Chitosan-Modified Smectite Clay and Study on Adsorption-Desorption of Urea

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This work presented a laboratory studies on the preparation of chitosan-modified clay and the study on urea adsorption-desorption. Modified clay was prepared by intercalating chitosan into layer structure of smectite clay; saponite and montmorillonite. Physicochemical character of the materials was conducted by using XRD, GSA, SEM-EDX and FTIR. Materials capability in adsorption-desorption of urea from aqueous solution was performed in a batch reactor and the urea content was determined by using HPLC analysis.

Results show that chitosan-modified clay exhibits the intercalation interaction as shown by increasing d_{001} of the clay structure while the specific surface area and pore volume were decreased. Stronger interaction between urea and the composites were identified from kinetics of adsorption and desorption and suggests the potency of the materials for designing slow release fertilizer.

1. Introduction

The growth of earth's population results in the increasing need for food. The depletion of agricultural potency is also the issue that needs to be solved. Besides of the limitation of agricultural area, the effectiveness of agriculture activity, which is related to the fertilizer is an important issue to be concerned with. Fertilizer is a main consumable chemical in agriculture since soil itself cannot supply enough nutrients for good plantation. Control release fertilizer (CRF) is a developing technology which promotes the green agriculture and green technology concepts (Essawy et al., 2016). CRF is a purposely designed manure that releases active fertilizing nutrients in a controlled, slow released in sequential needs of nutrients for plants and provide enhanced nutrient use efficiency along with enhanced yields (Budnyak et al., 2014). An ideal CRF is from the usage of fertilizer that supports the consistence leaching of active nutrients in soil as well as minimising the nutrient loss. Urea is the most consumed fertilizer and in the practical use, conventional urea is not so efficient which results in excessive nitrogen loss from the soil. This is the reason for developing slow release nitrogen (urea) fertilizer. There are many hybrid materials and super adsorbents used for the application of CRF such as zeolite, clay and other silica-alumina materials (Kyzas and Bikiaris, 2015). One of these that can be developed is polymer modified clay minerals. The main properties required for the super adsorbent for CRF is the ability to adsorb water and then desorb the nutrient slowly. The development of urea immobilised porous minerals and its combination with polymers are one of the most scheme for this purposes. Porous mineral of smectite clay is also involved for the scheme and based on the previous reports, its use in slow release designed composite works effectively with the addition of polymer. Biodegradability of the material is another aspect to be concerned with, which is also the reason that the utilisation of natural polymer is considered. Since Indonesia has huge potency of clay mineral, especially bentonite and montmorillonite, and chitosan source, this research aimed to produce CRF material in the form of polymer-clay composite using montmorillonite and chitosan as polymer (Kyzas and Bikiaris, 2015). The study on adsorption-desorption properties of the composite is crucial thing for further development. The comparison between the composite and clay standard, saponite, is explored. Research is aimed to study the physicochemical properties of chitosan-clay composite by comparing Indonesian montmorillonite and synthetic saponite and the evaluation on their adsorption-desorption kinetics.

2. Material and Method

Montmorillonite and chitosan were supplied from PT. Tunas Inti Makmur and LIPI Gunung Kidul, DIY. Semarang and chitosan was supplied from Center of Food, Indonesian Institute of Science (LIPI), Gunung Kidul, Yogyakarta, some chemicals including urea, acetic acid, citric acid, NaOH were purchased from Merck. Saponite (furthermore called as SAP) was supplied from Kuninime Ind. Japan and montmorillonite (furthermore called as MMt) sample was obtained from Boyolali, Jawa Tengah. The MMt sample was used without any purification step.

Preparation of chitosan-modified smectite was performed by mixing chitosan solution made by diluting chitosan flakes into acetic acid solution into clay suspension. The mixture was then stirred for a night before filtration and drying in oven for overnight. The samples obtained from these steps were designated as Chit-SAP and Chit-MMt.

X-ray diffraction (XRD) patterns were recorded on a X6000 Shimadzu using Ni-filtered Cu Kα (λ = 1.54 A) radiation. N$_2$ adsorption isotherms of the samples were measured in a Quantachrome NOVA 1200 instrument at liquid nitrogen temperature. The specific surface areas were calculated using the BET method. FTIR analysis was performed by using Perkin-Elmer UATR instrument. SEM images were obtained on a JSM-6060 (JEOL) operated at 200 kV.

