Comparison study on the adsorption of a synthetic textile dye using bentonite and surfactant modified bentonite

Mark Jeeva* & Wan Zuhairi Wan Yaacob

Geology Programme, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor
*Corresponding author email address: mgva85@gmail.com

Abstract: Dyes entering waterways are less focused on since there are more reports of heavy metals, organic and inorganic compounds pollution. The main aim of this paper was to evaluate the adsorptive potential of Natural Bentonite (NB), Cetyltrimethylammonium Bromide Modified Bentonite (CTAB-Ben) and Cetylpridium Bromide Modified Bentonite (CPB-Ben) on an Anionic Azo Dye. The materials used for adsorption of Acid Blue 25 (AB 25) dye from an aqueous solution were identified using physical characteristics such as XRD, SEM, SSA and various test effects. The test effects efficiency of natural and surfactant modified Bentonite in adsorption of AB 25 dye has been applied as a function of equilibrium concentrations, pH, contact times and temperatures using the batch technique. The adsorption of AB 25 by CTAB-Ben and CPB-Ben compared to NB showed a clear increase in adsorption for the effects of equilibrium concentrations (74.033 ± 0.153 and 59.833 ± 0.153 compared to 6.877 ± 0.001), pH (24.065 ± 0.002 and 23.578 ± 0.002 compared to 5.990 ± 0.003), contact times and temperatures (45.55 ± 0.05 and 37.42 ± 0.02 compared to 12.18 ± 0.01) respectively. Adsorption isotherm of CTAB-Ben and CPB-Ben resulted in ($R^2= 0.96$) and ($R^2= 0.93, 0.92$) for Langmuir and Freundlich compared to ($R^2=0.94$) and ($R^2=0.89$) of NB respectively. From the comparison showed by increase in adsorption percentages (80-88%), both surfactants were better compared to NB (20%). However, in modified materials, CTAB-Ben is better compared to CPB-Ben based on the Qe values of all the test effects.

Keywords: Acid Blue 25 Dye, natural bentonite, surfactant modified bentonite, CTAB, CPB

INTRODUCTION

The future of Earth's environment is a cause for concern. Due to the rapid technological advancements and industrial developments in recent decades, they have brought about to a rise of environmental issues, particularly pollution of water resources (Kiransan, 2014). Synthetic dyes are one of the major classes of pollutants causing problems in waterways which their complex molecular structure gives them a stability and difficulty in removal (Ozcan, 2004). The presence of very low concentrations of these effluents is highly visible and undesirable, and potentially inhibiting photosynthesis (Won *et al.*, 2006). Untreated disposal of this colored water, even in small concentrations (< 1.0 mg/L) into receiving water body causes damage to aquatic life and also severely damages human bodies (Baskaralingam *et al.*, 2006).

Acid Blue 25 (AB25) belongs to an acid class; anionic colored compounds that is highly soluble in water, have been used to dye wool, nylon, silk fibers because of their striking colour ranges and have reactive groups which are able to form covalent bonds between dye and fiber. It is an aromatic compound with diazoic properties which causes this dye to be resistant to colour change (Akl, 2013).

Various technologies have been developed for the removal of synthetic dyes from water and wastewater to decrease its environmental impacts. These include physical methods, such as membrane filtration processes and sorption techniques; chemical methods, such as coagulation, electroflotation, advanced oxidation processes and irradiation; and biological methods, such as aerobic and anaerobic microbial degradation and the use of enzymes. Although chemical and biological methods are effective at removing dyes, they require specialized equipment and are usually energy intensive; in addition, large amounts of by-products are often generated. Conversely, the physical methods are generally effective at removing dyes without producing unwanted by-products (Pereira & Alves, 2012).

In the wide ranges of methods, adsorption of synthetic dyes on inexpensive and efficient solid supports has been considered a simple and economical process for the removal of dyes from water and wastewater, producing high quality water; this process is an attractive alternative for the treatment of contaminated water, particularly where the sorbent is inexpensive and does not require a pre-treatment step before its application. Adsorption is superior to other techniques for water reuse in terms of initial cost, flexibility and simplicity of the design, and ease of operation (Pereira & Alves, 2012). Alternatively, low-cost, novel, locally available adsorbents are currently used for the removal of textile dye effluents from aqueous solutions, instead of activated carbon. For instance, clays such as Sepiolite (Ozcan & Oncu, 2006), Zeolite (Armagan *et al.*, 2003), Montmorillonite (Wang *et al.,* 2004), Smectite (Ogawa *et al.*, 1996) and Bentonite (Ozcan & Erdem, 2004) can be used in these respects.

