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THE EFFECTS OF VARIED pH ON PAHs ADSORPTION ONTO THAI CLAY MINERALS IN SYNTHETIC SEA WATER.

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ABSTRACT

It had been assumed that several physicochemical reactions, especially the adsorption processes were controlled by pH in sea water. This study was aimed to investigate the effect of pH on the adsorption processes of polycyclic aromatic hydrocarbons (PAHs) onto the dominant Thai clay minerals, i.e., kaolinite and montmorillonite. In acidic condition, the adsorption of B[a]P onto both minerals was higher than that in neutral and basic conditions. This was explained by surface roughness and surface area, which increased in acidic conditions due to dissolved surface structure. The adsorption of B[a]P on montmorillonite was higher than that on kaolinite because of its higher surface area. The highest distribution coefficients (K_p) in kaolinite and montmorillonite were 200.3 and 443.5 L/kg, respectively. The Langmuir adsorption isotherm indicated that B[a]P adsorption might not be a monolayer or that it occurred at a non-specific site.

Keywards: Benzo[a]pyrene (B[a]P), PAHs adsorption, kaolinite, montmorillonite.

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INTRODUCTION

PAHs are widespread persistent natural and anthropogenic organic toxicants, especially prominent in fresh water and coastal sediments (Brion and Pelletier, 2005; Boonyatumanond et al., 2006; Culotta, 2006; Bishnoi et al., 2009). They tend to adsorb onto solid substrates, such as suspended particles, and bottom sediments in water. It has been reported that sedimentary PAHs can be assimilated by aquatic organisms and transformed into dial-epoxide that can attach to DNA chain, which can disturb translation and transcription processes resulting in genetic deformation (Skarphéðoinsdóttir et al., 2003).

The main source of coastal sedimentary PAHs in Thailand is from human activities similar to those in other Southeast Asian countries (Boonyatumanond et al., 2006). PAHs enter the upper Gulf of Thailand by rivers, such as the Chao Phraya River with an average influx of 179 ng/g-dry (Boonyatumanond et al., 2006). These PAHs may finally find their ways through direct adsorption onto aquatic organisms (Björk, 1995; Baumard et al., 1998; Ching et al., 2000).

In spite of the advantage of the location near the river and estuarine areas in terms of raw material delivery and transportation, many industries may also release both solid waste and effluences from the processes into the ambient aquatic environment. The pH range of waste water is varied, such as that in the brewery and winery effluent, which the pH values are varied from 4.5 to 12.0 (Rao et al., 2007; Agustina et al., 2008). The value of pH in electroplating wastewater is about 2.0 (Shiao-Shing et al., 2007), while those in the rayon industry and the municipal waste are 3.0, and 7.2, respectively (Vlyssides et al., 2002; Ghosh et al., 2010; Yao-Xing et al., 2010). Moreover, the biological processes, such as increasing algal photosynthesis may be accelerated by the abundance of nutrient in wastewater effluence consuming CO_2 in both gaseous and bicarbonate ions forms resulting in high pH value (Tadasse et al., 2004). As generally known, the pH of solution has influence on many physical and chemical processes that occur in natural water, and may also affect the PAHs adsorption onto the surface of the sediment.

This study was aimed to investigate the effect of pH of solution on surface structure changes, and the capability of the adsorption of PAHs onto kaolinite and montmorillonite.

MATERIALS AND METHODS

B[a]P was used as a measure of the representative of PAHs because of its carcinogenic property in laboratory animals (Moorthy et al., 2002).

Clay minerals

Kaolinite and montmorillonite standards were used as absorbent clay minerals. Kaolinite consisting of 95% kaolinite, and 5 % $CaCO_3$ which was supplied by Siam Fine Clay Thailand, while 90% purity montmorillonite was purchased from Thai Nippon Chemical Industry Co., Ltd., Thailand. The residual organic compounds in clay samples were removed by continuous boiling for seven days using hydrogen peroxide (H_2O_2) extraction technique (Yoothong et al., 1997). This treatment removes surface organics with no physical alteration to the minerals (Yim et al., 2000). The mineral surface structure before and after the extraction was observed by using Scanning Electron Microscopy (SEM). The average sizes of the mineral grains in kaolinite and montmorillonite were 13.97 μm and 4.08 μm, respectively. The average mineral specific surface area estimated by N-BET was 16.6 m^2 per g, and 750.6 m^2 per g for kaolinite and montmorillonite, respectively.

