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Kinetic and isotherm studies for nickel (II) removal using novel mesoparticle graphene sand composite synthesised from sand and arenga palm sugar

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Abstract. Nickel (II) is one of the most toxic contaminants recognised as a carcinogenic and mutagenic agent which needs complete removal from wastewater before disposal. In the present study, a novel adsorbent called mesoparticle graphene sand composite (MGSC_{aps}) was synthesised from arenga palm sugar and sand by using a green, simple, low cost and efficient methodology. Subsequently, this composite was characterised and identified using field emission scanning electron microscope (FESEM), x-ray diffraction (XRD) and elemental mapping (EM). The adsorption process was investigated and optimised under the experimental parameters such as pH, contact time and bed depth. The results showed that the interaction between nickel (II) and MGSC_{aps} was not ion to ion interaction hence removal of Ni (II) can be applied at any pH. The results were also exhibited the higher contact time and bed depth, the higher removal percentage of nickel (II) occurred. Adsorption kinetic data were modelled using Pseudo-first-order and Pseudo-second-order equation models. The experimental results indicated pseudo-second-order kinetic equation was most suitable to describe the experimental adsorption kinetics data with maximum capacity of 40% nickel (II) removal for the first hour. The equilibrium adsorption data was fitted with Langmuir, and Freundlich isotherms equations. The data suggested that the most fitted equation model is the Freundlich with correlation $R^2=0.9974$. Based on the obtained results, it can be stated that the adsorption method using MGSC_{aps} is an efficient, facile and reliable method for the removal of nickel (II) from waste water.

1. Introduction

Waste water mainly contains a variety of organic and inorganic compounds of anthropogenics and natural origins, sediments, radioactive materials effluents and heavy metals [1], [2]. These pollutants; especially heavy metal are also contributed to the toxicity, bioaccumulation, non-biodegradable nature and contribute to the larger scale of extraction of metal release of hazardous wastes. Therefore, it is necessary to find a way to treat [3] and purify [4] wastewater contained with toxic metal ions to produce cleaner waste before releasing it to the environment. One of industrial wastewater may contain a large number of heavy metals in it. Nickel (II) is a non-biodegradable and toxic ion which present in wastewater. Increasing accumulation of nickel (II) in industrial wastewater has raised attention and concern. The main source of of nickel (II) pollution derived from processes such as galvanization, smelting, mining, dyeing operations, batteries manufacturing and metal finishing [5].



Most of them were discharged into the water sources without a proper treatment. Trace amounts of nickel (II) are beneficial to human organism as an activator of some enzyme systems. However, if it is beyond the scope of normal levels, different types of diseases such as lung cancer, renal enema, skin dermatitis and gastro intestinal disorder will occur. If nickel adsorbed into the body, it severely irritates gastrointestinal tract leads to circulatory shock and renal damage. Hence, the Water Sanitation and Hygiene under World Health Organization established the toxic limits of permissible concentration of nickel (II) and insoluble compounds of 1.0 mg/m^3 , soluble compounds of 0.1 mg/m^3 , nickel carbonyl of $0.05\text{-}0.12 \text{ mg/m}^3$ and nickel sulphide of 1.0 mg/m^3 [6]. The conventional method for removing nickel (II) from industrial wastewater includes the chemical oxidation or reduction, chemical precipitation, ion exchange, membrane separation, filtration, electrochemical treatment and adsorption. These methods require high reagent and energy requirements, and the generation of toxic sludge or wastes products which required disposal or treatment. However, the adsorption technique is one of the most popular and preferred methods to remove heavy metals. Adsorption by using activated carbon is preferred due to its high specific surface area, highly porous character, multiple adsorption, chemical stability and relatively low-cost. Thus recently, there are many researches on the removal of heavy metal ions from waste water effluents. Numerous materials have been used as adsorbents for the removal of nickel (II) processes including activated carbon, silica, ion exchange resins, rock materials, activated slag, agricultural wastes, microbial and plant derived biomass and chitin. Recently, graphene has become the hottest topic among researchers.

