



Facile fabrication of organobentonite–carboxymethyl chitosan hybrid film that absorbs organophosphate insecticides

DAU HUNG ANH¹ and KANCHANA DUMRI^{2,*}

¹Biogreen Material Research and Service Co. Ltd., Chiang Mai 50140, Thailand

²Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

*Author for correspondence (kanchana.d@cmu.ac.th, kdumri@gmail.com)

MS received 12 October 2016; accepted 25 January 2017; published online 7 September 2017

Abstract. Organophosphate (OP)-insecticide-absorbing hybrid film containing 10% (w/w) organobentonite and carboxymethyl chitosan (CMCh) was fabricated and tested. Bentonite clay was modified to organobentonite by two steps modification with (1) NaCl and (2) plant alkaloid monovalent cation berberine. CMCh was synthesized from commercial shrimp chitosan. Afterwards, organobentonite was immobilized into CMCh matrix via *in situ* polymerization of CMCh to cast a hybrid film with 0.5 mm thickness. Scanning electron microscopy images of organobentonite powder and the film revealed the porous material and layer-upon-layer structure, respectively, which is supposed to enhance the water permeability of the film. Fourier transform infrared spectrometry analysis revealed similarly chemical characteristics of the CMCh component in the film and synthesized CMCh polymer powder. The film was then investigated to remove four OP insecticides including profenofos, chlorpyrifos, methyl parathion and dimethoate of 5 ppm concentration in spiked water samples via batch filtration. High-pressure liquid chromatography analysis showed that the removal rates for profenofos, chlorpyrifos, methyl parathion and dimethoate after seven batches were 42, 39, 24 and 20%, respectively. Hence, absorptivity of this film for tested OP insecticides was demonstrated. Furthermore, the combination of organobentonite and natural chitosan is promising for novel absorptive film material generation with regard to environmental clean-up study.

Keywords. Organobentonite; carboxymethyl chitosan; hybrid film; organophosphate insecticides; batch filtration.

1. Introduction

Bentonite clay and carboxymethyl chitosan (CMCh) products are now commercialized world-wide and studied variously for environmental application. Bentonite is a well-known material for the development of environment clean-up techniques by its absorptivity for diverse materials from heavy-metal toxins, e.g., As (III), Cd (II), Cu (II, III), Ni (II) and Pb (II) [1–5], to agricultural herbicides and insecticides, e.g., atrazine, carbaryl, dichlofos, parathion, paraoxon [6–9], and hazardous polycyclic aromatic hydrocarbons, e.g. naphthalene, flouranthene, benzo[a]pyrene and benzo[a]anthracene [10,11]. For applications, bentonite can be chemically modified using a large selection of alkylammonium or quaternary ammonium cations, where these cations replace the interlaying inorganic cations in bentonite, e.g., Ca²⁺ and Na⁺, to form organobentonite. For example, bentonite types modified by plant alkaloid berberine (5,6-dihydro-9,10-dimethoxybenzo[g]-1,3 benzodioxolo[5,6-a]quinolinium), tetradecyltrimethyl ammonium bromide, dodecyltrimethyl ammonium bromide or hexadecyl trimethyl ammonium and phenyltrimethylammonium increasingly absorb pesticides malathion and butachlor, herbicides terbutylazine and diuron and industrial dyeing wastewater [12–15]. Among alkylammonium compounds, berberine is a selective

candidate for bentonite modification, which is a major alkaloid from *Coscinium fenestratum*. This plant is being used to date as a traditionally pharmaceutical component in Asian countries, e.g., Thailand, Vietnam and China [16]. The incorporation of berberine into different clays via cation exchange mechanism has been reported [14,17]. It resulted in the expansion of the basal spacing in the clay structures, which increased the absorptivity of the modified clay for the target pollutants [14,15]. CMCh, a water-soluble derivative polymer from biological chitosan molecules with high water solubility, has found applications in pharmacy and cosmetics. The hydrogel form of CMCh has biocompatibility and biodegradability properties, which have been applied for drug delivery and wound healing [18,19]. CMCh also behaves as an antimicrobial and antioxidant agent and emulsion stabilizer, which makes it an applicable matrix for cosmetics.

Interestingly, the combination of organobentonite or bentonite and chitosan yields new absorptive material bionanocomposites, which can absorb various industrial dyes and herbicides, e.g., cationic Rhodamine 6G, anionic Amido Black 10B or Bezactiv Orange V-3R and clopyralid, in wastewater treatment [20–24]. These materials have higher absorptive capacity for target absorbate than that of either organobentonite or chitosan [22,24]. The chitosan–bentonite nanocomposites also show antibacterial activity (both Gram

positive, e.g., *Bacillus subtilis* and *Staphylococcus aureus*, and Gram negative, e.g., *Escherichia coli*) as well as higher tensile strength in comparison with chitosan moiety [25,26].

The organophosphate (OP) insecticides tested in this work were chlorpyrifos, profenofos, dimethoate and methyl parathion. They are classified into class II (moderately toxic) and class IA (extremely toxic) for inhalation and ingestion by WHO, respectively [27]. Agricultural-product-exporting countries, e.g., Thailand, use these OP insecticides but the control of use is always problematic; therefore, their residues can be detected ubiquitously not only in harvested products but also in nearby agricultural water zones or even in fresh water sources due to rainfall event [28,29]. Towards this end, we fabricated a film composed of berberine-modified bentonite and synthesized CMCh. The film materials were tested to remove the four aforementioned OP insecticides in spiked water. The absorptivity of the film based on their structures and the interactions between film components and OP insecticides are described and discussed.

