INTERCALATION OF UREA INTO KAOLINITE FOR PREPARATION OF CONTROLLED RELEASE FERTILIZER

Article Highlights
• Urea was intercalated between elementary layers of kaolinite
• Urea-intercalated kaolinite was characterized using, XRD, FTIR and CHNS methods
• Urea-intercalated kaolinite was mixed with binder to prepare controlled release fertilizer granule
• The nitrogen release property of granules was investigated using UV-Vis spectroscopy
• Results showed that release property of granules conformed to the standard of controlled release fertilizers

Abstract
Urea was intercalated between layers of kaolinite by dry grinding technique to be used for preparation of controlled release fertilizer. X-ray powder diffraction (XRPD) patterns confirmed the intercalation of urea into kaolinite by the significant expansion of the basal spacing of kaolinite layers from 0.710 to 1.090 nm. Fourier transform infrared spectroscopy (FT-IR) also confirmed the hydrogen bonding between urea and kaolinite. Based on CHNS elemental analysis, 20 wt. % urea was intercalated between kaolinite layers. The urea-intercalated kaolinite was mixed with hydroxypropyl methylcellulose (HPMC) binder and was granulated to prepare the nitrogen-based controlled release fertilizer. To study the nitrogen release behavior of granules, ultraviolet/visible (UV-Vis) spectroscopy was used through the diacetyl monoxime (DAM) colorimetric method. The result of UV-Vis spectroscopy showed that intercalation of urea into kaolinite decreased the nitrogen release from 25.50 to 13.66% after 24 h and from 98.15 to 70.01% after 30 days of incubation in water. According to the results, the prepared controlled release fertilizer (CRF) behaved according to the standard for CRFs.

Keywords: kaolinite, urea, intercalation, controlled release fertilizer, nitrogen release.

The fertilization of agricultural soils with nitrogen (N) containing chemicals has been considered recently as one of the main sources of NOx emission and environmental pollution. Urea is the most widely used N fertilizer that contains 46% nitrogen. After application to soil, a large proportion of urea hydrolyzes before being absorbed by plants. Only a small portion of urea is actually consumed by plants [1,2].

To eliminate this environmental concern, controlled release fertilizers (CRFs) have been used as an alternative for conventional fertilizers [1,3,4]. CRFs release the nutrients at a slower rate than conventional fertilizers based on different mechanisms such as controlling water solubility of the material by semipermeable coating, occlusion of materials or by slowing the hydrolysis of low soluble chemicals. CRFs decrease the nutrient loss into the environment and have more efficiency in comparison to ordinary fertilizers [5]. One method to develop CRFs reported in previous studies is the occlusion of chemical sources of nutrients in natural porous minerals or between layers of clay minerals [6-10].

Correspondence: S.B.A. Rashid, Department of Chemical and Environmental Engineering, Faculty of Engineering, University Putra Malaysia, 43400 Serdang, Selangor D.E., Malaysia.
E-mail: suraya@eng.upm.edu.my
Paper received: 4 October, 2012
Paper revised: 19 December, 2012
Paper accepted: 10 January, 2013
Clay minerals are naturally occurring layered structure materials that consist of individual nanolayers connected via chemical bonds. These nanolayers have high surface areas and are suitable reactive sites for chemical reactions. In recent decades, these characteristics of clay minerals have been used in numerous studies to carry or reserve drugs using layered double hydroxide [11], to carry the herbicides using montmorillonite [12], to carry pesticides using calcined hydrotalcite [13] and to carry fertilizers for controlled release application using layered double hydroxide and montmorillonite [9,10].

Urea-intercalated clays have been used to prepare CRFs in previous studies [9,10]. However, the nutrient release behavior of products did not conform to the standard requirement of CRFs as outlined by the Comité Européen de Normalisation (CEN). According to this standard a fertilizer can be described as having controlled release properties if its nutrient release is not more than 15% after 24 h or not more than 75% after 30 days [5].

Man et al. [9] intercalated magnesium-urea complex between montmorillonite layers to prepare controlled release urea-based fertilizer. According to the reported result, about 80% of the intercalated urea was decomposed within 3 days in the soil. Also, Ureña-Amate et al. [10] developed a formulation of hydrotalcite-like layered double hydroxide (LDH) in the nitrate form mixed with the hydroxypropyl methylcellulose (HPMC) as the nitrogen-based CRF. The system with the highest LDH/HPMC ratio released around 87% of nitrogen during 180 h into the simulated soil solution. Thereby, the nitrogen release ratio in these two studies did not follow the standard of CRFs.

