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Methenamine-Smectite Clay as Slow Release Fertiliser: Physicochemical and Kinetics Study

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Slow release fertiliser (SRF) is one of the important materials, which provides benefit to the green chemistry and green chemical engineering in the agricultural applications. Various modifications on porous materials and super-adsorbent based composites have been developed to act as the host for fertilisers including nitrogen-based fertilisers. In this work, a scheme of organic nitrogen compound, methenamine, was used as the SRF compound and in order to increase the effectivity of the releasing nitrogen, immobilisation of the compound in montmorillonite clays has been conducted. Methenamine immobilised montmorillonite at varied methenamine contents (20 mmol/g; 50 mmol/g and 100 mmol/g) was prepared using intercalation process by employing microwave irradiation method. Study on the change of crystallinity and chemical structure of the composite was performed by x-ray diffraction (XRD) analysis, gas sorption analyser, and electronic microscope analysis. The kinetic study of the nitrogen release was conducted by FTIR and HPLC methods. Results showed that physicochemical character of the composite is affected by the methenamine content and the pH of the solution gives influence on the methenamine desorption from the composite.

1. Introduction

The increased activities in the industrial applications give impact to the changes in the environmental characteristics including the agricultural environment. Due to the increasing development in the agricultural field and technology, the application of fertilisers on soils to boost the productivity and the growth rate of agricultural products is considered as a necessity. Besides being advantageous for increasing the productivity of soils and plants, the use of fertiliser also affects significantly the characteristic alteration of the agricultural environment. For example, soil can lose its contained nutrients, which are beneficial for bacteria due to the rapid increase in the fertiliser addition and the use of bulk fertiliser may result in 40 – 75 % of leaching losses (Yamamoto et al., 2016).

To provide sustainable development in the agricultural industry through the applications of green technologies and green chemistry, the approach that can be considered for development is by releasing control chemicals into the environment, or specifically to be absorbed into the soils. In addition to providing positive impacts on the distribution of chemicals in the environment and prevent groundwater contamination, the use of fertilisers in the form of loose slow can provide the principle of atom economy. Several researches reported the use of super-adsorbent based composite as the matrix for slow release fertiliser (SRF). Zhan et al. (2004) prepared the super-adsorbent polymer with phosphate-based SRF using the esterification of polyvinyl alcohol (PVA) and phosphoric acid (H_3PO_4). Ni et al. (2009) proposed using double-coated, water retention urea based SRF using ethyl cellulose and crosslinked poly(acrylic acid-co-acrylamide) as its inner and outer coating materials as a method to mitigate the environmental pollution resulted from excessive usage of nitrogen fertiliser. Qiao et al. (2016) also developed a double-coated SRF using ethyl cellulose as its inner coating and starch-based super-adsorbent polymer as its outer coating. Xie et al. (2011) proposed the utilisation of wheat straw and attapulgite to form the super-adsorbent composite for nitrogen and boron based SRF.

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Basically, the SRFs are composed of hydrophobic inorganic and/or organic materials, which act as a barrier to suppress the “burst effect” of the fertilisers (Yamamoto et al., 2016). The effects of the combination of silica based materials with natural/synthetic polymer were reported by the authors.
Nitrogen fertiliser is an important nutrient for plants since it is established from the fact that its contained nutrient could not be replaced by other nutrients (Essawy et al., 2016). Nitrogen plays role in the formation of chlorophyll, proteides and proteins, and some other vital compounds like phytohormones. It is also the basic requirement for plant growth and is needed in greater amount than the other nutrients, with the exception of potassium. The use of some nitrogen compounds on the plants instead of urea was an effort to create an enhanced activity on the fertilizing effect (Li et al., 2016).
In the scheme of SRF preparation, besides zeolite and synthetic silica materials, clay based material is one of the important inorganic supports due to its sweallable properties (Qiao et al., 2016). Since there are abundant potency of clay in the ASEAN countries especially Indonesia, this work aimed to simulate the properties and kinetic study on clay mineral for SRF application. Smectite clays consist in natural kind, montmorillonite, was used for the study (Lateef et al., 2016). The interaction of nitrogen compound with the sweallable properties of smectite, which specifically refers to its structure, is pointed out on the study, and through this consideration, methenamine compound is selected.
Smectite is basically composed of silica-alumina sheets within the ratio of 2 : 1 and between the sheets, there are some exchangeable cations. The exchangeable sites can be replaced thermodynamically with bigger and higher potential molecules/ions including methenamine. This study presents the adsorption-desorption study of methenamine into smectite clays. The aim of this study is to evaluate the interaction of methenamine and smectite clay and the effect of methenamine content to the releasing rate of methenamine.