2. Experimental

2.1 Materials

The commercial bentonite or calcium bentonite (designated as bentonite) was purchased from Srichand United Dispensary Co., Ltd. (Bangkok, Thailand). Commercial grade shrimp chitosan of flake polymer type (molecular weight in the range 900–1,300 kDa) was purchased from Taming Enterprises (Samutsakon, Thailand).

All chemicals were of analytical grade. Berberine chloride (98%, designated as BBrCl) and OP insecticides (>97%, PESTANAL[®], including methyl parathion, chlorpyrifos, profenofos and dimethoate, were purchased from Sigma and Riedel de Haen (Germany) (figure 1). Stock solutions (100 mM) of insecticides were prepared in methanol (MeOH) and kept at 4°C until further use. Working insecticide solutions were prepared at 5 ppm in distilled water of pH 7.2.

2.2 Two steps modification of commercial bentonite by NaCl and BBrCl

In the first step, bentonite was modified by NaCl to form Na-bentonite; 100 g of bentonite was well dispersed in 1 litre of NaCl (0.1 M, pH 7.5) and vigorously stirred at 600 rpm for 8 h at room temperature. Afterwards, the reaction mixture was allowed to settle for 2 h and the supernatant was decanted. Later, the bentonite sediment was washed repeatedly 4–6 times by deionized water to eliminate the redundant NaCl. Subsequently, NaCl residue in the supernatant was tested using a Chloride Low Range Test Kit, Model 8-P, Hach (USA). The bentonite sediment was dried at 95°C for 12 h and ground to powder afterwards. This was designated as Na-bentonite. In the second step, 30 g of Na-bentonite was re-dispersed in 1 litre of deionized water and 10 ml homogeneous BBrCl solution (0.3 g BBrCl in 10 ml MeOH) was

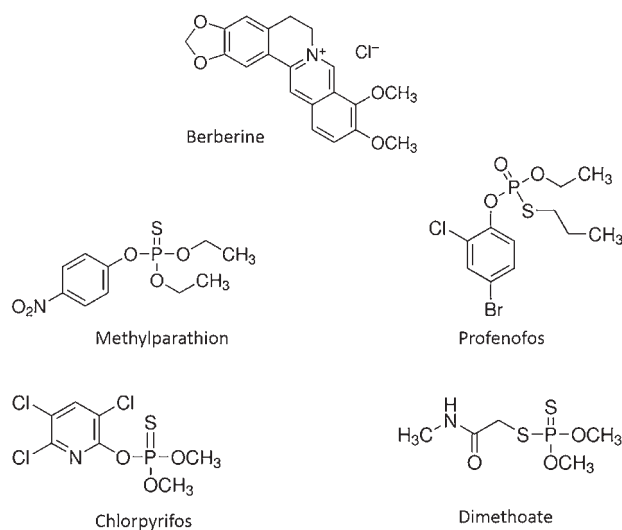


Figure 1. Structures of berberine chloride and tested OP insecticides.

pipetted step-wise (100 μ l in 10 s) into the Na-bentonite mixture with vigorous stirring. Subsequently, the reaction mixture was stirred at 600 rpm for 8 h. The yellow sediment was allowed to settle within 2 h, collected and dried at 95°C for 12 h. The dried sediment was ground to powder and sieved using a 300-mesh sieve (Gallenkamp and Co, London). The latter was used for all insecticides absorption tests throughout this work and it was designated as BBr-bentonite. Both Na-bentonite and BBr-bentonite are generally designated as modified bentonite in all following contexts.

2.3 Synthesis of CMCh

CMCh was synthesized by the procedure of Chen and Park [33]. The chitosan powder (25 g) was suspended in a solution of NaOH:*i*-propanol:H₂O (1:8:2) and stirred at room temperature for 1 h. The appropriate amount of monochloroacetic acid was added into the mixture and continuously stirred for 30 min. The mixture was covered with an aluminium foil and placed in an oven at 50°C for 4 h. Later, it was separated into liquid and solid phases. The solid phase was further suspended in MeOH and neutralized with glacial acetic acid. Subsequently, it was filtered and washed 5 times with ethanol (70% v/v EtOH) to remove undesirable products and the last time with absolute MeOH. The final product, designated as CMCh, was dried in the oven at 50°C for 18 h and kept in a sealed polyethylene bag until further use.

2.4 Casting of hybrid film containing organobentonite and CMCh

Modified bentonite (2 g, BBr-bentonite and Na-bentonite) was firstly added step-wise (50 mg in 10 s) into 500 ml distilled water at 80°C under 500 rpm stirring in a 1-litre glass beaker until a homogeneous grey suspension solution (Na/bentonite) or yellow suspension solution (BBr/bentonite) was formed.

Afterwards, 20 g of CMCh was added step-wise (50 mg in 10 s) into the above suspension solution while the temperature was maintained at 80°C; it was still under vigorous stirring until the polymerization of CMCh occurred and a homogeneous sticky grey or yellow suspension solution was formed; 100 ml of the latter was poured into a 30 cm × 15 cm × 2 cm transparent acrylic tray and kept at 25°C for 72 h to form a film with approximate thickness of 0.5 mm. These modified bentonite–CMCh films were designated as BBr-bentonite–CMCh and Na-bentonite–CMCh films.