Graphene is a single atomic layer of sp^2 -hybridized carbon arranged in a honeycomb structure. Several studies were made in term of heavy metals removal from waste water effluents by using different oxides of composite oxides. There were removal of Cu (II), Co (II), Zn (II), Cr (VI) and Pb (II) previously by using various types of adsorbents. However, it is remain necessary to develop a low cost, easily available, high adsorption capacity material for wastewater treatment to remediate environmental problems. The present research work focuses on exploiting exceptionally high adsorptive potential of graphene and using it for removal of nickel (II) ions from synthetic aqueous solutions. In this research, MGSC_{aps} was produced by using sand and sugar. The performance of MGSC_{aps} in removing nickel (II) from synthetic aqueous solution was investigated throughout the experimental works. MGSC_{aps} was prepared from sugar as it is a highly carbonaceous source [16]. The main objective of the research is to synthesise, characterise and analyse MGSC_{aps} on the effect of pH, contact time and bed depth criteria towards the adsorption capacity in removing nickel (II) from wastewater.

2. Methodology

2.1. Materials

The materials used to synthesis MGSC_{aps} were arenga palm sugar and sand which passed 2 nm sieve. Arenga palm sugar was obtained from arenga pinnata tree which abundantly available regions around the world especially in the tropical such as Malaysia, Indonesia, Thailand, Philippines and Vietnam. In this research, arenga palm sugar was supplied from Pahang, Malaysia. Sand was collected from river located in Pahang, Malaysia.

2.2. Chemicals

For chemicals used in this research, pure metal nickel, concentrated sulphuric acid and concentrated nitric acid were supplied from Permula Chemicals Sdn. Bhd. Distilled water as solvent was used throughout this experimental process.

2.3. Instrumentation for MGSC_{aps} Characterisation

MGSC_{aps} was subjected to several types of testing including FESEM, EM, XRD and Raman Spectroscopy.

2.3.1. Field Emission Scanning Electron Microscope. Field emission scanning electron microscopic (FESEM) was analysed by using FESEM JEOL JSM-6500F equipped with MiniFlex2 counter detector. It was also used fixed monochromator of diffracted beam monochromator.

2.3.2. Elemental Mapping. The growth and distribution of carbon on silica oxide surfaces was recorded by using elemental mapping equipment JEOL JSM-6500F.

2.3.3. X-Ray Diffraction. X-ray diffraction (XRD) was recorded to ascertain crystalline nature of graphene sand composite by using 30 kV; 15 mA x-ray with fixed monochromator at 1.0000 sec scan speed.

2.4. Synthesis Process of $MGSC_{aps}$

The synthesis of $MGSC_{aps}$ followed method mentioned in the literature [7] with a slight modification on the carbon source. 150 g arenga palm sugar was used as carbon source and was diluted in 150 g distilled water. The solution was then mixed with 150 g fine river sand before constantly stirred at 95 °C for 3 hours. The mixture then was put in the silica crucibles and burned in the nitrogen atmosphere furnace. The temperature of the furnace was set from the room temperature to 100 °C in 30 minutes to burn deleterious materials. The temperature was changed to 200 °C in another 30 minutes and was held for 1 hour to melt arenga palm sugar to confirm uniform coating on the sand surfaces. The temperature of the furnace then was ramped to 750 °C in 1 hour and held it for another 3 hours to ensure graphenisation process was completed. $MGSC_{aps}$ then allowed cooling to the room temperature gradually. After cooled, $MGSC_{aps}$ activated by using concentrated sulphuric acid for 30 minutes without disturbance to open pore sites which acted as adsorbent sites. $MGSC_{aps}$ is now ready for adsorption process before filtered as shown in Figure 1.



Figure 1. $MGSC_{aps}$ was successfully synthesised using arenga palm sugar as carbon source

2.5. Preparation of Synthetic Nickel (II) Solution

An amount of 5000 mg/L nickel (II) solution was prepared using 5 g pure nickel metal and dissolved in 20 ml of hot concentrated nitric acid. It was cooled and diluted with double distilled water. The stock solution was further diluted with distilled water before used.

3. Results and Discussion

3.1. $MGSC_{aps}$ Characterisation

3.1.1. Field Emission Scanning Electron Microscope. The morphological of $MGSC_{aps}$ was carried out through FESEM analyses. It was evident that the sand was coated uniformly which confirms the temperature setting for initial burning process was 200 °C successfully melted arenga palm sugar to

form a layer of carbon coating. This is in line with the previous researchers [8] which stated that the melting point of sucrose is approximately 186 °C. The graphenic morphology also was detected at the coating sheet's edges where thin wrinkles were formed as shown in Figure 2. The wrinkled edges of sheets that confirms the production of graphene, even after the formation of the composites, the structure of the composite remained the same where the wrinkles were still present [9].