Adsorption study was conducted in a batch system. Chit-SAP and Chit-MMt samples were mixed with urea solution with the concentration of 5 ppm at varied time of adsorption. The samples from the varied time were analysed using HPLC analysis with phosphoric acid as solvent and UV 254 nm. A HITACHI HLPC instrument was utilised for this analysis.

3. Result and Discussion

The main effect of clay modification during the CRF preparation is the change of clay structure. Modification of smectite minerals can be conducted by intercalation, pillarization and exfoliation mechanism. In this study, chitosan was inserted into the clay structure by intercalation mechanism (Madeira and Herney-Ramírez, 2010). Figure 1 and Figure 2 present XRD pattern of the modified materials compared to its raw forms.

From the figures, it can be seen that the modified samples give more crystallinity compared to the raw materials. Different patterns appeared as the result of modification in that smectite presents (001), (004) and (006) and reflections at around 2θ of 5 – 7°, 20° and 35°, while chitosan-modified samples formed intensive peak indicating the presence of quartz in saponite (Zhao et al., 2013) Theoretically, the intercalation mechanism causes the d$_{001}$ reflection to shift to lower angle. However, the results contradict with the expected results based on the theory (Cho et al., 2012). The patterns suggest the crosslinking mechanism of chitosan to clay structure as suggested in the works related to polymer modification to clay (Lebaron et al., 1999)
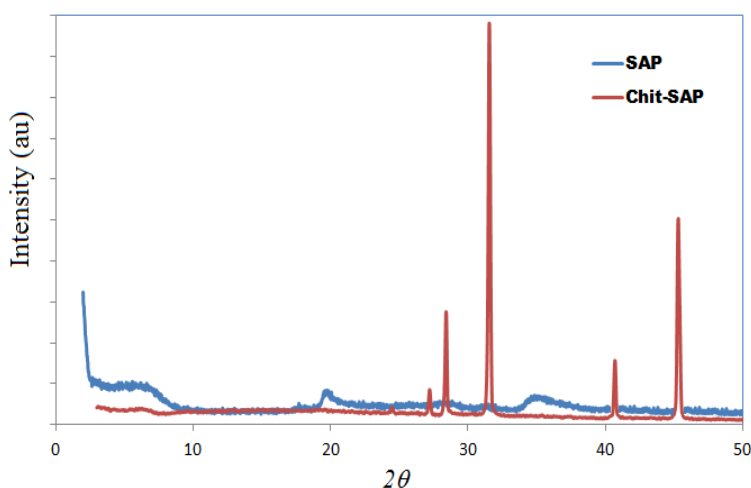

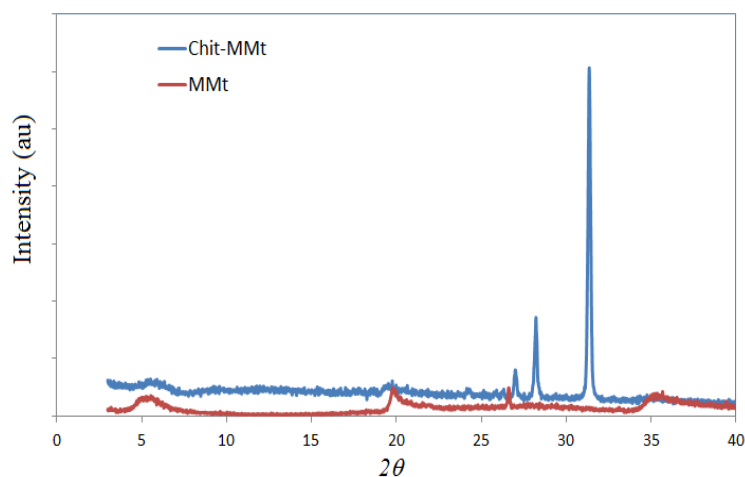Figure 1: XRD pattern of SAP and Chit-SAP

Figure 2: XRD pattern of MMt and Chit-MMt

Figure 3 expresses the effect of chitosan modification onto the surface parameter, expressed by the pattern change of adsorption-desorption process and Table 1 lists the calculated surface parameter data based on the isotherm data. The increasing specific surface area is exhibited by the modification for both smectite materials. The increase in specific surface area also increased the pore volume of the samples. The parameters suggest the higher capability of the samples to adsorb organic molecule theoretically.