2.5 Characterization of modified bentonites and modified bentonite–CMCh films by scanning electron microscopy

The morphologies of modified bentonite and modified bentonite–CMCh films were characterized by scanning electron microscopy (SEM; JEM 5910 LV and JEM 1010 JOEL Ltd., Japan) at accelerating voltage of 15 kV and fit magnification.

2.6 Characterization of modified bentonites and modified bentonite–CMCh films by Fourier transform infrared spectrometry

Chemical components of modified bentonite were identified by Fourier transform infrared spectrometry (FTIR) using a Bruker Tensor 27 (Bruker, USA) spectrometer. Samples were dried at 100°C overnight, ground mildly with KBr powder and subsequently pressed to form a disk, which was analysed further in the apparatus. For modified bentonite–CMCh films, the film materials were cut into 5 mm × 5 mm square pieces and placed on KBr plates for analysis.

2.7 Batch filtration to remove OP insecticides using modified bentonite–CMCh films

Modified bentonite–CMCh films were cut into round pieces of \varnothing 6 cm and 10 pieces were piled (approximately 10 g of film material) on the metal net bottom (1 mm × 1 mm mesh netting) of an acrylic column (\varnothing 6 cm × 20 cm). One upper net was finally piled on this film layer to prevent the floating; 100

ml of each OP insecticide solution (5 ppm in distilled water) was poured into the prepared column at room temperature. The flow-through aqueous solution was collected through a cone funnel and refilled back into the column for seven batches; 1 ml of sample from each batch was centrifuged at 20,627 g for 15 min at 4°C and the supernatant was analysed by high-performance liquid chromatography (HPLC, described in section 2.8) to evaluate the OP insecticide residues.

2.8 Analysis of OP insecticides by HPLC

HPLC was used to determine the residue of OP pesticides after absorption by modified bentonite following the procedure of Anh *et al* [30]. Samples (1 ml) were centrifuged at 20,627 g for 15 min, filtered using a VeriPure Nylon Syringe Filter (0.2 μ m pore size; Vertical[®]) and transferred to 2 ml HPLC vials. An Agilent HPLC system (series 1100; Agilent) equipped with a VertiSep[™] AQS reversed-phase (C18) column (4.6 mm × 150 mm, 5 μ m; Vertical[®]) was used for all analyses. Samples were analysed by applying a gradient of 20–80% acetonitrile (0 and 4 min, 20%; 4 and 12 min, 80%; 12 and 17 min, 20%) for 20 min at a constant flow rate of 1 ml min⁻¹. Degraded pesticides and pesticide residues were identified and quantified by means of authentic standards (chlorpyrifos, profenofos, methyl parathion and dimethoate).

3. Results and discussion

3.1 Two steps modification of bentonite by NaCl and BBrCl and characterization by SEM and FTIR

The modification of bentonite by NaCl and BBrCl aimed to enhance the absorption capacity of the original bentonite. Firstly, Ca-bentonite (commercial bentonite) or non-swelling bentonite was converted to Na-bentonite or swelling bentonite form [31] via the exchange of original Ca²⁺ by Na⁺ in NaCl solution. Later, Na-bentonite was converted to BBr-bentonite (figure 2b) when BBr⁺ displaced Na⁺ in Na-bentonite. The

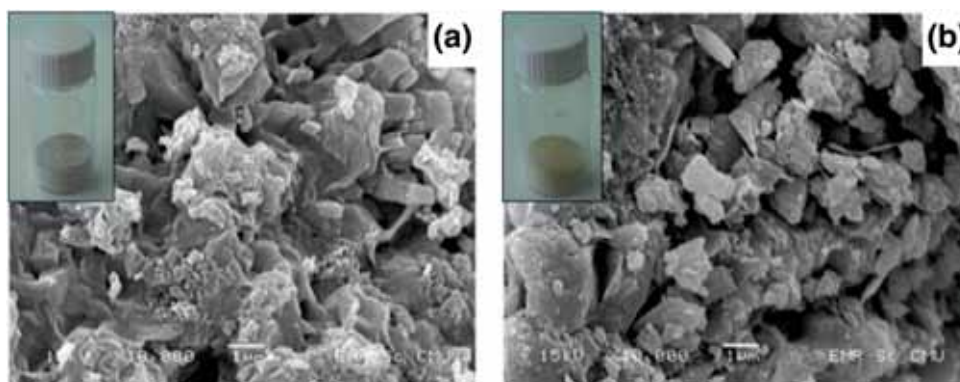


Figure 2. Typical SEM images of (a) Na-bentonite and (b) BBr-bentonite. Top-left insets are (a) grey Na-bentonite and (b) yellow BBr-bentonite powder samples.

