be due to homogenous distribution of active sites on steel slag surface since Langmuir equation makes assumption that the surface is homogenous (Foo and Hameed 2014). This concludes that Langmuir model is best model to explain the adsorption of Mn onto steel slag surface compare to Freundlich isotherm model. Moreover, figure 12 shows the graph of R_L versus initial concentration of Mn. The R_L value indicates whether the isotherm is suitable for the adsorbent. When $R_L = 1$, it indicates a linear relationship. The $R_L > 1$ value shows that the type of isotherm is not favorable, when $0 < RL < 1$, the isotherm is likely to be favorable and when $R_L = 0$ it shows an irreversible relationship. The graph shows that the value of RL fell within range $0 < R_L < 1$ which means that the adsorption of Mn onto steel slag is assume as favorable. Table 4 shows the value of R_L and level of favorable isotherm

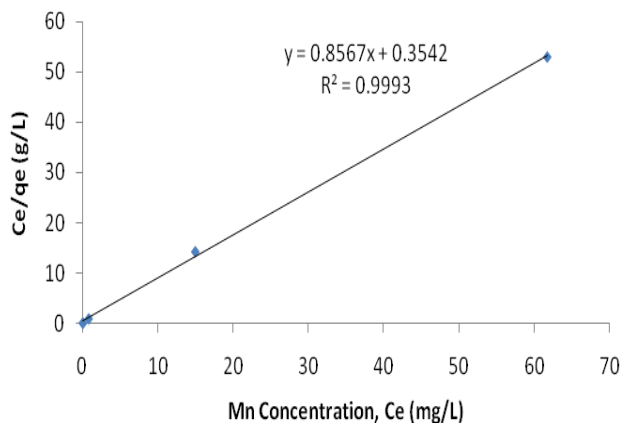


Figure 7: Langmuir plot for Mn adsorption onto steel slag

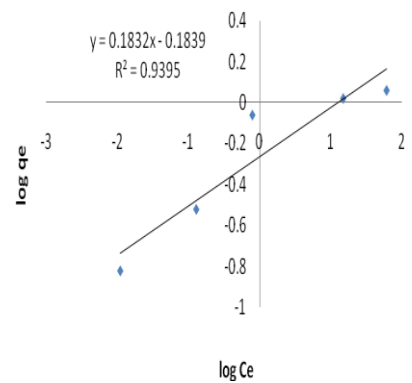


Figure 8: Freundlich plot for Mn adsorption onto steel slag

TABLE 3

Isotherm model constant of Langmuir and Freundlich isotherm model

Isotherm model	Parameters	Values
Langmuir isotherm	qm (mg/g)	1.1673
	b (L/mg)	2.4186
	R ²	0.993
Freundlich isotherm	k	0.6547
	1/n	0.1832
	R ²	0.9395