Solution phase

Synthetic sea water solution was prepared following the method of Kester et al. (1967), and Lopez et al. (2009). Sea water solutions at different pH conditions were obtained by adding 2-3 drops of 0.1 M of either NaOH or HCl. Salinity concentration used was 30 ppt prepared by adding appropriates amounts of deionized water (Milli-Q system, Millipore) to synthetic sea water.

B[a]P (Supelco, Thailand, No.48564) was dissolved in dimethylsulfoxide (DMSO) and subsequently added to sea water solutions at 0.5 mg/l. In order to avoid B[a]P biodegradations, 0.02% of sodium azide (w/v) was added as an antimicrobial agent in all experimental solution.

Batch experiments

The adsorption of PAHs on kaolinite and montmorillonite was determined in relation to pH at 4, 7, and 10, respectively. Clay minerals of 2 g were added to 30 ml of sea water containing 0.5 mg/l of B[a]P, and then mixed continuously. B[a]P in solution and the adsorbed ones were analyzed after 3, 6, 9, and 12 hours. Each experiment was run in a triplicate manner.

Solid and liquid phases of each solution were separated at the end of each experiment by centrifugation at 4,500 rpm for 15 min.

B[a]P analysis

The amount of B[a]P that adsorbed on clay surfaces was determined after samples were run freeze-dried process. B[a]P was extracted by the Soxhlet extraction method modified from several methods previously described by others (Suwanagosoom, 2001; Gfrerer et al., 2002; Hwang and Cutright, 2004), in which one gram of freeze-dried clay mineral was added to an extraction thimble, which fluorene was added as an internal standard. The thimble was then inserted into a 100 ml Soxhlet extractor filled with 150 solvent mixture of n-hexane – acetone (4:1, v/v). The extraction was run about 200 cycles for 24 h, and after the extraction, the solution was concentrated with a rotary evaporator and analyzed with a Gas Chromatography-Mass Spectrometer (GC-MS) (Agilent 6890/5973 GC/MS), with an Agilent HP-5ms Capillary GC Column. The initial temperature in the oven was increased to 90°C and maintained for 0.5 min, then sequentially increased at 17°C per minute to reach 200 °C, 9 °C per minute to reach 250 °C, and 10 °C per minute to reach 270 °C, after which it was maintained for 18 min.

The pH of solution was measured with a pH meter (DENVER Instrument UB-10) after it had been calibrated with US National Bureau of Standard buffers TEP 10 (pH 4, 7, 10, and Tris) obtained from WTW GmbH and Co. KG, Thailand.

RESULTS AND DISCUSSION

It was found that B[a]P was adsorbed on the surface of both minerals, and the adsorption was higher in an acidic (pH 4) condition than those in neutral pH (pH 7),and basic pH of sea water (pH 10) with statistic significant at $p < 0.05$, as shown in Figs. 1 and 2. The amount of B[a]P detected on kaolinite in acidic condition (pH 4) at the end of the experiment was 6.37 mg/kg, while that detected on montmorillonite was 6.74 mg/kg.

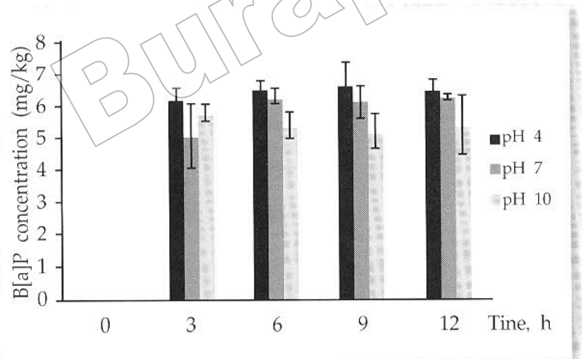

Figure 1. B[a]P concentration in kaolinite against time.

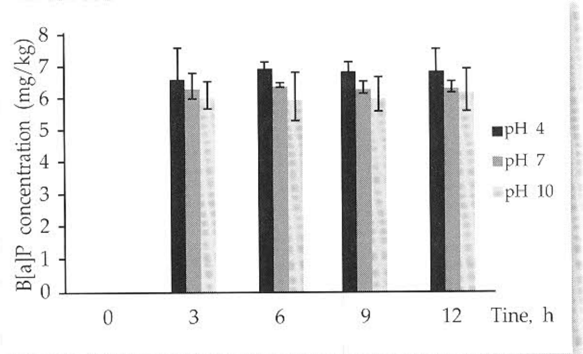

Figure 2. B[a]P concentration in montmorillonte against time.