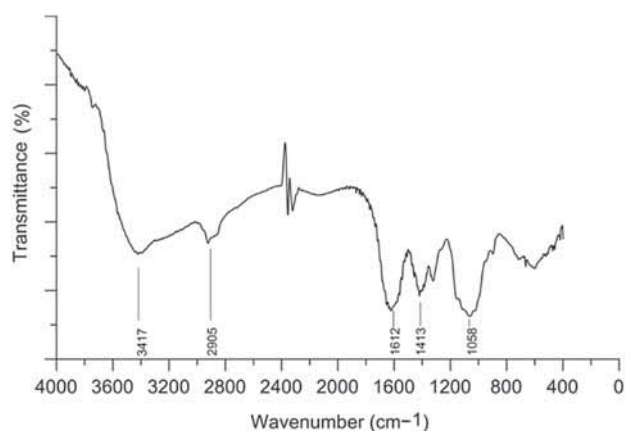


Figure 3. FTIR spectrum of sodium carboxymethyl chitosan.

Na-bentonite was grey whereas BBr-bentonite was yellow (figure 2a and b). At the magnification of $\times 10000$, the SEM image of Na-bentonite shows a matrix composed of polymorphic blocks and some cavities or the matrix was not hollow. This was similar in comparison to the SEM image of the microstructure of Na-bentonite in Danaja *et al* [32]. However, SEM image of BBr-bentonite shows a porous matrix composed of dispersed amorphous blocks. SEM image of BBr-bentonite in figure 2b is similar to the SEM image in the report about surficial morphology of BBr-modified bentonite of Rytwo *et al* [14]. BBr-bentonite was formed when BBr^+ displaced Na^+ and the basal spacings between bentonite sheets were increased [14,15]. Furthermore, the intercalation of BBr^+ into bentonite structure changed the originally exchangeable cations, i.e., Na^+ and Ca^{2+} , and generated more hydrophilic sites on the clay surface, which enhanced the interaction between BBr-bentonite and tested OP insecticides. In addition, BBr^+ cations were not desorbed from stable BBr-bentonite complexes [15].

3.2 Characterization of synthesized CMCh by FTIR

The CMCh material was used in this work due to its flexible water solubility over a wide pH range and temperature in comparison with native chitosan [33,34]. Under experimental conditions, commercial shrimp chitosan was converted to sodium salt CMCh form. The use of domestic shrimp chitosan was also significant in terms of low cost, especially because Thailand is a chitosan-exporting country. A typical FTIR spectrum of synthesized CMCh (figure 3) reveals characteristic peaks at 3417 cm^{-1} (O–H stretch), 2905 cm^{-1} (C–H stretch), $1574\text{--}1650$ and 1413 cm^{-1} ($-\text{COONa}$, $-\text{NH}_2$ and $=\text{CH}_2$ with sodium CMCh, respectively) and 1058 cm^{-1} (C–O stretch). These FTIR results are in agreement with previous reports of CMCh analysis from different shrimp sources [33,35–37].

3.3 Characterization of CMCh and Na-Bentonite–CMCh and BBr-Bentonite–CMCh films by SEM and FTIR

Three types of films were fabricated for OP insecticides filtration test. SEM and FTIR results revealed the relation between the films morphologies and chemical components in the absorptivity tests of OP insecticides. Figure 4a, c and e shows the morphologies of CMCh, Na-bentonite–CMCh and BBr-bentonite–CMCh films, and figure 4b, d and f depicts FTIR characteristics of these respective films. The CMCh film was transparent and colourless (inset in figure 4a) with smooth surface at magnification of $\times 2000$ (figure 4a). The Na-bentonite–CMCh film was opaque grey, whereas BBr-bentonite–CMCh film was opaque yellow (insets in figure 4c and e, respectively). At the magnification of $\times 3000$, their surfaces were rough; however, BBr-bentonite–CMCh film surface visually showed the density of blocks to be about three times higher than the surficial block density of Na-bentonite–CMCh film (figure 4e and c, respectively). Interestingly, the surface morphologies by SEM analysis of these films were different but their FTIR spectra were almost congruent to the FTIR of CMCh powder (figure 3). In the case of CMCh film, all FTIR peaks in figure 4b were obtuse but FTIR spectra of Na-bentonite–CMCh (figure 4d) and BBr-bentonite–CMCh films (figure 4f) both revealed clear characteristic peaks of CMCh powder as in figure 3. The different shapes of congruent peaks in FTIR spectra of different film types might be the result of sample preparation, where some samples needed heat treatment. The congruence between FTIR results of modified bentonite–CMCh films and CMCh powder implies that in both Na-bentonite–CMCh and BBr-bentonite–CMCh films, the CMCh component intercalated and enfolded all modified bentonite components tightly and flexibly.

3.4 Batch filtration to remove OP insecticides using modified bentonite–CMCh films

BBr-bentonite–CMCh and Na-bentonite–CMCh films (insets in figure 4e and c, respectively) were intensively used for filtration to remove 5 ppm OP insecticides from spiked water samples. This work was carried out based on our previous and selected reports elsewhere about: (i) the diverse absorptivity of bentonite to various OP insecticides [6,7,9,38–41]; (ii) the large water solubility of CMCh over a wide range of pH from 4 to 11 and temperature from 10 to 50°C , which is not influenced by ionic strength in aqueous solution [42,43]; (iii) the non-toxic nature of both bentonite and CMCh material to humans and the environment [19,34,44,45]. Apparently, the BBr-bentonite–CMCh film could absorb OP insecticides in water. With the design of filtration columns that contained 3 g of BBr-bentonite–CMCh film, profenofos, chlorpyrifos, methyl parathion and dimethoate were removed from the spiked water after seven batches at the rate of 42, 39, 24 and 20%, respectively (figure 5a). The Na-bentonite–CMCh film also removed these OP insecticides profenofos, chlorpyrifos, methyl parathion and dimethoate at the rate of 16,