2. Materials and Methods

2.1 Materials

Montmorillonite (MMt) was used as smectite clays model. MMt was obtained from Pacitan, East Java, Indonesia, and was activated by using HCl reflux for 6 h before using. Some chemicals including methenamine, HCl, and citric acid were purchased from Merck.

2.2 Methods

2.2.1 Samples preparation

Methenamine immobilised montmorillonite at varied methenamine contents (20 mmol/g; 50 mmol/g and 100 mmol/g) was prepared using the intercalation process by employing microwave irradiation method. The mixture of clay suspension with methenamine solution at varied concentrations in water was stirred for 24 h at room temperature. The suspension was irradiated using microwave oven at a low voltage power for 30 min. The suspension obtained was then filtered before drying at 60 °C. The obtained samples were designed as Meth/MMt-20, Meth/MMt-50 and Meth/MMt-100 to indicate the methenamine content.

2.2.2 Samples characterisation and analysis

Physicochemical characterisation of the composite was studied using x-ray diffraction (XRD) measurement, gas sorption analysis for BET surface area, pore volume and pore radius measurements and also SEM-EDX analysis. The desorption studies on the methenamine from the high concentrated solid was simulated in a flow desorption system by using citric acid as the leaching solution with a flow rate of 5 mL/min. The methenamine content in the filtrate was analysed by using HPLC. In order to evaluate the effect of pH on the composite, similar experiments were also conducted in varied pH of 4, 7 and 9.

3. Results and Discussion

3.1 Chemical Interaction Study

The basic principle of the SRF preparation is the preparation of the adsorbent-desorbent for methenamine releasing agent. The first study in this research is to investigate the chemical interaction between methenamine and montmorillonite by characterising the XRD pattern of the materials prepared from varied methenamine content.
Figure 1 shows the XRD patterns of MMts and Meth/MMts samples. From Figure 1, it can be shown that the peak intensities for MMt, Meth/MMt-20, Meth/MMt-50, and Meth/MMt-100 are 1.68 nm, 1.79 nm, 2.03, and 1.80 nm. The interlayer spacing in the sample of MMt clay increases from 0.11 nm to 0.35 nm (based on MMt and Meth/MMt-50 samples) after the intercalation of methenamine, which corresponds to the increase in the d (001) plane peak. The plotted data proves that the methenamine molecules are located in the interlayer space of MMT

layer. The highest peak intensity on the d_{001} plane was achieved as the methenamine content increased until the methenamine content reached 50 mmol/g but then reduced as the content increased to 100 mmol/g.

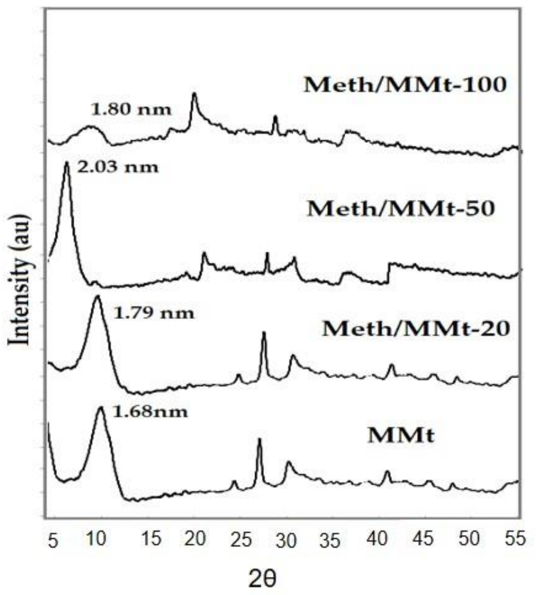

Figure 1: XRD pattern of materials

Since the samples characterisation from the XRD pattern shows that there is a chemical interaction between methenamine and the interlayer spacing of montmorillonite, there is a need for further investigation to determine the possible configuration based on the chemical interaction.