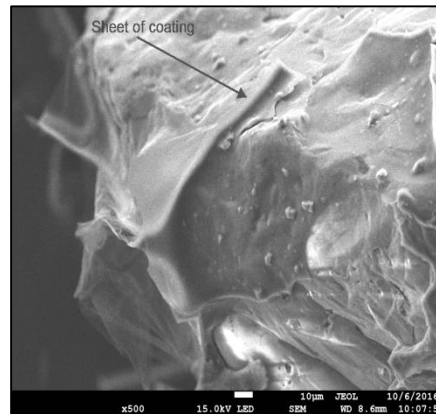


Figure 2. Sheet of coating was formed after arenga palm sugar melted and burned in furnace

3.1.2. Elemental Mapping. Major elements present were carbon, silicon and oxygen as presented in Figure 3. The presence of large carbon feature was originated from the carbonaceous material which was formed from melted arenga palm sugar on sand surface. Previous researchers [10] stated that the elements detected show that the sand was covered by carbon. The other elements; silicon and oxygen were also features in the major elements due to the usage of sand (SiO_2) hence validating the name of this composite in the research, mesoparticle graphene sand composite (MGSC_{aps}).

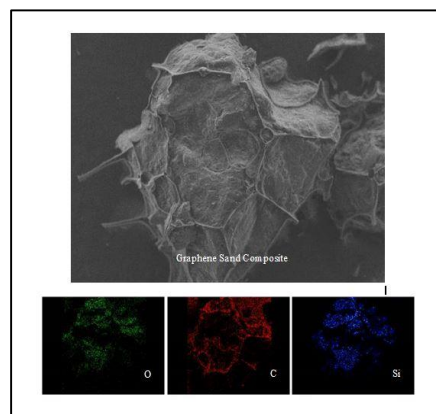


Figure 3. Elemental mapping on MGSC_{aps} surface

3.1.3. X-Ray Diffraction. An XRD analysis was conducted to measure the structure of MGSC_{aps} . The space group of MGSC_{aps} is 166: R-3m with hexagonal in shape whereas the figure of merit is 0.269. These two values validated the phase name of the composite where graphite-3R element was found during the test. The strongest diffraction peak located at 26.652 ° which indicates the formation of the crystalline of the MGSC_{aps} that gives glowing effect to the composite due to the light reflection. The d spacing of pristine MGSC_{aps} is 0.525 nm. The value in this research of d spacing is higher than previous researcher [8]. This is supported by another researcher [9] which stated that the activation process by using concentrated sulphuric acid on the graphene sand composite resulted in the formation of multiple layers which produced higher d spacing. Due to the reason, the MGSC_{aps} structures were exhibited multilayer of graphene structures simultaneously. The all diffraction peaks and

corresponding reflections which at 266.652° (0,0,3), 44.36° (1,0,1) 54.706° (0,0,6) and 77.58° (1,1,0) were showing the basic characteristic of graphene similar to the previous research. Figure 4 presents the result of MGSC_{aps} upon x-ray diffraction test.

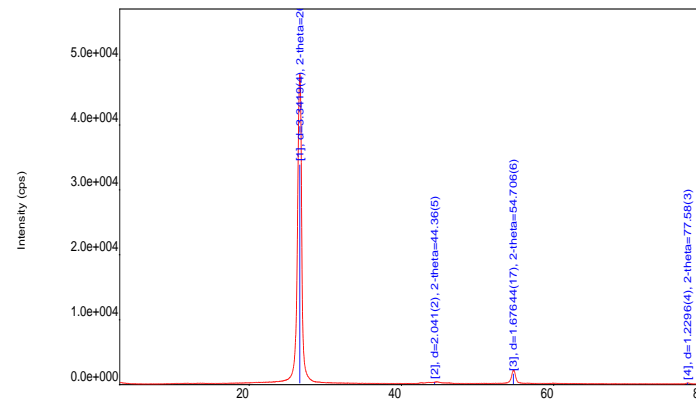


Figure 4. The structure of MGSC_{aps} was determine using x-ray diffraction

3.2. Adsorption Study

The adsorption study is an important stage to determine adsorbency patterns in every different parameter set of MGSC_{aps}. Further discussion presented in subchapters as follows:

3.2.1. Adsorption Kinetic. The adsorption data was fitted to two kinetic models namely Pseudo-first-order and Pseudo-second-order. The interaction of nickel (II) and MGSC_{aps} was investigated as a function of time by using column batches experiment to determine its ability to remove nickel (II) at the maximum capacity. The adsorption capacity, q was showed in the Equation 1.

$$q = [(C_i - C_f)V]/W \quad \text{Equation 1}$$

Where C_i is the initial concentration in mg/L, C_f is the final concentration in mg/L, V is the volume of nickel (II) solution in ml whereas W is the weight of MGSC_{aps} in g, used as adsorbent. The calculations were made to find adsorption capacity as a function of time, q_t . The calculations were repeated to find development curve throughout the adsorption period. In this case, adsorption period was taken at 600 minutes due to the stagnant data starting from 540 minutes which were recorded as adsorption at equilibrium, q_e . The pseudo first order and pseudo second order can be expressed as:

$$\ln(q_e - q_t) = \ln(q_e - k_1 \cdot t) \quad \text{Equation 2}$$

$$\frac{t}{qt} = \frac{1}{k_2 qe^2} + \frac{t}{qe}$$

$$\text{Equation 3}$$

The values of q_e were calculated from the experimental data before plotting $\ln(q_e - q_t)$ versus t and t/qt versus t to find k_1 and k_2 . The value of k_1 and k_2 is calculated from the slope of the function $y = mx + C$. From the curves it was found that k_1 value is -0.003 whereas for k_2 is 1.815. It is also exhibited the increment of adsorption capacity is increasing as the interaction time increase. However, the adsorption is still happening despite of the lower increment on the nickel (II) adsorption at the later time of interaction. It was successfully to adsorb 40% of nickel (II) at the first hour of contact time before the adsorption increment has reached stagnant phase after 960 minutes of interaction, suggesting the whole process of adsorption was achieved the equilibrium phase [11], [12]. The

experimental data was compared to the two different models to analyse and determine the most suitable model for the experimental data plotted. The pseudo first order given $R^2= 0.9867$ whereas pseudo second order given better correlation with $R^2= 0.9921$. Thus, this experiment showed that the pseudo-second-order equation is more appropriate in indicating better curve fitting to describe experimental data as compared to the other model; pseudo-first order. Longer time was needed for graphene sand composite to completely saturate with the nickel (II) similar with literature review. This is in line with the previous researches[13], where other researchers [14], [15] suggested that saturation of adsorbent and solution influences breakthrough curve. Longer breakthrough is indicated by residual percentages of nickel (II) in waste water where longer point is needed to replace and regenerate graphene sand composite to remove more nickel (II) as shown in Figure 5.

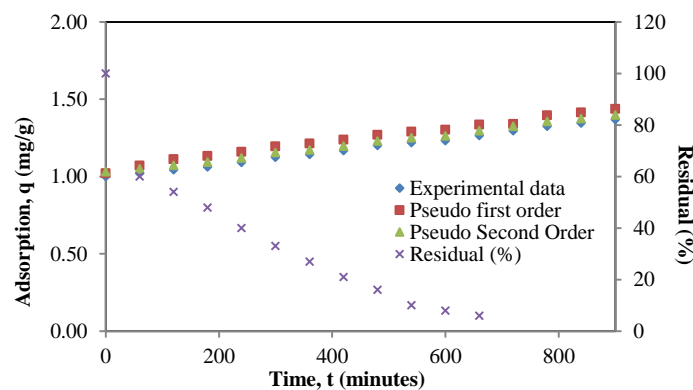


Figure 5. Adsorption of nickel (II) and it's residual in a factor of time

3.2.2. Adsorption Isotherm. For adsorption equilibrium, the data was fitted to two isotherm models namely Langmuir and Freundlich isotherm models. Langmuir model describes the equilibrium of the monolayer of adsorption onto the surface of containing finite identical active sites. This model assumes that there is uniform energy of adsorption onto the surface of adsorbent and no transmigration of the solution in the surface plane. On the other hand, Freundlich model is commonly used to describe heterogeneous surface of the adsorption characteristics. The equations of Langmuir and Freundlich are presented as follow.