The intercalation of kaolinite with the chemical composition of \( \text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4 \) by urea has also been studied in numerous works [14–24]. However, the previous studies have focused only on the intercalation of urea as the guest molecule rather than on their nitrogen release behavior. The aim of this work was to use urea-intercalated kaolinite to prepare a controlled release fertilizer and investigate the release behavior of the prepared CRF. Urea was intercalated between the layers of kaolinite by dry grinding technique. Urea-intercalated kaolinite was mixed with HPMC and was granulated to make CRF. Finally, nitrogen release property of CRF was measured by ultraviolet-visible (UV-Vis) spectroscopy.

**EXPERIMENTAL**

**Intercalation of urea between layers of kaolinite**

The kaolinite used in this study was hydrated aluminum silicate (KM 40) which was provided from Kaolin Malaysia Co. Physicochemical properties of kaolinite are shown in Table 1. The urea powder with a melting point of 132–135 °C and density of 1.33 g/ml was obtained from Sigma-Aldrich. For intercalation of urea between layers of kaolinite (K), 50 g of kaolinite was dry ground with 12.5 g of urea (U) powder (weight ratio of U/K = 1/4) using a Fritsch Pulverisette type planetary monomill for 1 h at room temperature. The mixture was washed three times by isopropanol to remove the non-intercalated urea followed by drying at 50 °C overnight. Also, 2.5 g of urea was mixed with 50 g of kaolinite by hand to make a non-intercalated control sample with the same urea content as the washed intercalated sample.

**Preparation of nitrogen-based fertilizer granules**

The dried urea-intercalated kaolinite and also non-intercalated urea-kaolinite mixtures (U-K) were mixed with aqueous solution of 25 wt.% hydroxypropyl methylcellulose (HPMC) (Sigma Aldrich) as a binder in the ratio of HPMC/U-K = 1/10. HPMC is a water-soluble polymer with an average molecular weight of 90,000. The mixtures were then granulated (Table 2) using a lab scale granulator following by drying of the granules in an oven at 30 °C overnight.

To study the nitrogen release behavior of granules, 1 g of urea-intercalated kaolinite fertilizer (UIKF), non-intercalated urea-kaolinite fertilizer (NIUKF) and...
conventional urea fertilizer (CUF) were immersed in beakers containing 200 ml water. The beakers were sealed and kept at ambient room temperature for 30 days [5]. There were three replicates for each sample kept in the same conditions. After 1, 2, 3, 5, 10, 15, 20, 25 and 30 days of incubation, the urea content of 0.1 ml of each sample was measured using UV-Vis spectroscopy.

Characterization methods

The XRPD patterns for the urea-intercalated kaolinite and pure kaolinite were obtained to measure the basal spacing of kaolinite using a Philips PW 3710 diffractometer. The applied radiation was CuKα from a broad-focus Cu tube, operating at 50 kV and 40 mA. Intercalation ratio (IR) for urea-kaolinite powder was calculated using the following equation [19]:

\[ IR = \frac{I}{I_0 + I} \]

where \( I \) is the intensity of the peak attributed to the basal spacing of pure kaolinite and \( I_0 \) is the intensity of the basal spacing of urea-intercalated kaolinite powder.

In addition, infrared spectra were recorded to investigate the interaction of urea with kaolinite. The spectra were obtained for samples in KBr pellet form with an AEM Thermo Nicolet FT-IR collected at a spectrum resolution of 4 cm\(^{-1}\) with 32 co-added scans over the range from 4,000 to 400 cm\(^{-1}\). Elemental analysis method (CHNS analysis) was carried out to measure the intercalated urea between the kaolinite layers using a LECO TruSpec CHNS determinator.

The crushing strength of UIKF, NIUKF and CUF granules was measured using an Instron 3365 machine with a capacity loading of 5 kN at a running speed of 1 mm/min. Table 2 shows the characteristic of all granules.

Determination of the urea release was carried out according to the diacetyl monoxime (DAM) colorimetric method using a UV-Vis spectrometer presented by Douglas and Bremner [23]. This method is based on the reaction of urea with DAM under acidic conditions provided by reagents and measuring the color absorbency of the reaction product by UV-Vis spectrophotometer at a maximum absorbance of 527 nm. The DAM and other reagents such as phenylmercuric acetate (PMA), potassium chloride (KCl), thiosemicarbazide (TSC), phosphoric acid and sulfuric acid were obtained from Sigma-Aldrich.