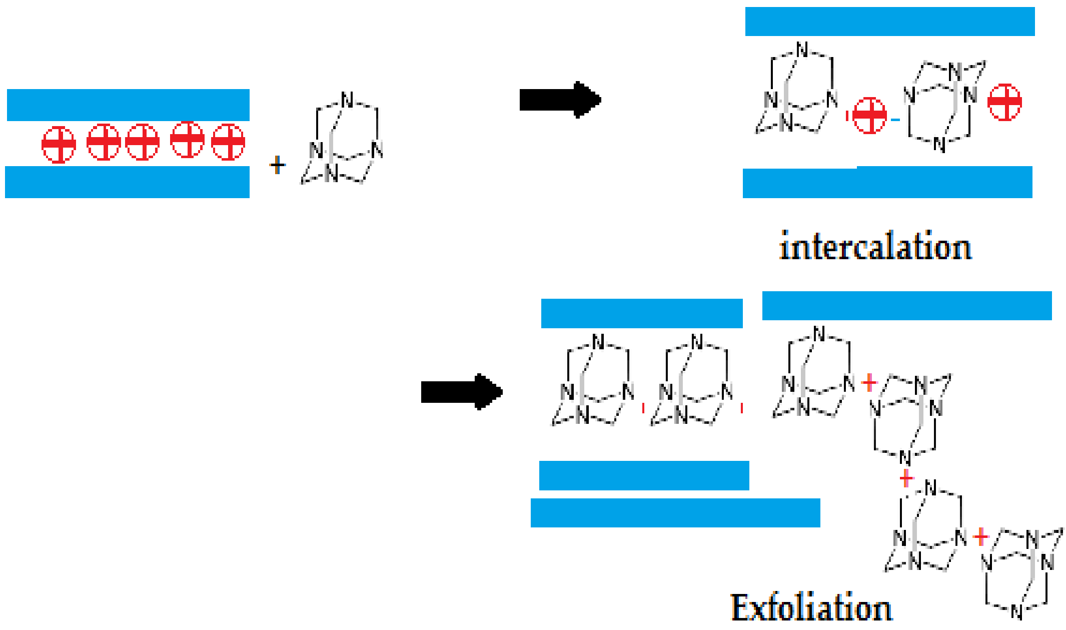

Figure 2: Schematic representation of intercalation and exfoliation of methenamine molecules in smectite clay

The possible configuration of methenamine in the interlayer of montmorillonite space in higher content is partial exfoliation as described in Figure 2. Initially, the methenamine molecules in smectite clay went through the intercalation process and as the methenamine content increased, the molecules in the interlayer of montmorillonite space proceed for the partial exfoliation process.

The confirmation on the different conformations is represented by the gas sorption analysis data. Adsorption-desorption curve exhibited in Figure 3 displays the evolution of adsorption-desorption pattern. The graph shows an increasing volume profile pattern for every MMt sample. The patterns show that there is an increasing adsorption capacity with methenamine intercalation.