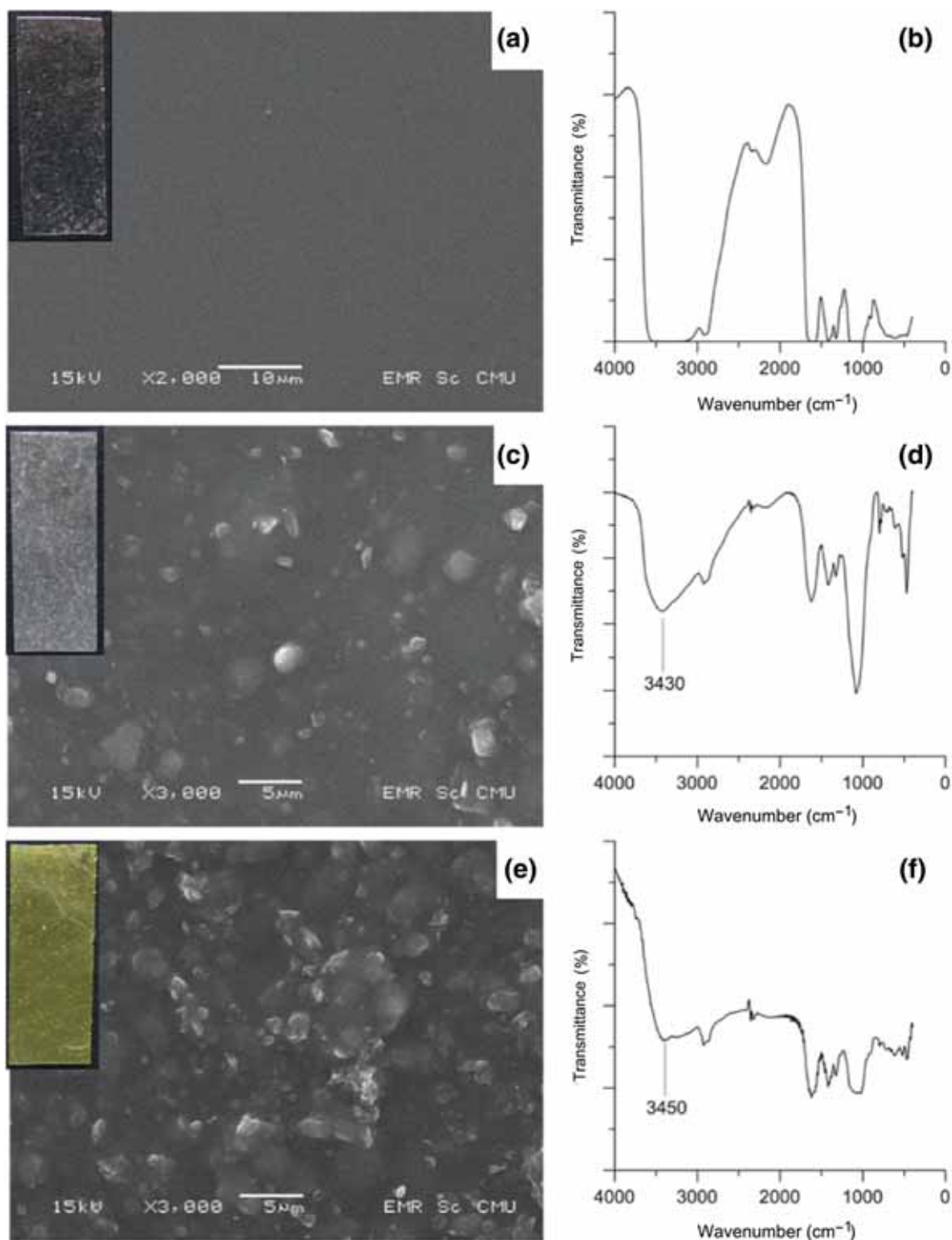


Figure 4. Typical (a, c and e) SEM images and (b, d and f) FTIR spectra of CMCh, Na-bentonite–CMCh and BBr-bentonite–CMCh films. Inset in SEM images are (a) CMCh, (c) Na-bentonite–CMCh and (e) BBr-bentonite–CMCh film samples.

16, 11 and 12% after seven batches of filtration, respectively (figure 5b). In most of the previous works, modified bentonite was dispersed in aqueous solution of OP insecticides

for the absorption study. Chlorpyrifos and methyl parathion were absorbed when modified bentonite in cationic micelles form was suspended in insecticides solution [9,38,46]. The