The surface parameter of the samples is also expressed by the SEM analysis profile in Figure 4. The rougher profile of smectite is presented by the modification indicating the insertion of the chitosan as modifier. The rougher profile was due to the insertion of chitosan polymer in between the layer of structure.
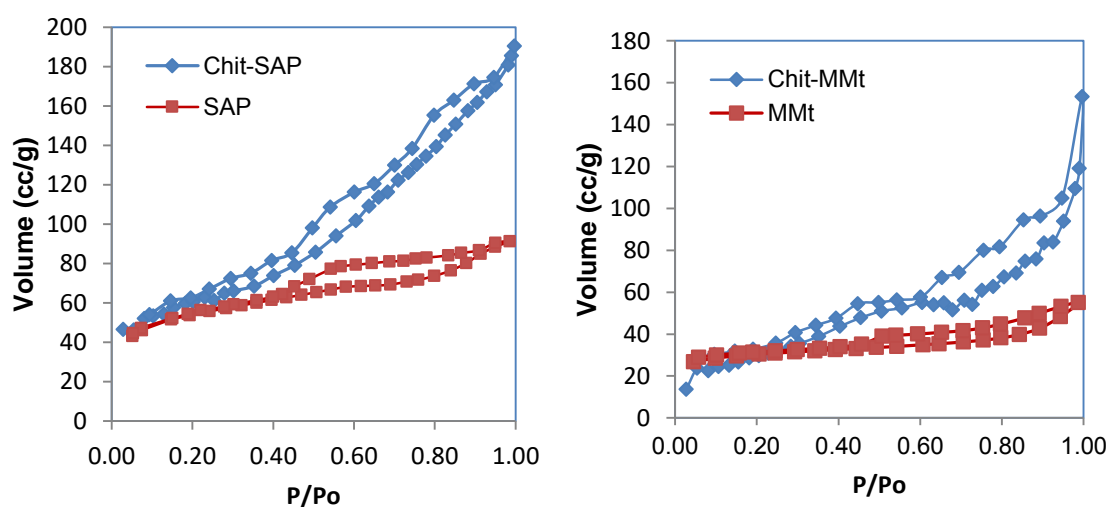

Figure 3: Adsorption-desorption profile of materials

Table 1: Surface parameter of material

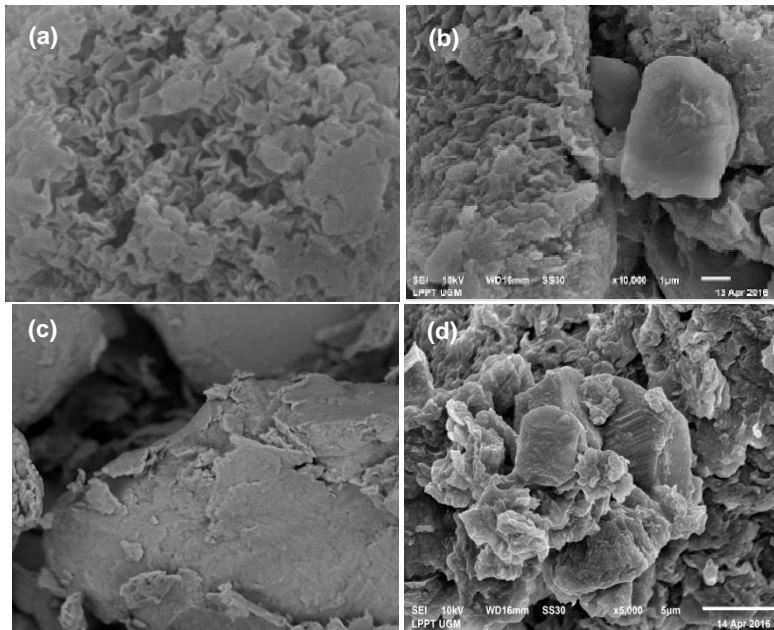| Sample	Specific surface area (m^2/g)	Pore Volume (cm^3/g)	Pore Radius (Å)
MMt	69.08	2.34×10^{-3}	11.9
Chit-MMt	174.08	3.65×10^{-2}	12.3
SAP	99.56	6.57×10^{-3}	12.8
Chit-SAP	167	3.77×10^{-2}	13.2