One of the clay minerals, which namely Bentonite, is composed of units made up of two Silica Tetrahedral sheets with a central Al Octahedral sheet. It has permanent negative charges that increase owing to the isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} for Al^{3+} in the octahedral layer. This negative charge is balanced by the presence of exchangeable cations (Na^+, Ca^{2+}, etc.) in the lattice structure. Acid and reactive dyes are water soluble anionic dyes, negatively charged and used

to dye textile fibers. As the non polar and water pollutants such as anionic dyes are negatively charged which causes weak adsorption, the negative surface of the natural clays has to be modified to increase the adsorption ability. Due to the absorption of anionic dyes that have weak attraction on the negative surface of bentonite, the clay is modified with loading of surfactant to eliminate anionic dyes. It is made possible by cation exchange mechanism using long chain or short chain cationic surfactants as the structure of clayey surfaces are permanently negative (Baskaralingam *et al.*, 2006). The frame of clay stores the surfactants on the outer surface where it forms a bilayer which alters the surface charge into positive, allowing anions and rejecting cations. The surfactant is then withheld in between bentonite layers (Li & Bowman, 1997). The adsorption of dye is by the mechanism of anionic exchange between the high amount of anions and the contaminant tail from the surfactant (Ma, 2011). Moreover, the occupation of exchange sites on the bentonite surface by organic cations (such as cationic surfactants) will change the surface properties from hydrophilic to hydrophobic to adsorb pollutants for low polarity. Therefore, there has been much interest in the use of modified bentonites as adsorbents to prevent and remediate environmental organic contamination. Thus, this modification with the introduction of organic cation increases the clay's adsorption capacity to compare with natural clay mineral and it can be used as an adsorbent for the adsorption of dyes (Ozcan & Erdem, 2004; Shen, 2001).

The main aim of this paper was to evaluate the adsorptive potency of Natural Bentonite (NB) compared to Cetyltrimethylammonium Bromide (CTAB) Modified Bentonite (CTAB-Ben) and Cetylpridium Bromide Modified Bentonite (CPB-Ben) on an anionic diazo dye. NB, CTAB-Ben and CPB-Ben were compared to effective adsorbents for Acid Blue 25 (AB25) dye from aqueous solution. The effects of experimental conditions on the removal amount, included adsorption time, pH, Zero Point Charge (pH_{zpc}), temperature, and equilibrium AB25 concentration were studied. The adsorption isotherm of AB25 onto NB, CTAB-Ben and CPB-Ben was determined by the equilibrium concentration and adsorption amount (Qe). Specific Surface Area (SSA), FTIR and XRD spectrums of AB25 adsorption using NB, CTAB-Ben and CPB-Ben were also studied to explain the differences and effectiveness of surfactant modified Bentonite in dye adsorption.

MATERIALS AND METHODS
Materials
The natural Bentonite (NB) material was purchased from R&M Pte. Ltd. All chemicals used in this study were of analytical reagent grade. Surfactants used were Cetyltrimetylammonium Bromide (CTAB), molecular weight 364.45 g/mol and Cetylpyridium Bromide (CPB), molecular weight 384.44 g/mol purchased from Merck Group. The dye used in this research was purchased from Sigma Aldrich. The NB was oven dried at 90°C, screened through a 110-mesh sieve and then stored in a desiccator

Table 1: Physical-chemical properties of Bentonite and modified Bentonite.

Parameters	NB	CTAB-Ben	CPB-Ben
Size (μm)	80-190	80-190	80-190
XRD	Quartz, Montmorillonite, Bentonite	Quartz, Montmorillonite, Vermiculite	Quartz, Montmorillonite, Vermiculite
CEC (meq/100g)	160	189	187
SSA (m²/g)	13.6	7.42	6.9
pH in distilled water	6	6.5	6.8

XRD- X-Ray Diffraction; CEC- Cationic Exchange Capacity; SSA- Specific Surface Area

prior to use. Selected physical-chemical properties of the Bentonite and modified Bentonite were listed in Table 1.