Statistical methods

Descriptive statistics such as mean and standard deviation were calculated for samples of each experiment. Analysis of variance based on the completely randomized design (CRD) was done to show the differences among samples with different characteristics. All data showed a normal distribution, so analysis of variance (ANOVA) was performed using statistical analysis software (SAS 9.1). The means were compared by Duncan’s multiple range test (DMRT).

RESULTS AND DISCUSSION

To monitor the intercalation of urea, the XRPD patterns of washed urea-intercalated kaolinite and pure kaolinite were obtained (Figure 1). The curve attributed to the pure kaolinite shows the (001) reflection at \( 2\theta = 12.2^\circ \) with the basal spacing of 0.710 nm. The curve related to the intercalated kaolinite displays

![Figure 1. XRPD Patterns of pure kaolinite and washed urea-intercalated kaolinite.](image-url)
a new peak at $2\theta = 8.4^\circ$ with a d-value of 1.090 nm indicating the expansion of basal spacing of kaolinite layers by the intercalation process. Also, the value of intercalation ratio of urea into kaolinite was 1, indicating a complete intercalation of urea after 1 hour of grinding the urea-kaolinite mixture.

The content of urea in the sample of washed urea-intercalated kaolinite was measured using CHNS analysis. From the results, the content of urea in the sample was 20.01-20.08 wt.%, which was in good agreement with the results of previous experimental and simulation works [21,24].

To investigate the chemical interaction of urea molecules with kaolinite, the FT-IR spectra for pure kaolinite and washed urea-intercalated kaolinite are shown in Figure 2. The spectra for the original kaolinite shows characteristic O–H stretching bands at 3696 and 3653 cm$^{-1}$ attributed to the inner surface hydroxyl groups. The intensity and location of these bands usually change upon intercalation of urea. Another characteristic band at 3620 cm$^{-1}$ is related to the stretching of the inner hydroxyl groups and would be unaffected by intercalation [24,25]. After intercalation of urea into kaolinite, the 3653 cm$^{-1}$ peak disappeared completely and a new peak appeared at 3503 cm$^{-1}$, which is attributed to the formation of hydrogen bond between NH$_2$ groups and the oxygen of the tetrahedral sheets. The band at 3620 cm$^{-1}$ remains unaffected and the newly formed band at 3384 cm$^{-1}$ confirmed the asymmetric and symmetric NH$_2$ stretching frequencies involved in weak H-bonding with the inner surface hydroxyls [17,20,21]. The absorption bands at 1680 and 1600 cm$^{-1}$ resulted from contributions of both CO stretching and NH$_2$ bending motions. Furthermore, the band which appeared at 1470 cm$^{-1}$ is attributed to CN stretching [22].

To investigate the controlled release efficiency of granules, the nitrogen release behavior of UIKF, NIUKF and CUF granules are compared in Figure 3. The released nitrogen after 1 day and after 30 days is also shown in Table 3. It is illustrated in the results that CUF released more than 80 wt.% nitrogen into the water during the first day of incubation (Figure 3, curve a) and after 2 days all the nitrogen content of CUF granule was released. Meanwhile, although after 1 day and 30 days NIUKF granules released around 25 and 99 wt% nitrogen respectively (Figure 3, curve b), which is significantly slower than CUF, these results showed that NIUKF still did not conform to the standard of CRFs outlined by the CEN.

On the other hand, intercalated granules released around 13 and 70 wt.% nitrogen after 1 day and 30 days respectively which is acceptable for CRFs. It can be concluded from the results that inter-
Intercalation of urea into kaolinite caused a remarkable decrease in the ratio of urea release during 30 days incubation of IUKF granules (Figure 3, curve c).

It is speculated that the mechanism for nitrogen release from prepared CRF into water can be explained by the following steps. Initially, the water is absorbed on the surface of granule and then penetrates into the granule through tiny porosities on the granule surface. Subsequently, the penetrated water enters into the interlayer spacing of kaolinite and dissolves the soluble urea molecules which were bonded to the surface of nanolayers through hydrogen bonds. Finally, the dissolved urea diffuses out from the interlayer spacing and is released out into the water through dynamic exchange of free water. However, further work is currently being carried out to support these claims. Nevertheless, the XRPD patterns of urea-intercalated kaolinite before and after immersion in water were obtained to show that complete release of urea from the CRF after 30 days incubation in water had occurred, as shown in Figure 4.

Comparing the two curves shows that after 30 days immersion in water, the peak reflected at $2\theta = 8.4^\circ$ which corresponds to $d = 1.090$ nm was completely removed. Removal of this peak is attributed to the removal of urea from the interlayer basal spacing of kaolinite.