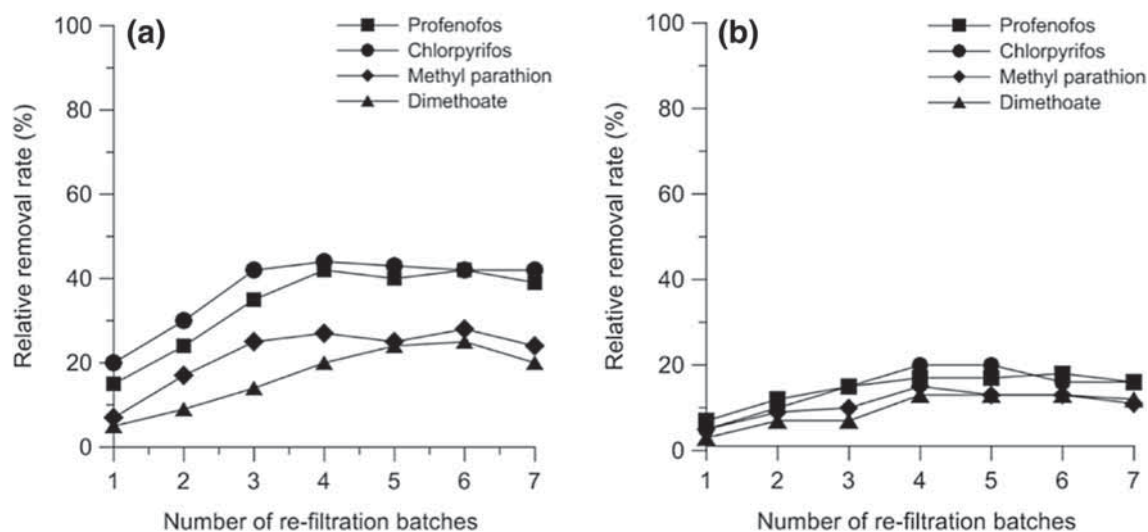


Figure 5. Removal rate of OP insecticides by modified bentonite–CMCh films by batch filtration. Data points are means of three parallel measurements (SD < 15%). Filtration mode using (a) CMCh–BBr–bentonite film and (b) CMCh–Na–bentonite film.

adsorption of profenofos and dimethoate used soils and clays as adsorbents in aqueous solution [41,47]. Dispersed bentonite was also applied to remove various herbicides and pesticides in aqueous solution [6,40,48]. Numerous works proved the absorptivity of modified bentonite to the various insecticides. However, the collection of the insecticide-absorbing bentonite remained technically as a ‘bottle neck’ for field application. It was difficult to separate the insecticide-absorbing bentonite in field application. Apparently, this work showed that OP insecticides were partly removed from contaminated water via batch filtration using modified bentonite films. Thus, OP-insecticide-absorbing film can be simply collected and replaced by new film materials.

The higher removal rate to OP insecticides of BBr-bentonite–CMCh film than that of Na-bentonite–CMCh film was deduced from the larger basal spacing between structural sheets of BBr-bentonite than that of Na-bentonite [17]. The absorption mechanism of tested OP insecticides possibly also followed the ‘C-type’ [15,49]. This described that the increase of the organic content alkaloid berberine in clays enhanced the absorption of diluted organic pesticide, e.g., metolachlor. Noticeably, there are possible hydrogen bond acceptors (=O, –Cl, –Br, –NO₂) in structures of tested OP insecticides, which are about 4, 5, 6 and 5 sites for profenofos, chlorpyrifos, methyl parathion and dimethoate, respectively (figure 1). Hence, water bridges can be formed between berberine and those insecticides to enhance the absorptivity of BBr-bentonite–CMCh film to tested OP insecticides.

Additionally, at the same concentration of 5 ppm in water, tested OP insecticides removal rate was in the order profenofos > chlorpyrifos > methyl parathion > dimethoate. This result is in accordance with the soil organic carbon water partition coefficient (K_{oc}) value of related insecticides, where ‘higher K_{oc} values correlate to low-mobility organic

chemicals while lower K_{oc} values correlate to more mobile organic chemicals’ [50]. K_{oc} in clay soils of profenofos, chlorpyrifos, methyl parathion and dimethoate takes values from 869 to 3162, 4381 to 6129, 366 to 1516 and 5.2 to 50, respectively [51,52]. As regards K_{oc} values, it was assumed that profenofos and chlorpyrifos were less mobile in modified bentonite or they were captured tightly by modified bentonite, whereas methyl parathion and dimethoate were more mobile in modified bentonite. This also reflected the higher profenofos and chlorpyrifos removal rates than methyl parathion and dimethoate removal rates by using modified bentonite.

3.5 Influence of film form and its microstructure on the absorption of tested OP insecticides

In this work, the modified bentonite was immobilized in CMCh via *in situ* polymerization of CMCh to form the modified bentonite–CMCh film material. Due to the water solubility property of CMCh, dispersal of modified bentonite inside the polymerized CMCh matrix is uniform when both materials can be mixed well before the casting of the film. The immobilized modified bentonite not only functions as an OP insecticide absorbent but also enhances the physical property of the hybrid film. FTIR spectra of BBr-bentonite–CMCh and Na-bentonite–CMCh film show peaks at 3450 and 3430 cm⁻¹, respectively, representing the vibration bands of the N–H bonded O–H between film components, e.g., hydroxyl group in hydroxylated silicate layers of bentonite might form hydrogen bonds to amine group in CMCh. The intercalation of BBr⁺ generated more cationic charge of modified bentonite, which interacted with anionic carboxyl group in CMCh. Thus, the film formation might be a result of strong electrostatic interaction between modified bentonite and CMCh