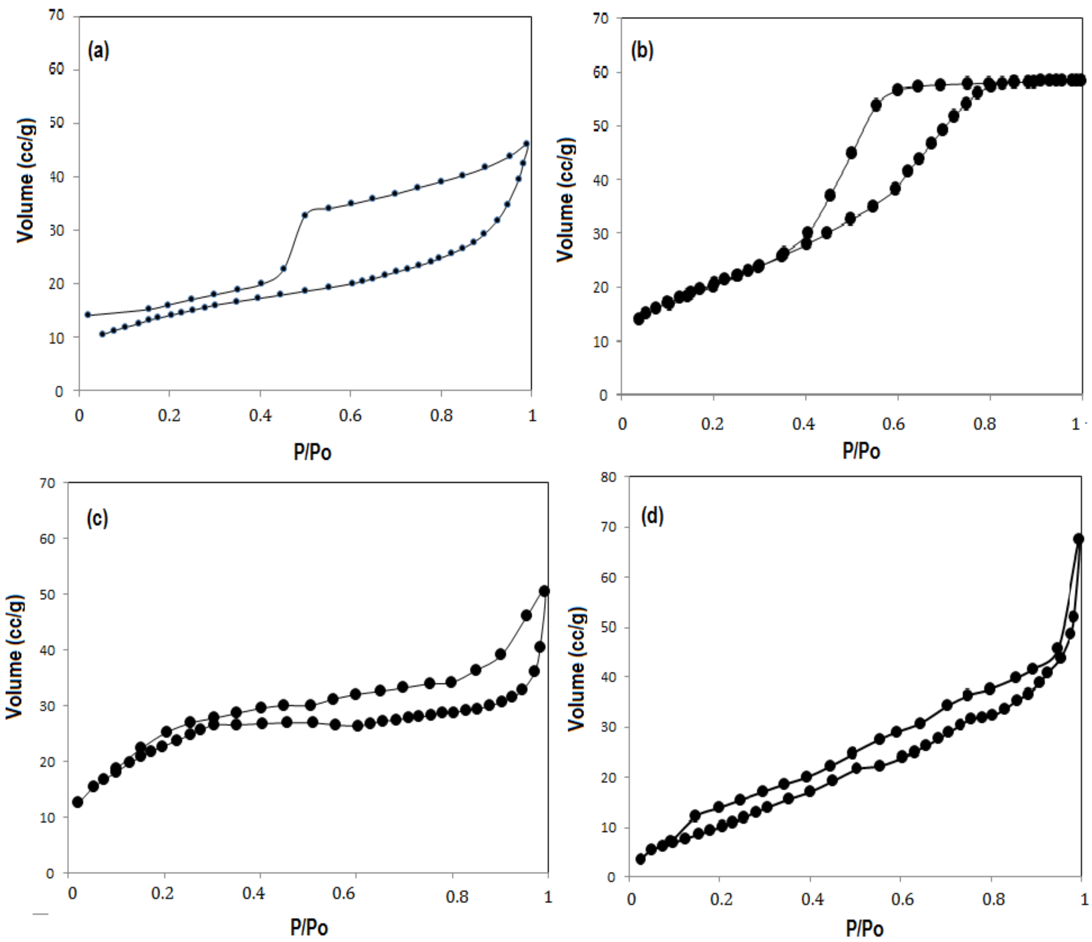

Figure 3: Adsorption-desorption profile of (a) MMt (b) Meth/MMt-20 (c) Meth/MMt-50 (d) Meth/MMt-100

Based on the gas sorption analysis data, the specific surface areas of the samples can be determined to identify the effects of increasing the methenamine content on the chemical interaction based on the methenamine intercalation process.

Table 1: Specific surface area, pore volume and pore radius of materials

Sample	Specific surface area (m^2/g)	Pore Volume (cm^3/g)	Pore Radius (Å)
MMt	67.98	0.235	11.85
Meth/MMt-20	101.56	0.597	12.02
Meth/MMt-50	134.26	0.811	12.33
Meth/MMt-100	84.12	0.432	11.03

The calculated specific surface areas of the materials are listed in Table 1. Based on the data, the specific surface area of the samples increased as the methenamine content increased until 50 mmol/g. The results are in line with the d_{001} change since the Meth/MMt-50 has the highest peak intensity value of 2.03 nm.

The surface morphology of the MMt after methenamine intercalation also changed to become flakier as represented in Figure 4. The presence of N indicated from the EDX data suggesting the increase in N content as methenamine increased in varied concentration.

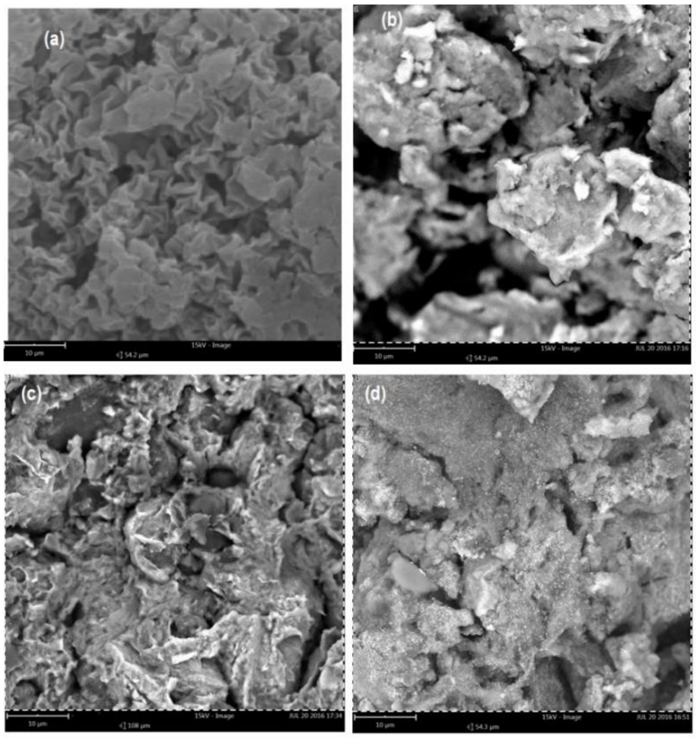

Figure 4: SEM profile of (a) MMt (b) Meth/MMt-20 (c) Meth/MMt-50 (d) Meth/MMt-100