$$\text{Langmuir model, } qe = (qm \cdot K_L \cdot Ce) / (1 + K_L \cdot Ce) \quad \text{Equation 4}$$

$$R_L = 1 / (1 + K_L Ce) \quad \text{Equation 5}$$

$$\text{Freundlich model, } qe = K_F \cdot Ce^{1/n} \quad \text{Equation 6}$$

Where qe is the amount of nickel (II) adsorbed in mg/g, Ce is the equilibrium concentration of nickel (II) in mg/L, qm is the maximum adsorption capacity in mg/g, K_L is the Langmuir isotherm constant in L/mg, K_F is the Freundlich isotherm constant in mg/g whereas n is the adsorption intensity. The graph of Ce/qe as a function of Ce is plotted to find the parameters of Langmuir isotherm model which are qm , K_L , R_L and R^2 . The slope and interception of the curve is equal to $1/qm$, and $1/(qm \cdot K_L)$ respectively. Whereas to find the parameters of Freundlich isotherm model which are K_F , n and R^2 , the graph $\log qe$ versus $\log Ce$ was plotted. The slope of the graph is equal to n value and K_F is calculated based on the fundamental logarithm's principal as follow:

$$\begin{aligned} \log_{10} K_F &= 0.8037 \\ K_F &= 10^{0.8037} \\ K_F &= 6.364 \end{aligned} \quad \text{Equation 7}$$

Figure 6 exhibits the adsorption equilibrium of nickel (II) adsorbed by MGSC_{aps}. From the graph, it is suggested that the nickel (II)'s concentration would reflecting the same towards adsorption equilibrium. The equilibrium data is fitted with Freundlich isotherm model best with $R^2 = 0.9989$ as compared to the other isotherm model, Langmuir isotherm model with $R^2 = 0.9873$ due to the heterogeneous characteristic of MGSC_{aps} consisting different active sites to be adsorbed. This is in complete agreement with the experimental data in kinetic study.

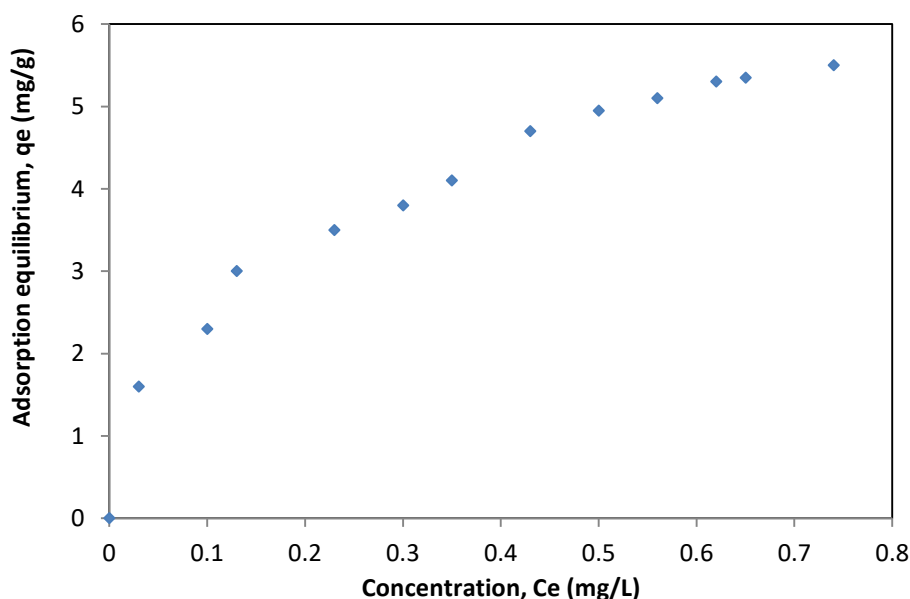


Figure 6. Adsorption equilibrium against concentration of nickel (II) solution

4. Conclusion

The kinetic and isotherm study shows that the surface of the MGSC_{aps} is heterogeneous and favourable to adsorb at the lower temperature due to the exothermic process of it. It is proposed to carry out further research on the effect of reusability and regeneration on the removal nickel (II) or any other heavy metals in waste water.

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