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Research paper

Chemical modification of commercial kaolin for mitigation of organic pollutants in environment *via* adsorption and generation of inorganic pesticides

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ABSTRACT

Contamination of water supplies with different organic pollutants from industrial and agricultural activities has received high concern recent years. Thus, efficient removal of these organic pollutants and minimize their usage in environment are highly recommended. Herein, we report hydrothermal chemical modifications of commercial kaolin (CK) in presence of sodium hydroxide (alkaline-modified kaolin; AMK) and disodium hydrogen phosphate (phosphate-modified kaolin; PMK) reagents. Interestingly, these chemical modifications altered the physico-chemical characteristics of CK in term of morphology, surface area and functionality which enhanced the adsorption capability of organic pollutants (*i.e.* methylene blue; MB) as well as offered an alternative inorganic pesticide that might reduce the consumption of organic pesticides. The results showed that, the equilibrium of MB adsorption is well described by Langmuir isotherm with maximum monolayer capacity of 434.78 and 476.19 mg/g for AMK and PMK, respectively. Furthermore, AMK and PMK revealed reasonable latent entomotoxic effect against cotton leafworm (*S. littoralis*) compared to a highly toxic organic pesticide (*i.e.* Methomyl). Therefore, the naturally abundant kaolin can be utilized efficiently to mitigate the organic pollutants in environment through sequestering of organics and generation of alternative inorganic pesticides for green plant protection.

1. Introduction

With the rapid development of chemical industry, different kinds of organic pollutants, such as phenols, aromatic hydrocarbons, dyes, pesticides and pharmaceuticals were produced and unavoidably released into the natural environment, which could cause serious deleterious impacts to aquatic and human health even at lower concentrations (Uddin et al., 2009; Wang et al., 2017). During the last decades, many researchers have focused on efficient sequestering of organic pollutants from aqueous solution. A variety of techniques have been adopted such as coagulation (Cañizares et al., 2006; Shi et al., 2007), chemical oxidation (Wu et al., 2008), membrane filtration (Lee et al., 2006), photocatalytic degradation (Jiang et al., 2012; Sánchez-Cantú et al., 2017), and adsorption (Anbia et al., 2010; Shi et al., 2011; Hegyesi et al., 2017). Among these methods, adsorption is an effective and widely applied method for removal and reclaim of various organic and inorganic adsorbents. Methylene blue (MB) is an aromatic heterocyclic organic compound with charged groups (SO_3^-, Na^+, $=NH^+$) used in rubbers as coloring agents and disinfectors, varnishes, pharmaceuticals, and pesticides industries. Although, it was listed as an essential medicine by world health organization, it has many side effects including mutations, allergic dermatitis, cancer, skin irritation, eye burns, cyanosis, methemoglobinemia, convulsions, dyspnea, tachycardia, gastrointestinal nausea, tract, diarrhea and vomiting in humans and animals (Vargas et al., 2011; Rehman et al., 2012). Therefore, MB containing wastewater should be treated before discharge to environment.

On the other hand, the rapid development of several agricultural activities leads to exaggerate using of several organic pesticides. As a result, over than 2.8 million tons of organic pesticides are consumed annually over the world. It has been estimated that only 0.1% of applied organic pesticides reach the target pests and leaving their bulk (99.9%) released to soil and water supplies and then were accumulated in food (Alavanja, 2009). According to the European Union (EU), the permissible concentrations of individual pesticides in drinking water and food of plant origin are 0.1 μg/L and 0.05 mg/kg, respectively (Chaara et al., 2010). Thus, several agricultural strategies were developed to reduce the consuming of agrochemicals including genetically

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engineered crops and integrated pest management. Recently, we have developed silica nanoparticles with different size and shape for cotton leafworm (*S. littoralis*) control. It was observed that, the pesticidal activity is significantly affected by particle size and surface functionality of nanosilica. However, the cost of the starting materials is still the major challenge for inorganic pesticides commercialization (Ayoub et al., 2017).

Kaolin is naturally abundant and low-cost material; widely used in many environmental, industrial and agricultural applications because it offers many interesting characteristics such as high mechanical and thermal stability and large surface area (Belver et al., 2002; Khraisheh et al., 2005; Sdiri et al., 2016). Kaolinite ($Al_2Si_2O_5(OH)_4$) is the major mineral component of kaolin. It is structurally consists of two interlinked layers, tetrahedral SiO_4 layer and octahedral $AlO_2(OH)_4$ layer (Bhattacharyya and Gupta, 2008). The net layer charge of kaolinite is zero, but in nature, kaolinite has a small net negative change arising from broken edges on its crystals which neutralized by the presence of Na^+ and K^+ ions. Metakaolinite (MK) is a metastable phase obtained by dehydroxylation of kaolinite at 550–950 °C. Many applications of CK have been recently reported such as catalyst support, adsorbent of many organic and inorganic toxins, paper-coating, filler added to plastic and rubber compounds, pigment additive in paints and pharmaceuticals (Sdiri et al., 2016). For adsorption of organic pollutants, montmorillonite, nontronite (Gürses et al., 2006), laponite (Schoonheydt and Heughebaert, 1992), sepiolite (Aznar et al., 1992) and smectitic (Abayazeed and El-Hinnawi, 2011) were used for adsorption of MB. However, the adsorption capability is relatively low. Therefore, the attention was turned to fabricate highly surface area carbon-based materials although they are expensive. Further, clay materials played an important role in agricultural processes *i.e.* nutrient cycling, plant growth and plant protection products (Zbik and Smart, 1998; Stucki, 2006). In the present manuscript, we report hydrothermal chemical modifications of commercial kaolin in presence of NaOH and Na_2HPO_4 reagents. The physicochemical features of modified CK are evaluated and explored to mitigate the organic pollutants in environment through study of MB adsorption and formulate alternative inorganic pesticides. The results revealed new perspectives on the MB adsorption and inorganic pesticide development against *S. littoralis*.