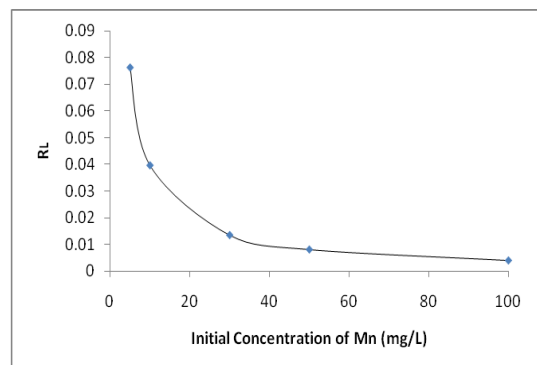


Figure 9: Value of RL against initial concentration of Mn

TABLE 4

R_L and Level of favorable isotherm

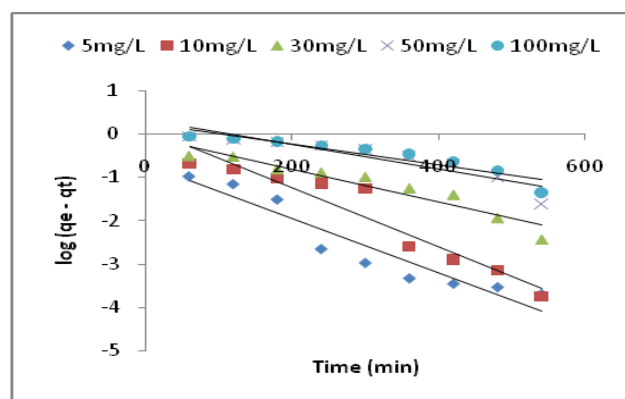
Value	Indicator
$(0 < R_L < 1)$	Favorable
$(R_L > 1)$	Unfavorable
$(R_L = 1)$	Linear
$(R_L = 0)$	Irreversible

H. Kinetic Test

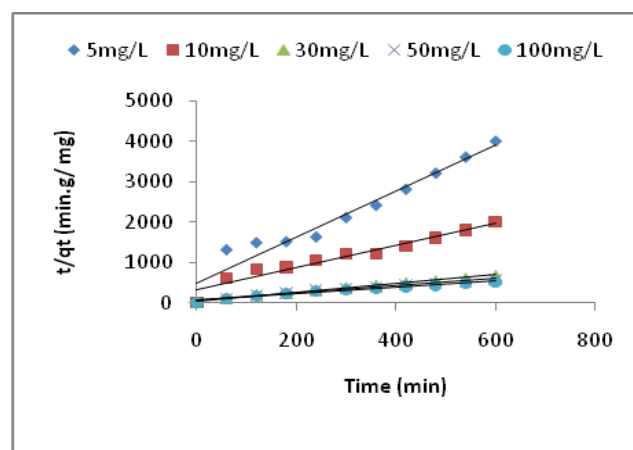
Figure 10 shows the linear form of the kinetics model that had been chosen to describe the kinetic adsorption of manganese onto steel slag. Table 5 shows the rate constant and other parameter for each kinetic model. The theoretical q_e values obtained from the pseudo first order and pseudo second order linear were compared with experimental q_e value and there is large difference for pseudo first order compared to pseudo second order. The correlation coefficient R^2 for pseudo second order at different initial concentration shows better agreement (≥ 0.9436) compared to the correlation coefficient R^2 (≥ 0.8702) for pseudo first order at different initial concentration which indicate that the adsorption of manganese onto steel slag fit well with the pseudo second order model. The pseudo second order model are based on the assumption that the rate limiting step may be chemical adsorption involving valent forces through sharing or the exchange of electrons between adsorbent and adsorbate (Ho and Mackay, 2000). One of the advantages of the pseudo second order equation for estimating q_e values is its small sensitivity to the influence of random experimental errors (Aly *et al.* 2014).

The intra particle diffusion model are also presented in this study to analyze the adsorption kinetic data due to the result from pseudo second order model that are insufficient to predict diffusion mechanism (Akar *et al.* 2008). Generally, the kinetic process of adsorption is always controlled by liquid film diffusion or intra particle diffusion in which one of the process should be the rate limiting step (Qiu *et al.* 2008). Intra particle diffusion plots may represent multi-linearity, which considered two or three steps are involved in this adsorption process. In this form, the external surface adsorption or instantaneous adsorption occurs in the first step; the second step is the gradual adsorption step, where intra particle diffusion is controlled; and the third step where the solute moves slowly from large pores to micro-pores causing a slow adsorption rate (Wu, Tseng and Juang 2009). A plot of q_e vs $t^{1/2}$ would yield a straight line with a slope of k_i when the intra particle diffusion is a rate-limiting step (Qiu *et al.* 2008). If the graph passes through origin, the intra particle diffusion process would not only be involved in adsorption process, but would be a rate limiting step