Figure 4: SEM profile of (a) SAP, (b) Chit-SAP, (c) MMt, and (d) Chit-MMt

The interaction of chitosan with the clay materials as the host is represented by FTIR analysis depicted in Figure 5. The spectra at around 2,800 - 3,000 cm^{-1} represented the vibration of C-H bonding while the spectra at around 1,580 cm^{-1} came from -NH_2 bonding which was related to the presence of chitosan. The data indicated the shift of -NH_2 bonding in raw chitosan which was reported to be in around 1,550 cm^{-1}. The shift was caused by the interaction of spectra and chitosan while the raw materials, montmorillonite and saponite, were expressed by silica and alumina bonds from Al-O-Si and Si-O-Si vibration (Budnyak et al., 2014).
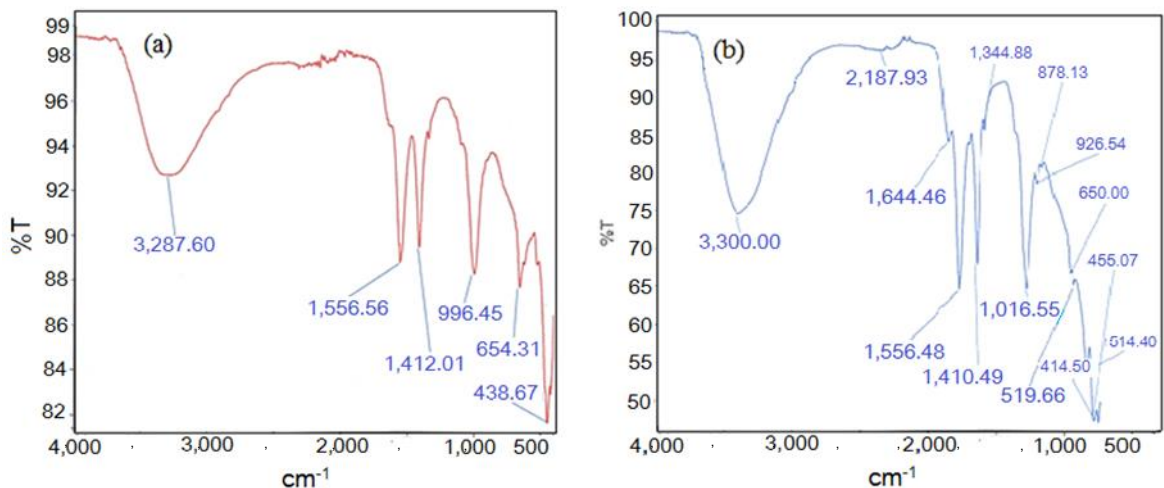