2. Experimental

2.1. Chemicals

All chemicals were used as received without any further purification. Methomyl (HPLC 99.7), methylene blue (MB), cetyltrimethyl ammonium bromide (CTAB), triton-X100 (TX-100), HCl, NaOH, Na_2HPO_4 were supplied from Sigma-Aldrich LTD. Commercial kaolin (CK) was purchased from MORGAN chemicals, Egypt. All solutions were prepared using double distilled water (> 18 Ωcm).

2.2. Cotton leafworm control

Laboratory strain of cotton leafworm (*Spodoptera littorals*) was cultured on leaves of the castor oil plant (*Ricinus communis* L) under constant laboratory conditions of 25 ± 2 °C and 65 ± 5% relative humidity (R. H) in Plant Protection Research Institute, A. R. C., Dokki – Giza, Egypt. The second instar larval stage of the insect was used in the pesticidal activity evaluation.

2.3. Modification of kaolin

Hydrothermal chemical treatment of CK was carried out in presence of NaOH and Na_2HPO_4 at relatively high temperature (Fig. S1, in supporting information). For AMK, 1.0 g of CK was mixed with 0.5 g of cetyltrimethyl ammonium bromide (CTAB) as soft template and dissolved in 50 mL solution of 10 M NaOH. The PMK was modified by mixing of 1.0 g of CK and 10 g Na_2HPO_4 and then dissolved in 50 mL of distilled water. After sonication for 30 min, both mixtures were transferred to Teflon-lined stainless steel autoclaves. The autoclaves were maintained at 160 °C for 12 h, and then allowed to cool down to room temperature. The precipitates were collected, washed several times with a mixture of water/ethanol until reach neutral pH and then dried in air at 60 °C for 1 h. The kaolin and modified kaolin materials were thermally treated at 550 °C for 6 h.

2.4. Characterization of kaolin materials

X-ray diffraction (XRD) of kaolin samples were performed using X-ray diffractometer (Model FW 1700 series, Philips, Netherlands) using with monochromatic CuK_α radiation ($\lambda = 1.54$ Å), employing a scanning rate of 0.060 min^{-1} and 2θ ranges from 4 to 80°. The diffraction data were analysed using the DIFRAC plus Evaluation Package (EVA) software with the PDF-2 Release 2009.

ATR-FTIR spectra of kaolin samples were recorded between 4000 cm^{-1} and 400 cm^{-1} on a Bruker ALPHA FTIR spectrometer. The FTIR spectrum was recorded in a refection mode since the layer is too flexible to be ground into a powder.

The textural surface properties and pore size distribution were determined by N_2 adsorption/desorption isotherms at 73 K with a NOVA 3200 apparatus, USA. The specific surface area (S_{BET}) was calculated using the Brunauer-Emmett-Teller (BET) method with multipoint adsorption data from the linear segment of the N_2 adsorption isotherm. The pore size distribution was determined from the analysis of desorption branch of isotherm using Barrett-Joyner-Halenda (BJH) method.

The morphology of kaolin samples was investigated using scanning electron microscopy (SEM JEOL model 5400 LV). Kaolin powders were ground and fixed onto a specimen stub using double-sided carbon tape. Then, a 10 nm Pt film was coated on kaolin sample using anion sputtering (Hitachi E-1030) at room temperature. The SEM was operated at 20 keV to obtain high-resolution SEM images. Transmission electron microscopy (TEM) was performed using a JEOL JEM model 2100 microscope. TEM was conducted at an acceleration voltage of 200 kV to obtain a lattice resolution of 0.1 nm. The TEM images were recorded using a CCD camera. The kaolin samples were dispersed in ethanol solution using an ultrasonic bath and then dropped on a copper grid. Prior insertion of the samples into the TEM column, the grid was dried for 20 min.

2.5. Adsorption studies of MB

Adsorption isotherms were performed *via* batch adsorption procedure by adding a suitable amount of kaolin or modified kaolin (25 mg) to a serious of 100 mL glass bottles containing 50 mL of MB solutions. The glass bottles were sealed and placed on a magnetic stirrer at 25 °C. After the adsorption experiment, the bottles samples were filtrated and separated from the adsorbent through a 0.45 μm membrane. Finally, the concentration of MB in filtrate samples was analysed by a UV–Vis spectrophotometer (JASCO V-770) at 665 nm. The equilibrium adsorption capacity of MB, q_e (mg/g), was evaluated by using the mass balance equation;

$$q_e = \frac{(C_o - C_e) \times V}{m}$$

where C_o and C_e are the initial and equilibrium concentrations of MB (mg/L), V is the volume of solution (L), and m is the mass of adsorbent used (g).The removal efficiency was calculated using the following equation;

$$(\text{removal}\%) = \frac{(C_o - C_e) \times 100}{C_o}$$

The influence of pH on MB adsorption was determined by carrying out the adsorption experiment in different solution pHs at 25 °C. The