Preparation of modified adsorbent and dye sorption solutions
In order to synthesize surfactant modified CTAB-Ben/CPB-Ben nanomaterial, 10 g NB was first dispersed in 100 mL distilled water and stirred for 10 h at a stirring speed of 250 rpm to swell and to reach homogeneity. Then a desired amount of CTAB/CPB was slowly added. The amounts of surfactants were 0.3, 0.5, 0.7, 0.9, 1.1, 1.3, 1.5 of the CEC of NB thus, making modified Bentonite samples of 0.018, 0.029, 0.041, 0.053, 0.064, 0.076 and 0.0878 g of CTAB/CPB adsorbed in 1g of Bentonite. The mixture was stirred for 1 hour, then stirring was stopped and the resulted CTAB-Ben/CPB-Ben was filtered and washed with distilled water for several times to remove excess salts, tested with $AgNO_3$ solution to remove bromide ions and then dried at 90°C in an oven. The product was ground and sieved using standard sieves to obtain chemically modified adsorbent (Kiransan *et al.*, 2014). Stock solutions of AB 25 of different concentrations were prepared by dissolving different amounts of the dye in distilled water. 0.1 mol/L HCl or 0.1 mol/L NaOH solution was used for the pH adjustment (Jin *et al.*, 2013).

Chemical analysis and physical characterization
The FTIR spectra of NK and HMK were obtained using a Fourier Transform Infra Red (FTIR) Spectrometer (Fourier-380FT-IR, America). The spectrum was recorded from 400 to 4000 cm-1 with a resolution of 2 cm-1 using a pressed KBr pellet. X-ray diffraction (XRD) spectroscopy was collected by the DIFFRAC.EVA software operated at 40 kV and 40 mA. The XRD pattern was recorded from 1.5 to 50° of 2θ with a 2θ scanning speed of 0.028 of per second. Morphology of kaolinite particles and average particle size were determined by Field Emission Scanning Electron Microscopy (FESEM) Zeiss Supra 55VP. The SSA was determined using the Sears' Method (1956) which the

results were comparable to (±0.5 to ±1.0 difference) BET-N$_2$ method. 0.5 g of each clay was acidified with 0.1 M HCl to a pH 3–3.5. The volume was made up to 50 mL with distilled water after addition of 10.0 g of NaCl. The titration was carried out with standard 0.1 M NaOH in a thermostatic bath at 298 ± 0.5 K to pH 4.0, and then to pH 9.0. The surface area was computed from the following equation:

$$S \ (m^2/g) = 32V - 25 \qquad (1)$$

Where S = specific surface area of the adsorbent, V= volume of NaOH required to raise the titrate pH from 4.0 to 9.0.

Adsorption experiment

The adsorption of AB 25 dye by NB and CTAB-Ben/CPB-Ben was studied using batch experiments under the different conditions, included contact times (from 1 to 60 min), pH (from 2.0 to 11.0), initial AB 25 concentrations (from 10 to 200 mg/L) and temperatures (25 to 75°C). Batch experiments were performed in 50 mL capped plastic centrifuge tubes containing 50 mg/L AB 25 solutions (40 mL) and either NB or CTAB-Ben/CPB-Ben (0.1 g) in a shaker incubator at the desired temperature and 200 rpm. After shaking for 1 hour, the suspensions were centrifuged at 3000 rpm for 10 min (Jin et al., 2013; Unabonah et al., 2008). The dye concentration remained in the solution was determined by UV-VIS spectrophotometry. The amounts of AB 25 adsorbed by NB and CTAB-Ben/CPB-Ben were calculated by difference using the following formula:

$$Qe = \frac{(Co - Ce)V}{m} \qquad (2)$$

where Qe = the amount of dye adsorbed onto the natural Bentonite or modified Bentonite (mg/g), Co is the initial concentration dye (mg/L), Ce = the final value of dye concentration in the adsorbate (mg/L), V = the volume of dye used (ml) and m = weight of natural Bentonite or modified Bentonite used (mg).