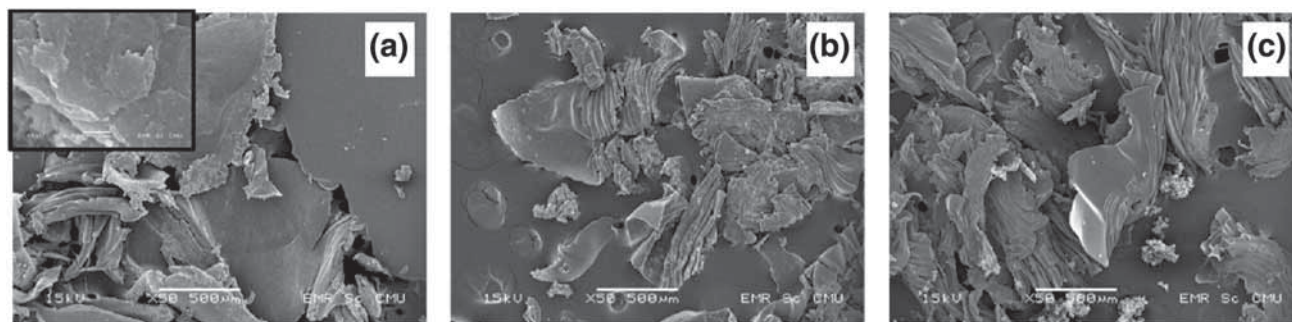


Figure 6. SEM images of surfaces of (a) profenofos-absorbing BBr-bentonite–CMCh, (b) Na-bentonite–CMCh and (c) CMCh film after three batches of filtration. Inset in a is the SEM of BBr-bentonite–CMCh film at magnification of $\times 20,000$.

components. The addition of 10% (v/v) BBr-bentonite or Na-bentonite increased the tension strength of both CMCh–BBr-bentonite and CMCh–Na-bentonite by approximately 15% in comparison with CMCh–bentonite, respectively (data not shown). Potassium persulphate-modified bentonite increased the tensile strength and restricted the degradation of the relevant chitosan–bentonite nanocomposites [26]. Another work showed that the addition of 3% (v/v) Na-bentonite into chitosan acetate solution also increased the stiffness and strength of the final film by 100% [53]. Thus, the modified bentonite–CMCh film form is easy to handle for absorption procedures.

A typical BBr-bentonite–CMCh film is revealed in figure 6a with sheets, and gaps between sheets. The inset image shows a structural ‘layer-upon-layer’ (top left inset in figure 6a). However, Na-bentonite–CMCh (figure 6b) and CMCh films (figure 6c) mostly composed of folding and twisting blocks and less space between these blocks. SEM results suggested that aqueous OP insecticide solution fluently flowed through the BBr-bentonite–CMCh film. The contact surface area between the tested OP insecticide solutions and BBr-bentonite–CMCh film (figure 6a) was obviously larger in comparison with that of Na-bentonite–CMCh film (figure 6b). Therefore, tested OP insecticide molecules probably interact at higher frequency with absorptive material in case of BBr-bentonite–CMCh film and it contributed to its higher OP insecticides removal rate than that of Na-bentonite–CMCh film.

4. Conclusions

A film composed of berberine-modified bentonite and CMCh is simply fabricated and applied for OP insecticides removal. The modified bentonite in the film can absorb OP insecticides from aqueous solution via rebatch filtration remarkably. The commercial bentonite clay, natural berberine powder and chitosan from shrimp are non-toxic and low-cost products; therefore, it is promising to develop an economic, eco-friendly and suitable film material to remove agricultural insecticide residues in agricultural run-off water zones.

Acknowledgements

We are thankful to the Department of Chemistry, Faculty of Science, and Microscope Unit of Chiang Mai University for HPLC analysis and SEM analysis supports.

References

- [1] Peng X, Luan Z, Zhang H and Tian B 2005 *J. Environ. Sci. Health A Tox. Hazard Subst. Environ. Eng.* **40** 1055
- [2] Yadanaparthi S K, Graybill D and von Wandruszka R 2009 *J. Hazard Mater.* **171** 1
- [3] Turan N G and Ozgonenel O 2013 *Sci. World J.* **2013** 342628
- [4] Naseem N and Tahir S S 2001 *Water Res.* **35** 3982
- [5] Barati A, Asgari M, Miri T and Eskandari Z 2013 *Environ. Sci. Pollut. Res. Int.* **20** 6242
- [6] Davies J E and Jabeen N 2003 *J. Incl. Phenom. Macrocycl. Chem.* **46** 57
- [7] Tha-in S, Dau H A and Dumri K 2013 *Int. J. Environ. Sci. Dev.* **4** 415
- [8] Mircioiu C, Voicu V A, Ionescu M, Miron D S, Radulescu F S and Nicolescu A C 2013 *Toxicol. Lett.* **219** 99
- [9] Bowman B T and Sans W W 1977 *Soil Sci. Soc. Am. J.* **41** 514
- [10] Wiles M C, Huebner H J, McDonald T J, Donnelly K C and Phillips T D 2005 *Chemosphere* **59** 1455
- [11] Ake C L, Wiles M C, Huebner H J, McDonald T J, Cosgriff D, Richardson M B *et al* 2003 *Chemosphere* **51** 835
- [12] Pal O R and Vanjara A K 2001 *Sep. Purif. Technol.* **24** 167
- [13] Celis R, Trigo C, Facenda G, Hermosin M C and Cornejo J 2007 *J. Agric. Food Chem.* **55** 6650
- [14] Rytwo G, Varman H, Bluvshstein N, König T N, Mendelovits A and Sandler A 2011 *Appl. Clay Sci.* **51** 43
- [15] Rytwo G, Gonen Y and Afuta S 2008 *Appl. Clay Sci.* **41** 47
- [16] Rojsanga P, Gritsanapan W and Suntornsuk L 2006 *Med. Princ. Pract.* **15** 373
- [17] Chulkov A N, Deineka V I, Tikhova A A, Vesentzev A I and Deineka L A 2012 *Russ. J. Phys. Chem. A* **86** 429
- [18] Giri T K, Thakur A, Alexander A, Badwaik A H and Tripathi D K 2012 *Acta Pharm. Sin. B* **2** 439
- [19] Upadhyaya L, Singh J, Agarwal V and Tewari R P 2013 *Carbohydr. Polym.* **91** 452