An H^+ ion, in acidic pH condition, attaches to the silica and alumina surfaces of mineral structures that have negative charges which is known as protonation (Daqing et al., 1998; Bertsch and Seaman, 1999), and subsequently bring down the total surface charge to near zero, which resulting in an increase in its hydrophobicity (Wang et al., 1997; Kılıç and Hoşten, 2010). There is no change in the charge of B[a]P in this pH range at near zero charge of B[a]P molecule (Yang et al., 2001). Both phenomena contribute to the adsorption of B[a]P, which is a hydrophobic interaction under acidic conditions (Luthy et al., 1997; Li and Qu, 2007).

The adsorption capabilities of both minerals can be written in the form of distribution coefficient (*Kp*) as described in equation 1 and are illustrated in Figs. 3 and 4. An adsorption capability of montmorillonite was higher than that of kaolinite with statistic significant at $p < 0.05$. The highest *Kp* value of both minerals occurred at low pH, as 200.2 l/kg for kaolinite and 443.5 l/kg for montmorillonite, respectively. The higher adsorption capability of B[a]P on montmorillonite in our study was in agreement with that previously observed by Bowman et al. (2002) and may relate to its higher surface area.

$$\mathrm{Kp} = \frac{C_s}{C_w} \qquad (1)$$

This equation describes how the distribution coefficient is estimated, where C_s is the concentration of B[a]P that adsorbed on the mineral surface, and C_w is the concentration of B[a]P in the solution (Means, 1995; Tremblay et al., 2005).

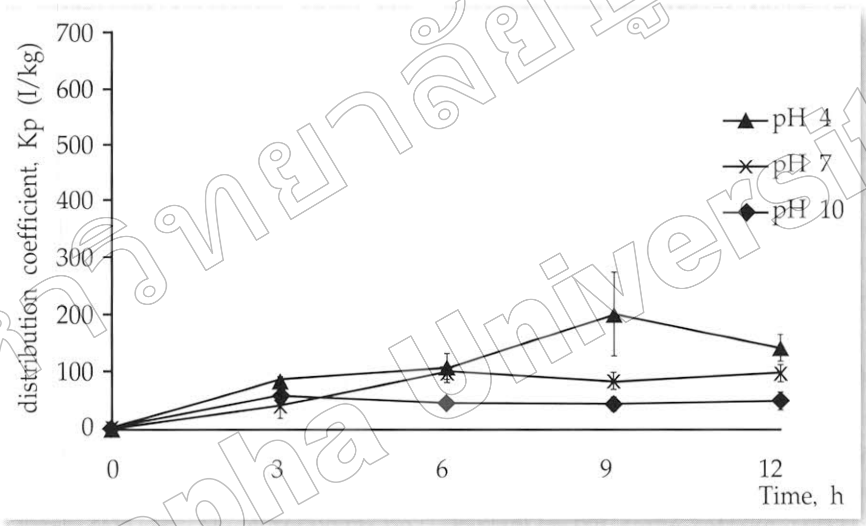

Figure 3. Kp values at different pH of kaolinite against time

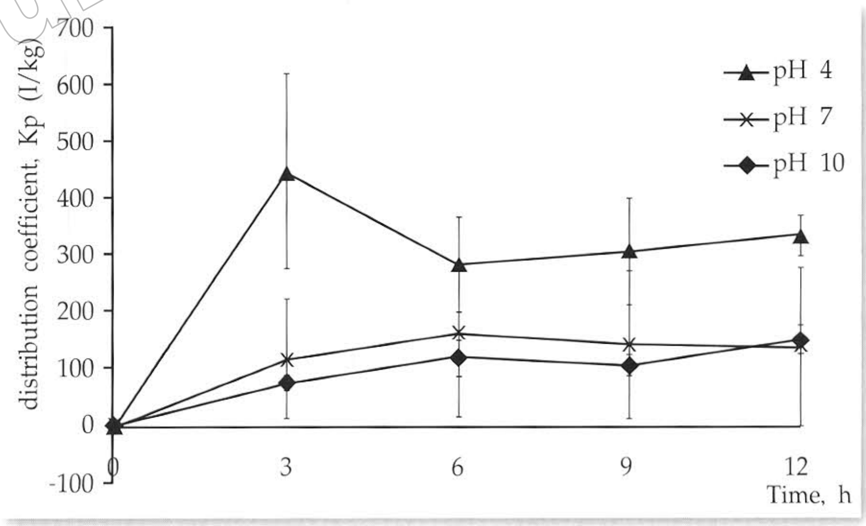

Figure 4. Kp values at different pH of montmorillonite against time

The adsorption capability data of B[a]P were applied to the Langmuir equation which is a general equation for adsorption study based on the assumption of monolayer adsorption and specific localized site (Czepirski et al., 2000). The correlation coefficient (R^2) was relatively low for both minerals (range from 0.344 to 0.770). Thus, it might be concluded that the adsorption of B[a]P is either multilayer or occurred at a non-specific site.