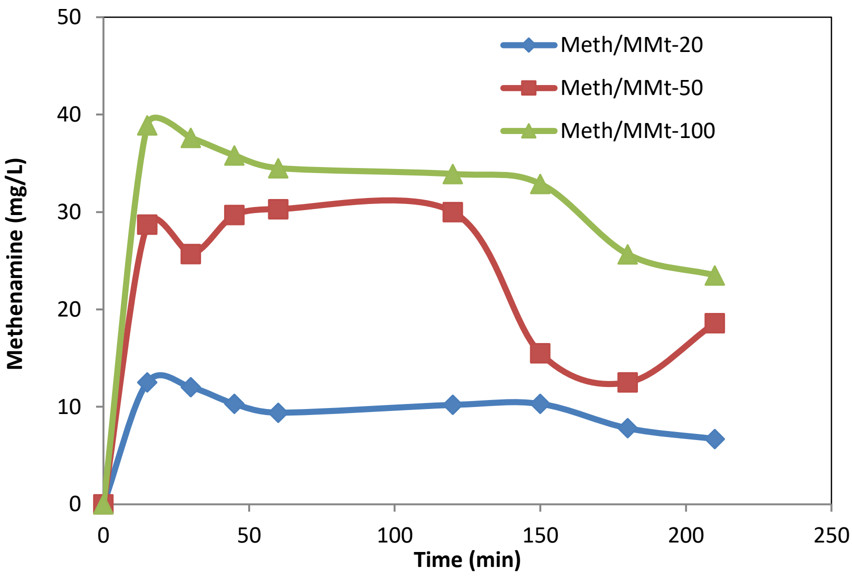

Figure 5: Kinetic of methenamine desorption at varied time of leaching

3.2 Desorption Study

The most important SRF properties is the slow desorption rate of the fertiliser. In order to study the properties, methenamine desorption by the materials is conducted in varied pH. The kinetics data is presented in Figure 5. From the pattern, it is confirmed that all prepared materials give slow release methenamine as the stable content for all varied materials. The trend is that the stable release was achieved after an hour and the rate got lower at increasing time. The higher methenamine content in the material, the higher released in all varied time, suggesting the chemical equilibrium controlling for the desorption mechanism.

The effect of pH on the releasing rate is exhibited by the graph in Figure 6. The highest releasing rate was achieved by all materials at the pH of 4. It suggests that acid condition gives strong interaction to replace interlayer molecules within the clay interlayer regions.

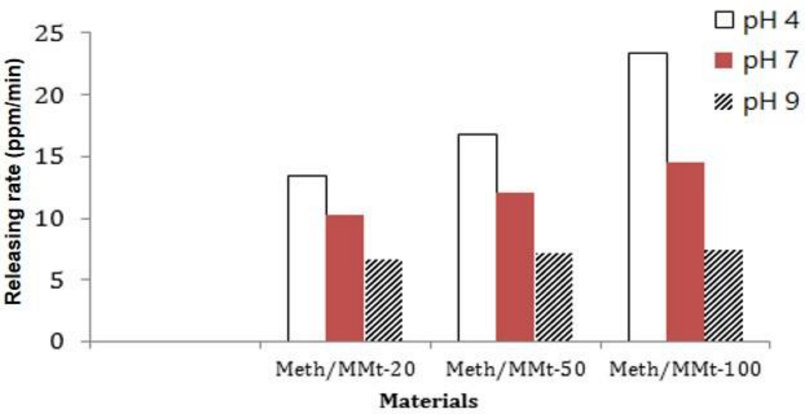

Figure 6: Effect of pH on methenamine releasing rate

4. Conclusions

From the research data, it can be concluded that methenamine gives chemical interaction with smectite clay structure and is affected by the methenamine content. From desorption studies, it is confirmed that all materials give stable releasing rate and are affected by the change in pH. The lower pH gives the higher releasing rate.

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