Adsorption equilibrium is usually described by an isotherm equation which parameters express the surface properties and affinity of a solute on an adsorbent. Adsorption isotherms can be described by various models, of which the Langmuir and Freundlich models are the most common used (Unabonah et al., 2008). Adsorption equilibrium is usually described by an isotherm equation which parameters express the surface properties and affinity of a solute on an adsorbent. The Langmuir model assumes that adsorption of molecules occurs on a surface of adsorbent at a fixed temperature, forming a monolayer without any interaction between molecules adsorbed on the surface. The model can be described by the following equation:

$$\frac{Ce}{Qe} = \frac{1}{KlQm} + \frac{1}{Qm} \times Ce \qquad (3)$$

where Q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L); and Q_m (mg/g) and K_l (L/mg) are Langmuir constants.

Freundlich's equation can also be used to describe adsorption of solute on a heterogeneous surface and is expressed as:

$$\log Qe = \log Kf + \frac{1}{n}\log Ce \qquad (4)$$

where Qe is the amount adsorbed (mg/g), Ce is the equilibrium concentration of the adsorbate (mg/L); and KF ($mg^{1-1/n} \ L^{1/n} \ g^{-1}$) and n (g/L) are the Freundlich constants, representing characteristics of the system, such as the adsorptive capacity and the adsorption intensity, respectively (Jin et al., 2013).

Effects of temperature, pH, Point of Zero Charge (PZC), equilibrium concentration and time

Adsorption experiments were carried out at various constant temperatures in ranges of 25-75°C under the same adsorption isotherm experiments to explore the effect of temperature on adsorption of dye onto NB and CTAB-Ben/CPB-Ben. The effect of pH on dye adsorption by NB and CTAB-Ben/CPB-Ben was also examined in the initial pH ranges of 2 to 10 using Mettler-Toledo pH meter. The adsorbate was 40 ml of dye and solution pH was adjusted with 0.1 M NaOH and 0.1M HCl. The time effect was assigned to be in the ranges between 1 and 60 minutes. The equilibrium concentration value ranged from 1 mg/L to 500 mg/L in testing the adsorption extent of NB and CTAB-Ben/CPB-Ben toward AB 25 dye. Adsorbent (0.1g) was added in each adsorbate and reacted in the shaker for 24 h at 25°C.

The Point of Zero Charge (PZC) is an important characteristic of a solid phase immersed in a liquid medium and by knowing the PZC, conclusions on the sign of surface charge can be made, e.g. metal oxides are positively charged at pH<pH$_{PZC}$ and negatively charged at pH>pH$_{PZC}$, which give a better understanding of adsorption phenomena. Verification on the Point of Zero Charge was carried out using the technique adapted from Lazarevic et al. (2007). Initial pH values (pH$_i$) of 20mL of KCl solutions (concentrations 10−2 M) were adjusted in pH ranges of 2–11 using 0.01M of HCl or NaOH. Then, 0.1g of Bentonite was added to each sample. Equilibration was carried out by shaking, in a water shaker and incubator at 200rpm for 2h at 25±1°C. The dispersions were then filtered and the final pH of the solutions (pH$_f$) was determined. The point of zero charge was found from a plot of pHf versus pHi.

RESULTS AND DISCUSSIONS
Optimization of CTAB-Ben and CPB-Ben

Figure 1 shows the amount of CEC ratio of Bentonite to be used as an intercalated mass of CTAB in increment removal of AB 25. Adsorbent modification of CTAB-Ben and CPB-Ben with CEC value of 0.7 on 1g of Bentonite produced the most adsorbing amount of 44.2 mg/g and 354.2 mg/g respectively (Table 2), had a stable result compared to other CEC values. The intensity of the peak disappeared with further increasing of the amount of CTAB, implying the formation of the dominantly exfoliated nanostructure in CTAB-Ben for CEC of 0.8. As for CEC of 1.0 and 1.5,

Table 2: Sample replication statistical results for Figure 1.