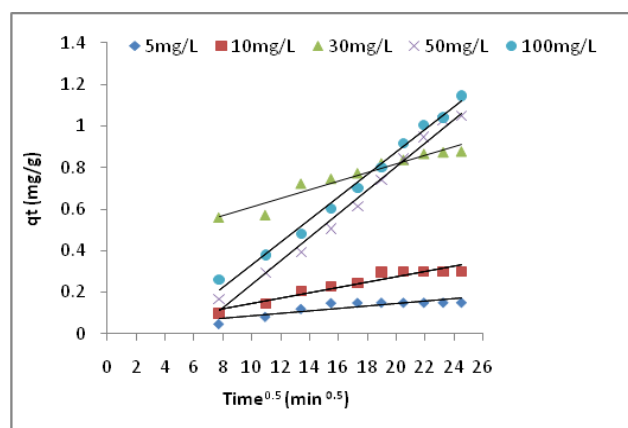
(Aly *et al.* 2014). Based on figure 10, the linear form obtained from a plot of q_e vs $t^{1/2}$ did not pass through origin thus indicate that the intra particle diffusion mechanism is not the sole rate determining step.



a) Lagergren's pseudo first order



b) Pseudo second order



c) Intraparticle diffusion

Figure 10: Kinetic model for adsorption of manganese onto steel slag a) Pseudo first order b) Pseudo second order c) Intra particle diffusion

TABLE 5

Initial concentration (mg/L)	Experimental q_e (mg/g)	Pseudo 1 st order			Pseudo 2 nd order			Intraparticle diffusion model	
		k_1 (min ⁻¹)	q_e (mg/g)	R^2	k_2 (g/mg min)	q_e (mg/g)	R^2	k_i (mg/g min ^{1/2})	R^2
5	0.1499	0.0143	0.1927	0.9045	0.0694	0.1748	0.9517	0.0058	0.7478
10	0.2997	0.0157	1.2868	0.9187	0.0244	0.3606	0.9436	0.0128	0.9198
30	0.8764	0.0085	0.8652	0.9091	0.025	0.9261	0.9907	0.0207	0.9383
50	1.0508	0.0064	2.0403	0.8361	0.0135	1.109	0.9743	0.0566	0.9874
100	1.146	0.0056	1.7227	0.8702	0.0112	1.2323	0.9724	0.0544	0.9909

The rate constant and other parameter for each kinetic model

IV. CONCLUSION

The results from 24 hours contact time shows rapid removal percentage at first 2 hours and optimum time was achieved at 10 hours of contact time, with the removal percentage of 97.4 %. After 10 hours, the removal percentage shows no significance difference of removal. Therefore, the equilibrium time is considered to be 10 hours which is enough to remove Mn from solution It was found that the size of adsorbent also influences the removal percentage of Mn from solution. From the experiment, the small size adsorbent shows higher percentage removal compared to the large size. Higher adsorbent dosage leads to increase rate of adsorption and starts to become constant after reaching equilibrium amount. Higher adsorbent dosage also leads to the decrease of adsorption capacity. Even in low pH (e.g. pH 3 and 4), the steel slag still had ability to remove Mn from solution above 93%. The removal percentages of Mn from solution reached constant removal at pH ranged between 5.7 - 8. The best results were obtained at pH 6. The final pH of solution ranged between pH 8 and 9. Higher initial concentration (e.g. 100 mg/L) leads to the decrease in percentage removal of Mn from solution, but increase in adsorption capacity. The Langmuir isotherm models fit well with data of Mn adsorption on steel slag compared to the Freundlich isotherm model. Although the maximum adsorption capacity of manganese onto steel slag is not as high

compared to other previous studies, steel slag is still capable to remove high percentage of Mn from aqueous solution (>95%) thus showing potential for real application.