CONCLUSIONS

Intercalation of 20 wt.% urea between layers of kaolinite was carried out by dry grinding of urea-kaolinite mixture. Urea-intercalated kaolinite was mixed

![Figure 3. Release behavior of nitrogen for: a) CUF, (b) UIKF and c) granules (error bars represent the standard deviation for three replicates).]

![Figure 4. XRPD Patterns for a sample of urea-intercalated kaolinite a) before immersion in water and b) after 30 days immersion in water.]

<table>
<thead>
<tr>
<th>Granule</th>
<th>After 1 day (mean ± standard deviation)</th>
<th>After 30 days (mean ± standard deviation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UIKF</td>
<td>13.66±0.80 c</td>
<td>70.01±0.52 c</td>
</tr>
<tr>
<td>NIUKF</td>
<td>25.50±1.54 b</td>
<td>98.15±0.49 b</td>
</tr>
<tr>
<td>CUF</td>
<td>81.10±1.15 a</td>
<td>99.00±0.82 a</td>
</tr>
</tbody>
</table>

Table 3. Released nitrogen from fertilizer granules (%) after 1 day and 30 days in terms of mean ± standard deviation; the means with different letter are significantly different ($p \leq 0.01$) based on DMRT.
with a binder and was used to prepare CRF granules. Investigation of the release properties of incubated CRF in water showed that the intercalation of urea into kaolinite decreased the urea release ratio remarkably (13.66% of nitrogen release after 24 h) in comparison with non-intercalated urea-kaolinite granules (25.50% of nitrogen release after 24 h). The results show that urea-intercalated kaolinite granules behaved according to the standard of CRFs and hence would find good application in agriculture. However, trying other techniques to load more urea into the kaolinite is highly recommended for future research, as the final product would be more applicable in agriculture.

Acknowledgement

We wish to acknowledge Ministry of Education (MOE), Malaysia, for the Long-term Research Grant Scheme (Enhancing sustainable rice production) and University Putra, Malaysia, for funding this research project and technical support.

Nomenclature

ANOVA Analysis of variance
CEN Comité Européen de Normalisation
CRF Controlled release fertilizer
CUF Conventional urea fertilizer
DAM Diacetyl monoxime
DMRT Duncan multiple range test
FT-IR Fourier transform infrared spectroscopy
IR Intercalation ratio
HPMC Hydroxypropyl methylcellulose
K Kaolinite
LDH Layered double hydroxide
NIUKF Non-intercalated urea-kaolinite fertilizer
PMA Phenylmercuric acetate
SAS Statistical analysis software
TSC Thiosemicarbazide
U Urea
UIKF Urea-intercalated kaolinite fertilizer
UV-Vis Ultraviolet-visible
XRPD X-ray powder diffraction

REFERENCES

INTERKALACIJA UREE U KAOLINIT ZA PRIPREMU ĐUBRIVA SA KONTROLISANIM OSLOBAĐANJEM

U ovom radu urea je umetnuta između slojeva kaolinita tehnikom suvog mlevenja koja se koristi za pripremu dubriva sa kontrolisanim oslobađanjem. Metodom rendgenske difrac-cije na polikristalnim uzorcima (XRPD) potvrđena je interkalacija ureje u kaolinit na osnovu značajnog proširenja osnovnog razmaka u slojevima kaolinita od 0,710 do 1,090 nm. Infracrvena spektroskopija sa Furijeovom transformacijom (FT-IR) takođe potvrđuje vodo-nične veze između ureje i kaolinita. Na osnovu CHNS elementarne analize je dokazana interkalacija 20% ureje između slojeva kaolinite. Kaolinit sa interkaliranim urejem je pomešan sa hidroksipropilmetilcelulozom (HPMC) kao vezivom i posle granuliranja je iskorišćen za pripremanje azotnog dubriva sa kontrolisanim oslobađanjem. Sposobnost granula da oslobađa azot je ispitana UV-Vis spektrofotometrijskom metodom sa diacetil monoksimom (DAM). Rezultati UV-Vis spektrofotometrije pokazuju da interkalacija ureje u kaolinit opada oslobađanjem azota inkubacijom u vodi, i to: za 24 sata od 25,50 do 13,66%, a za 30 dana od 98,15 do 70,01%. U skladu sa ovim rezultatima pripremljeno dubriva sa kontrolisanim oslobađanjem (CRF) se ponaša u skladu sa CRF standardom. Ključne reči: kaolinit, urea, interkalacija, dubriva sa kontrolisanim oslobađanjem, oslobađanje azota.