CEC value	CTAB-Ben Qe1	CTAB-Ben Qe2	CTAB-Ben Qe3	Mean	Standard deviation	Relative standard deviation	Standard error
0.3	13.3	13.4	13.5	13.40	0.1	0.746	0.058
0.7	44.2	44.4	44.3	44.30	0.1	0.226	0.058
1	42.2	42.4	42.3	42.30	0.1	0.236	0.058
1.5	40.6	40.8	40.4	40.60	0.2	0.493	0.115

CEC value	CPB-Ben Qe1	CPB-Ben Qe2	CPB-Ben Qe3	Mean	Standard deviation	Relative standard deviation	Standard error
0.3	10	11	10.5	10.50	0.5	4.762	0.289
0.7	34.2	34.4	34.3	34.30	0.1	0.292	0.058
1	32.2	32.4	32.6	32.40	0.2	0.617	0.115
1.5	30	31	30.5	30.50	0.5	1.639	0.289
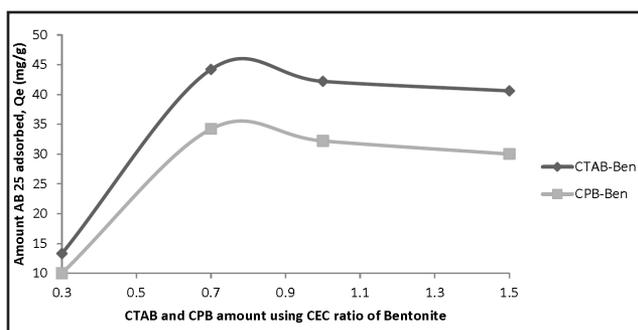
Figure 1: Relationship between amount of CTAB-Ben and CPB-Ben with amount of AB 25 adsorbed.

the stack density of organic cations in the interlayer space increases and the arrangement of organic cations changes because of the variety of charge in different layers (Kiransan *et al.*, 2014).

Characterization
FTIR analysis

FTIR results (Figure 2) of CTAB-Ben and CPB-Ben formed from NB showed the strong bands at 2932 and 3104 cm^{-1} attributed to asymmetric and symmetric stretching vibrations of C–H groups. A sharp peak located at 1572 cm^{-1} can be related to bending vibrations of NH_4^+, supported the intercalation of surfactant molecules between the silica layers. In the case of NB, the band in the region of 950–1104 cm^{-1} (stretching vibration of Si–O group divided into a sharp band at 1059 cm^{-1} and a shoulder around 1104 cm^{-1}) attributed to perpendicular Si–O stretching. The band shape changed and its frequency shifted to a lower wave number after the modification to CTAB-Ben. The absorption band of –OH and bending vibration of H_2O of NB shifted significantly from 1650 cm^{-1} (NB) to a low frequency of 1640 cm^{-1} after the modification (CTAB-Ben and CPB-Ben), which indicated the removal of water molecules and the change in the hydrophobicity of NB nanomaterial. This makes the CTAB to produce slightly more adsorption sites compared to CPB to increase in adsorption capacity of anionic dyes such as AB 25 (Ozcan & Oncu, 2006).
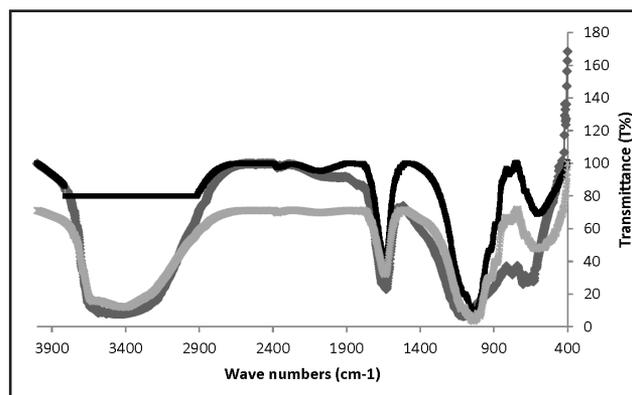
Figure 2: FTIR patterns of NB, CTAB-Ben and CPB-Ben.
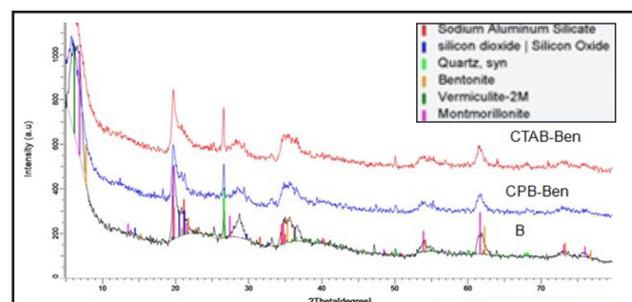
Figure 3: XRD patterns of NB, CPB-Ben and CTAB-Ben.