V. REFERENCES

- [1] Akar, T., Ozscan, A.S., Tunali, S., and Ozscan, A. (2008). "Biosorption of a textile dye (Acid Blue 40) by cone biomass of Thuja orientalis : Estimation of equilibrium, thermodynamic and kinetic parameters," *Bioresources Technology* 99(8), 3057-3065.
- [2] Almasi, A., Omidi, M., Khodadadian, M., Khamutian, R., and Gholivand, M. B. (2012). "Lead(II) and cadmium(II) removal from aqueous solution using processed walnut shell: kinetic and equilibrium study," *Toxicological & Environmental Chemistry* 94 (4), 660-671.
- [3] Aly, Z., Graulet, A., Scales, N., and Hanley, T. (2014). "Removal of aluminium from aqueous solution using PAN-based adsorbent: characterization, kinetics, equilibrium and thermodynamics studies," *Environmental Science and Pollution Research* 21(5), 3972-3986.
- [4] Aziz, A. S., Manaf, L. A., Man, H. C., and Kumar, N. S. (2014). "Equilibrium studies and dynamic behavior of cadmium adsorption by palm oil boiler mill fly ash (POFA) as a natural low-cost adsorbent," *Desalination and Water Treatment* , 1-13.
- [5] Aziz, A. S., Manaf, L. A., Man, H. C., and Kumar, N. S. (2014). "Kinetic modeling and isotherm studies for copper (II) adsorption onto palm oil boiler mill fly ash (POFA) as a natural low-cost adsorbent," *BioResources* 9 (1), 336-356.
- [6] Beh, C. L., Chuah, L., Choong, T. S., Kamarudzaman, M. Z., and Abdan, K. A. (2010). "Adsorption study of