The changes in surface structure indicated that it was dissolved in acidic conditions due to an H^+ ion interacts with oxygen atom causing dissolution to form water molecules. This interaction is led to the increase of surface roughness and surface area (Fig. 5). This phenomenon suggested that higher adsorption capability of B[a]P occurred in acidic conditions in our experiment.

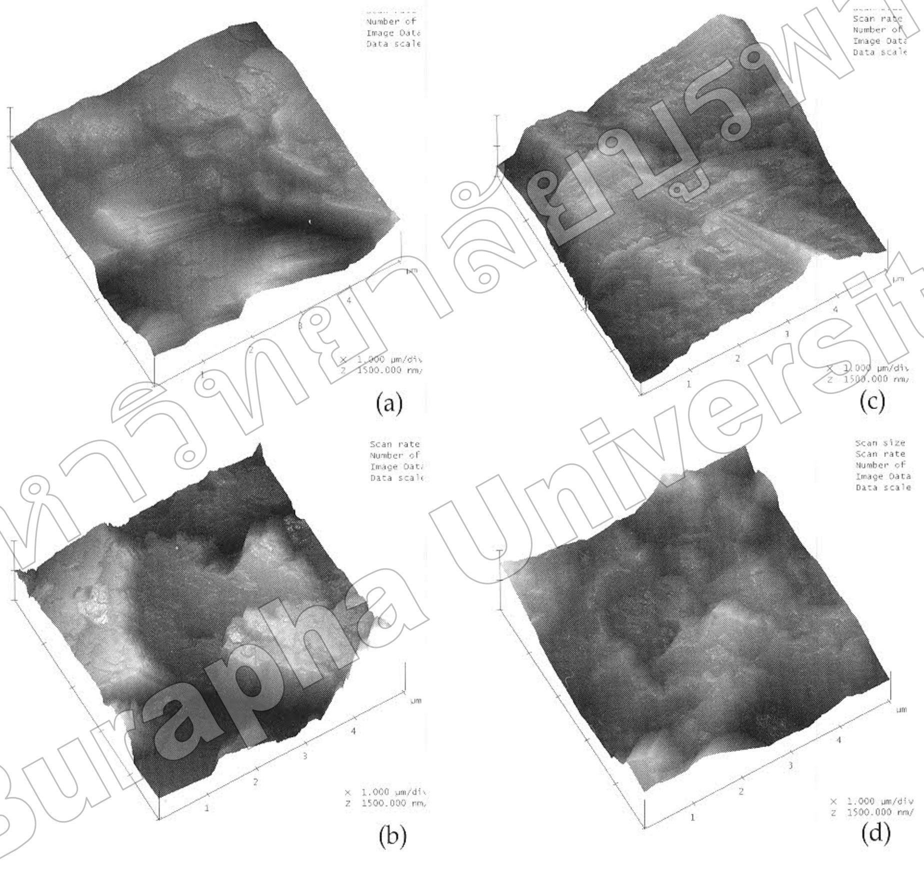

Figure 5. The Atomic Force Microscopic (AFM) images of mineral surfaces; kaolinite at 3 h (a) and 12 h (b), montmorillonite at 3 h (c) and 12 h (d).

In conclusion, after receiving partially treated and untreated wastewater from rivers, especially which from the Chao Phraya River, which flows through agricultural, industrial, and municipal areas, the pH in coastal sea water is varied due to the influence of receiving wastewater.

In general, the pH range of sea water in the upper Gulf of Thailand is between 6.8-7.6 (Cheevaporn and Menasveta, 2003). However, the wastewater discharged from several activities as previously mentioned, the pH value can turn to be more acidic levels (Rao et al., 2007; Shiao-Shing et al., 2007; Agustina, 2008; Ghosh et al., 2010). The results from this study indicated that B[a]P can be adsorbed onto the surface of clay minerals more in acidic conditions. Thus, other PAHs or toxic chemicals with similar hydrophobic properties can also be increasingly adsorbed on particular or sedimentary surfaces resulting in increasing its retention time in coastal environment.

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