XRD and SEM analysis

The XRD patterns of NB, CTAB-Ben and CPB-Ben were given in Figure 3, which showed the peaks of Bentonite and quartz for NB and peaks of Montmorillonite and Vermiculite for CTAB-Ben and CPB-Ben. The XRD patterns showed no significant difference between NB, CTAB-Ben and CPB-Ben indicated the surfactants were not incorporated into the layers but covered the surface of NB after modification. The values signify difference from peaks of NB, CTAB-Ben and CPB-Ben because of ion-exchange, which intensity increment happens when the cationic sites of CTAB and CPB are modified on the surface of NB (Jin *et al.*, 2013). SEM micrographs of NB, CTAB-Ben and CPB-Ben were shown in Figure 4. The basal surface morphology of NB was not smooth but showed a very

complex surface structure on the extensive (basal) plane with flaky inter layers and ragged, broken nano-sized edges which supported the adsorption of CTAB and CPB. As a result, the surfactants were evenly spread on the surface of NB with a cluster layering formation (Ozcan, 2004). Despite the evenly spread surfactants, CTAB was more adsorbed on the surface of NB compared to CPB.

Test effects on NB, CTAB-Ben and CPB-Ben
Effects of pH
    The effect of pH on AB 25 removal was investigated overnight in the pH ranged 2.0–11.0 at 25°C with an AB 25 volume of 40 ml in 50 mg/L. From Figure 5, it showed that the maximal adsorption capability of NB was 5.99 mg/g compared with 23.578 mg/g for CPB-Ben and 24.065 mg/g for CTAB-Ben at pH 2.0 to pH 3.0 (Table 3). The pH significantly impacted more on the adsorption of AB 25 on CTAB-Ben > CPB-Ben > NB. As AB 25 was presented in solution as an anionic species, NB could hardly adsorb any AB 25 at any pH. The adsorption capacity of AB 25 with CTAB-Ben and CPB-Ben was increased with a general increase of pH values. Adsorption of clays at lower pH was higher and suggested that CTAB and CPB modification covered the NB surfaces with positive charges and increased electrochemical interactions between anionic AB 25 dye molecules and the modified clay surfaces. Negatively charged environment by AB 25 was readily adsorbed on positively charged clay surfaces due to stronger attractive forces at lower pH values. The high adsorption capacity was due to strong electrostatic interaction between the $N^+(CH_3)_3$ of CTAB, CPB and $Na_2O_9S^-$ tails of AB 25 dye. Moreover, at higher pH, more protons will be free resulted in electrostatic repulsions, has caused a decrease in AB 25 adsorption. Similar findings have been reported by Baskaralingam *et al*. (2006) and Jin *et al*. (2013). Adsorption of AB 25 on NB, CTAB-Ben and CPB-Ben is high in the pH ranged from 2.0 to 5.0, matched the value of PZC in Figure 6 with a similarity in initial and final adsorption at pH 2 to pH 3. Following these results, pH was corrected as 3 in the adsorption of AB 25 on NB, CTAB-Ben and CPB-Ben for all further test effect experiments.

    The dependence of final pH (pHf) versus initial pH (pHi) was plotted in Figure 6. The value of the Point of Zero Charge was obtained as the pH value at which the curve plateau appeared. At this pH value, a change in surface charge from positive to negative or vice versa has occurred. According to Figure 6, the plateau obtained at a pH value of 11 corresponded to the Point of Zero Charge of the CTAB-Ben and CPB-Ben (Table 4). Shift of the curves towards lower pHPZC with increasing ionic strength for the KCl solutions may have attributed to the formation of $SO^-·K^+$ surface complexes due to coulombic interactions (Ijagbemi *et al*., 2009).