- electric arc furnace slag for the removal of manganese from solution," *American Journal of Applied Sciences* 7 (4), 442-446.
- [7] Crossgrove, J., and Zheng, W. (2004). "Manganese toxicity upon overexposure," *NMR in Biomedicine* 17(8), 544-553.
- [8] Dal Bosco, S. M., Jimenez, R. S., Vignado, C., Fontana, J., Geraldo, B., and Figueiredo, F. C.(2006). "Removal of Mn(II) and Cd(II) from wastewaters by natural and modified clays," *Adsorption* 12 (2), 133-146.
- [9] Das, B., Prakash, S., Reddy, P. S., and Misra, V. N. (2007). "An overview of utilization of slag and sludge from steel industries," *Resources, Conservation and Recycling* 50 (1), 40-57.
- [10] Duan, J., and Su, B. (2014). "Removal characteristics of Cd(II) from acidic aqueous solution by modified steel-making slag," *Chemical Engineering Journal* 246, 160-167.
- [11] Emmanuel, K. A., and Rao, A. V. (2008). "Adsorption of Mn (II) from aqueous solutions using pithacelobium dulce carbon," *Rasayan Journal of Chemistry* 1 (4), 840-852.
- [12] Foo, K. Y., and Hameed, B. H. (2010). "Insights into the modeling of adsorption isotherm systems," *Chemical Engineering Journal* 156 (1), 2-10.
- [13] Han, R., Zou, W., Zhang, Z., Shi, J., and Yang, J. (2006). "Removal of copper(II) and lead(II) from aqueous solution by manganese oxide coated sand: I. Characterization and kinetic study," *Journal of Hazardous Materials* 137 (1), 384-395.
- [14] Ho, Y.S., and McKay, G. (1998). "Sorption of dye from aqueous solution by peat," *Chemical Engineering Journal* 70 (2), 115-124.
- [15] Ho, Y.S., and McKay, G. (2000). "The kinetics of sorption of divalent metal ions onto sphagnum moss peat," *Water Research* 34 (3), 735-742.
- [16] Ho, Y.S. (2004). "Citation review of Lagergren's kinetic rate equation on adsorption reactions," *Scientometrics* 59 (1), 171-177.
- [17] Kour, J., Homagai, P. L., Pokhrel, M. R., and Ghimire, K. N. (2012). "Adsorptive Separation of Metal Ions with Surface Modified *Desmostachya bipinnata*," *Nepal Journal of Science and Technology* 13 (1), 101-106.
- [18] Kumar, P. S., and Kirthika, K. (2009). "Equilibrium and kinetics study of adsorption of nickel from aqueous solution onto bael tree leaf powder," *Journal of Engineering Science and Technology* 4 (4), 351-363.
- [19] Kwon, J. S., Yun, S. T., Lee, J.H., Kim, S. O., and Jo, H. Y. (2010). "Removal of divalent heavy metals (Cd, Cu, Pb, and Zn) and arsenic(III) from aqueous solutions using scoria: Kinetics and equilibria of sorption," *Journal of Hazardous Materials* 174 (1-3), 307-313.
- [20] Lohani, M. B., Singh, A., Rupainwarb, D. C., & Dharc, D. N. (2008) . "Studies on efficiency of guava (*Psidium guajava*) bark as bioadsorbent for removal of Hg (II) from aqueous solutions," *Journal of Hazardous Materials* 159 (2-3), 626-629.
- [21] Lu, C., Liu, C., and Rao, G. P. (2008). "Comparisons of sorbent cost for the removal of Ni²⁺ from aqueous solution by carbon nanotubes and granular activated carbon," *Journal of Hazardous Materials* 151 (1), 239-246.
- [22] Omri, A., and Benzina, M. (2012). "Removal of manganese(II) ions from aqueous solutions by adsorption on activated carbon derived a new precursor: *Ziziphus spina-christi* seeds," *Alexandria Engineering Journal* 51 (4), 343-350.
- [23] Qiu, H., Pan, B.C., Zhang, Q.J., Zhang, W.M., and Zhang, Q.X. (2008). "Critical review in adsorption kinetic models," *Journal of Zhejiang University SCIENCE A* 10(5), 716-724.
- [24] Ragheb, S. M. (2013). "Phosphate removal from aqueous solution using slag and fly ash," *HBRC Journal* 9 (3), 270-275.
- [25] Roccaro, P., Barone, C., Mancini, C., and Vagliasindi, F. G. (2007). "Removal of manganese from water supplies intended for human consumption: a case study," *Desalination* 210 (1-3), 205-214.
- [26] Silva, A. M., Cunha, E. C., Silva, F. D., and Leao, V. A. (2012). "Treatment of high-manganese mine water with limestone and sodium carbonate," *Journal of Cleaner Production* 29-30, 11-19.
- [27] Vijayaraghavan, K., Padmesh, T. V., Palanivelu, K., and Velan, M. (2006). "Biosorption of nickel(II) ions onto *Sargassum wightii*: Application of two-parameter and three-parameter isotherm models," *Journal of Hazardous Materials* 133 (1-3), 304-308.
- [28] Wang, F. Y., Wang, H., and Ma, J. W. (2010). "Adsorption of cadmium (II) ions from aqueous solution by a new low-cost adsorbent—Bamboo charcoal," *Journal of Hazardous Materials* 177 (1-3), 300-306.
- [29] Weber, W. J., Morris, J.C. (1962). "Advances in water pollution research : removal of biologically resistant pollutant from waste water by adsorption", in : *Proceedings of 1st International conference on water pollution symposium*, vol. 2, Pergamon Press, Oxford, 231-236.
- [30] Wu, F.C., Tseng, R.L., and Juang, R.S. (2009). "Initial behavior of intraparticle diffusion model used in the description of adsorption kinetics," *Chemical Engineering Journal* 153 (1-3),
- [31] Yusuf, M., Chuah, L. A., Mohammed, M. A., and Shitu, A. (2013). "Investigations of Nickel (II) removal from Aqueous Effluents using Electric Arc Furnace Slag ," *Research Journal of Chemical Sciences* 3 (12), 29-37.
- [32] Yusuf, M., Chuah, L., Khan, M. A., and Choong, T. S. (2014). "Adsorption of Nickel on Electric Arc Furnace Slag: Batch and Column Studies," *Separation Science and Technology* 49 (3), 388-397.