- [20] Vanamudan A, Bandwala K and Pamidimukkala P 2014 *Int. J. Biol. Macromol.* **69** 506
- [21] Liu Q, Yang B, Zhang L and Huang R 2015 *Int. J. Biol. Macromol.* **72** 1129
- [22] Nestic A R, Velickovic S J and Antonovic D G 2012 *J. Hazard Mater.* **209** 256
- [23] Celis R, Adelino M, Hermosin M C and Cornejo J 2012 *J. Hazard Mater.* **209** 67
- [24] Guo J, Chen S, Liu L, Li B, Yang P, Zhang L *et al* 2012 *J. Colloid Interface Sci.* **382** 61
- [25] Wang X, Du Y, Yang J, Tang Y and Luo J 2008 *J. Biomed. Mater. Res. A* **84** 384
- [26] Tan W, Zhang Y, Szeto Y and Liao L 2008 *Compos. Sci. Technol.* **68** 2917
- [27] WHO 2004 *The WHO recommended classification of pesticides by hazard and guidelines to classification* (Geneva: International Program on Chemicals Safety)
- [28] Panuwet P, Siriwong W, Prapamontol T, Ryan P B, Fiedler N, Robson M G *et al* 2012 *Environ. Sci. Policy* **17** 72
- [29] Wanwimolruk S, Kanchanamayoon O, Boonpangrak S and Prachayasittikul V 2015 *Environ. Health Prev. Med.* **20** 204
- [30] Anh D H, Cheunrungsikul K, Wichitwechkarn J and Surareungchai W 2011 *Biotechnol. J.* **6** 565
- [31] Kogel J E, Trivedi N C, Barker J M and Krukowski S T 2006 *Industrial minerals and rocks—commodities, markets, and uses* (New York: Society for Mining: Metallurgy, and Exploration Press)
- [32] Dananaj I, Frankovská J and Janotka I 2005 *Appl. Clay Sci.* **28** 223
- [33] Chen X G and Park H J 2003 *Carbohydr. Polym.* **53** 355
- [34] Jimtaisong A and Saewan N 2014 *Int. J. Cosmet. Sci.* **36** 12
- [35] Brugnerotto J, Lizardi J, Goycoolea F M, Argüelles-Monal W, Desbrières J and Rinaudo M 2001 *Polymer* **42** 3569
- [36] Shigemasa Y, Matsuura H, Sashiwa H and Saimoto H 1996 *Int. J. Biol. Macromol.* **18** 237
- [37] Jaidee A, Rachtanapun P and Luangkamin S 2012 *Adv. Mater. Res.* **506** 158
- [38] Suciú N A and Capri E 2009 *J. Environ. Sci. Health B* **44** 525
- [39] Shabeer T P A, Saha A, Gajbhiye V T, Gupta S, Manjaiah K M and Varghese E 2015 *Water Air Soil Pollut.* **226** 1
- [40] Ye P and Lemley A T 2008 *J. Agric. Food Chem.* **56** 10200
- [41] Spliid N H, Helweg A and Heinrichson K 2006 *Chemosphere* **65** 2223
- [42] Pang H T, Chen X G, Park H J, Cha D S and Kennedy J F 2007 *Carbohydr. Polym.* **69** 419
- [43] Thanou M, Verhoef J C and Junginger H E 2001 *Adv. Drug Deliv. Rev.* **52** 117
- [44] Williams L B and Haydel S E 2010 *Int. Geol. Rev.* **52** 745
- [45] Haydel S E, Remenih C M and Williams L B 2008 *J. Antimicrob. Chemother.* **61** 353
- [46] Seger M R and Maciel G E 2006 *Environ. Sci. Technol.* **40** 797
- [47] Kanazawa J 1989 *Environ. Toxicol. Chem.* **8** 477
- [48] Shabeer T P, Saha A, Gajbhiye V T, Gupta S, Manjaiah K M and Varghese E 2014 *Environ. Technol.* **35** 2619
- [49] Sparks D L 1995 *Environmental soil chemistry* (London: Academic Press)
- [50] EPA U S 1996 *Soil screening guidance: technical background document* EPA/540/R-95/128
- [51] <https://pubchem.ncbi.nlm.nih.gov/>
- [52] Howard P H 1991 *Handbook of environmental fate and exposure data for organic chemicals* (Florida: Taylor and Francis Group; CRC Press)
- [53] Giannakas A, Grigoriadi K, Leontiou A, Barkoula N M and Ladavos A 2014 *Carbohydr. Polym.* **108** 103