Effect of equilibrium concentration
    Initial AB 25 concentrations were adjusted in the ranges of 10-500 mg/L for adsorption on NB, CTAB-Ben and CPB-Ben at pH 10 and 25°C for 24 hour interaction. As shown in Figure 7, increment in equilibrium AB 25 concentration resulted in an increase in adsorption of AB 25 on NB, CTAB-Ben and CPB-Ben. When concentration of AB 25 increased from 1 to 500 mg/L, the adsorption of AB 25 increased from 6.877 to 74.033 mg/g as the highest increase overall. The maximal adsorptive capacity of AB 25 on CTAB-Ben, CPB-Ben and NB were 74.033, 59.833 and 6.877 mg/g respectively (Table 5). Thus, the adsorptive capacity for AB 25 of CTAB-Ben increased about 9 times (88% increase) compared to NB. CTAB-Ben and CPB-Ben have more adsorption active sites available for further adsorption compared to NB as it saturated and plateau rapidly.
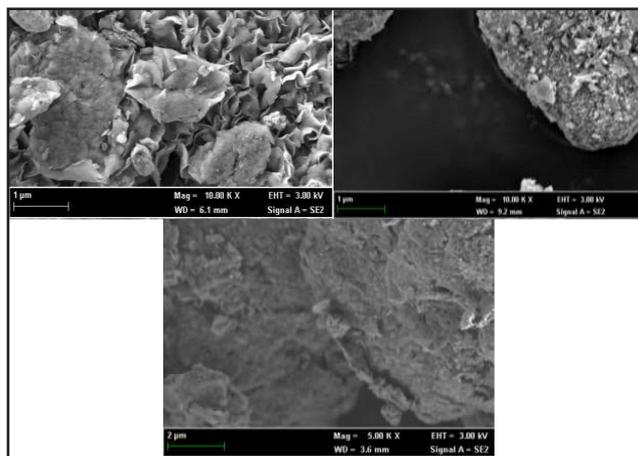
Figure 4: FESEM micrographs on CPB-Ben (left), CTAB-Ben (right) and NB (below).
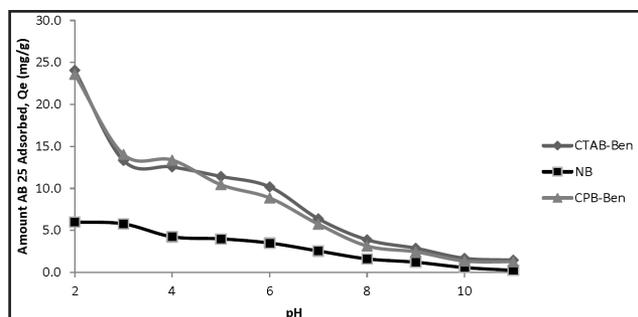
Figure 5: Effect of pH on the adsorption of AB 25 on NB, CTAB-Ben and CPB-Ben.
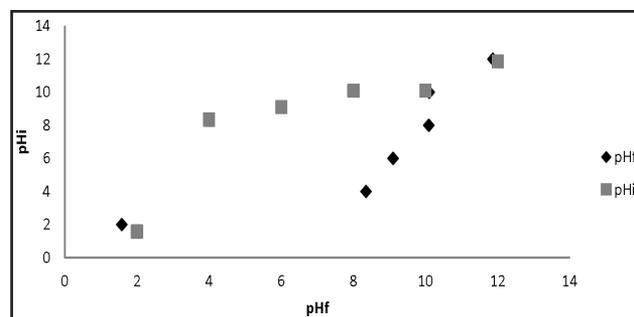
Figure 6: Dependence of pHf on pHi during equilibrium of 0.1g of CTAB-Ben and CPB-Ben with KCl to determine PZC.

Table 3: Sample replication statistical results for effect of pH.

pH	NB Qe1	NB Qe2	NB Qe3	Mean	Standard deviation	Relative standard deviation	Standard error
2	5.987	5.99	5.992	5.990	0.003	0.042	0.001
3	5.768	5.77	5.772	5.770	0.002	0.035	0.001
4	4.231	4.232	4.234	4.232	0.002	0.036	0.001
5	3.987	3.99	3.988	3.988	0.002	0.038	0.001
6	3.487	3.488	3.489	3.488	0.001	0.029	0.001
7	2.540	2.55	2.56	2.550	0.010	0.392	0.006
8	1.600	1.62	1.61	1.610	0.010	0.621	0.006
9	1.200	1.22	1.24	1.220	0.020	1.639	0.012
10	0.567	0.568	0.57	0.568	0.002	0.269	0.001
11	0.232	0.233	0.234	0.233	0.001	0.429	0.001