Figure 5: FTIR spectra of (a) Chit-SAP and (b) Chit-MMt

Figure 6 exhibits the urea adsorption desorption profile of chitosan-modified montmorillonite and saponite, and Figure 7 depicts the pattern of urea adsorpsion-desorption over raw montmorillonite and saponite. It is concluded that the modified smectite gives higher urea adsorption capability compared to that of raw material. The rate of desorption is lower compared to the adsorption rate in the same time of measurement. The pattern of adsorption-desorption profile is fit for CRF application. A slower release rate is attributed to the interaction between the entrapped urea and many sites within the network structure of the superabsorbent (Essawy et al., 2016).
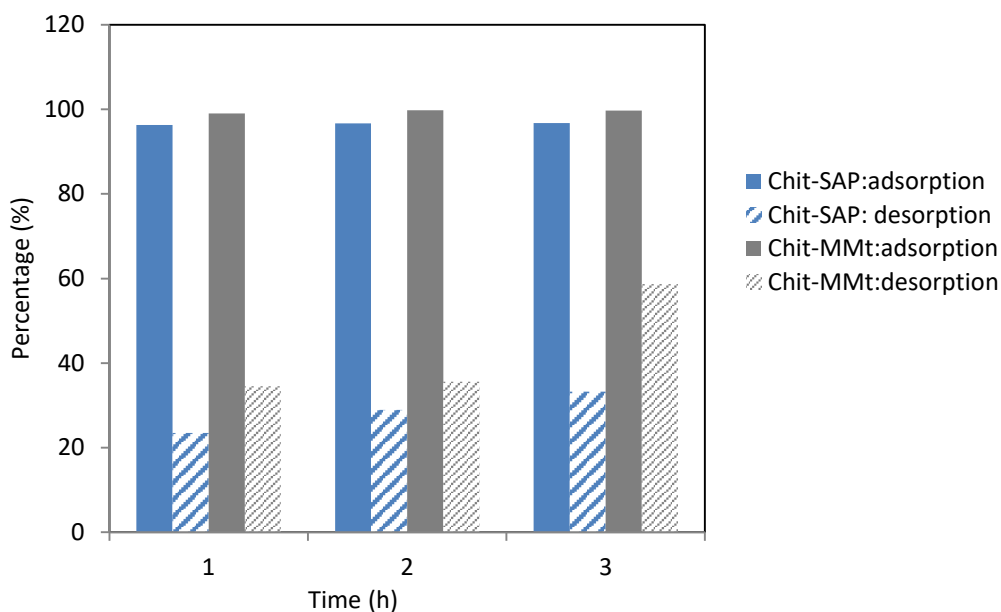
Figure 6: Urea adsorption-desorption profile of chitosan-saponite and chitosan-montmorillonite
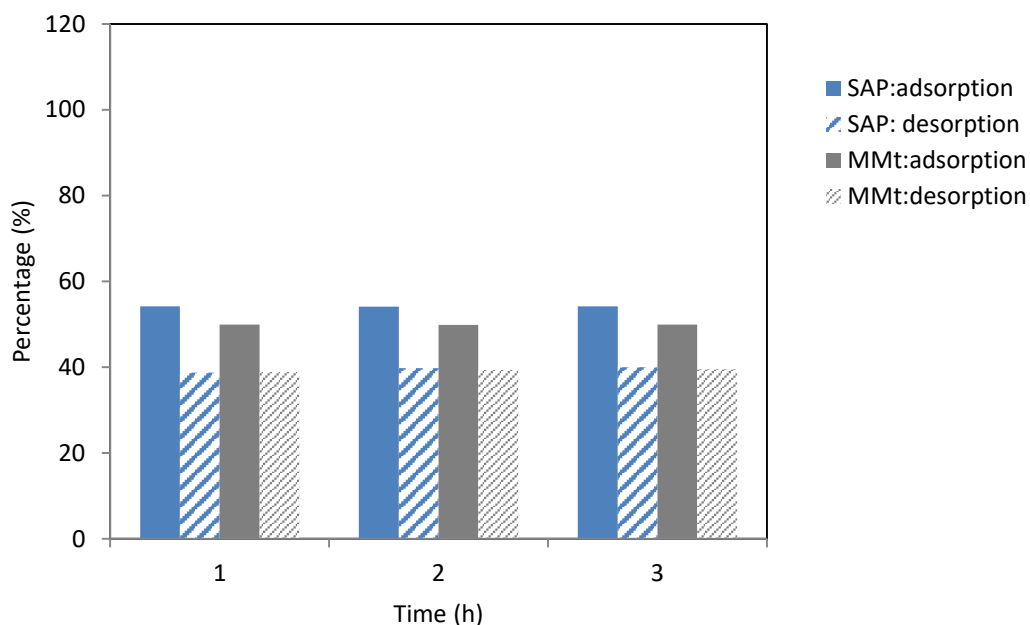

Figure 7: Urea adsorption-desorption profile of raw saponite and raw montmorilonite

4. Conclusions

This study shown that formation of chitosan-smectite composite was observed with increasing physical parameters such as surface area. These results are confirmed with the adsorption-desorption profile of the material towards urea.

Acknowledgments

Reference

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Zhao Y., Abdullayev E., Vasiliev A., Lvov Y., 2013, Halloysite nanotubule clay for efficient water purification. Journal of Colloid and Interface Science 406, 121–129.