pH	CTAB-Ben Qe1	CTAB-Ben Qe2	CTAB-Ben Qe3	Mean	Standard deviation	Relative standard deviation	Standard error
2	24.063	24.065	24.07	24.065	0.002	0.007	0.001
3	13.318	13.32	13.32	13.319	0.001	0.009	0.001
4	12.553	12.555	12.56	12.555	0.002	0.016	0.001
5	11.416	11.418	11.42	11.418	0.002	0.019	0.001
6	10.180	10.182	10.18	10.181	0.001	0.008	0.000
7	6.377	6.378	6.38	6.378	0.002	0.028	0.001
8	3.877	3.88	3.879	3.879	0.002	0.046	0.001
9	2.865	2.866	2.868	2.866	0.002	0.058	0.001
10	1.671	1.672	1.674	1.672	0.002	0.102	0.001
11	1.455	1.456	1.458	1.456	0.002	0.108	0.001

pH	CPB-Ben Qe1	CPB-Ben Qe2	CPB-Ben Qe3	Mean	Standard deviation	Relative standard deviation	Standard error
2	23.576	23.578	23.58	23.578	0.002	0.008	0.001
3	14.045	14.046	14.05	14.046	0.002	0.011	0.001
4	13.367	13.368	13.37	13.368	0.002	0.011	0.001
5	10.435	10.436	10.44	10.437	0.002	0.020	0.001
6	8.854	8.855	8.856	8.855	0.001	0.011	0.001
7	5.734	5.375	5.376	5.495	0.207	3.767	0.120
8	3.134	3.135	3.138	3.136	0.002	0.066	0.001
9	2.435	2.436	2.438	2.436	0.002	0.063	0.001
10	1.345	1.346	1.347	1.346	0.001	0.074	0.001
11	1.254	1.255	1.256	1.255	0.001	0.080	0.001

Effect of temperature and time

Initial adsorption of AB 25 on CTAB-Ben and CPB-Ben was rapid and adsorption capacity increased with increasing contact time within the first 20 min (Figure 8), and remained almost constant suggested that the adsorption occurred on the exterior surface of the clay compared to the flat rate of slow adsorption of NB. Therefore, a contact time range of 90 minutes was allowed for maximum adsorption as the remained concentration of AB 25 after peaking was almost asymptotic to the time axis. Following the increasing adsorption during the final 10 minutes, diffusion into the internal clay particles controlled the adsorption rate as the exterior surface of the clay became saturated.

After the equilibrium time, the rate of AB 25 adsorption reached plateau and amount of AB 25 adsorbed remained the same. Temperature ranged from 25°C till 65°C (Figure 8) where the results indicated an extensive increase of AB 25 adsorption on CTAB-Ben and CPB-Ben ranged from 36.667 to 46.55 mg/g, compared to the flat readings of NB (Table 6). Increasing adsorption capacity with increasing temperature shows that the adsorption of NB is controlled by an endothermic reaction (Jin *et al.*, 2013).

Adsorption isotherm

As listed in Table 7, linear plots of Ce/Qe versus Ce were used to determine Q_{max} and K_L. The Langmuir

Table 4: Sample replication statistical results for PZC.

PZC	pH1	pH2	pH3	Mean	Standard deviation	Relative standard deviation	Standard error
2	1.58	1.63	1.6	1.60	0.025	1.570	0.015
4	8.35	8.45	8.4	8.40	0.050	0.595	0.029
6	9.1	9.2	9.15	9.15	0.050	0.546	0.029
8	10.09	10.15	10.1	10.11	0.032	0.318	0.019
10	10.1	10.15	10.13	10.13	0.025	0.249	0.015
12	11.87	11.9	11.85	11.87	0.025	0.212	0.015

Table 5: Sample replication statistical results for equilibrium concentration effects.

Ce NB	Qe1	Qe2	Qe3	Mean	Standard deviation	Relative standard deviation	Standard error
0.755	0.245	0.246	0.247	0.246	0.001	0.407	0.001
18.010	1.987	1.99	1.988	1.988	0.002	0.077	0.001
47.500	2.543	2.545	2.544	2.544	0.001	0.039	0.001
96.200	3.789	3.79	3.788	3.789	0.001	0.026	0.001
195.710	4.287	4.288	4.29	4.288	0.002	0.036	0.001
294.000	5.964	5.965	5.966	5.965	0.001	0.017	0.001
393.600	6.389	6.39	6.388	6.389	0.001	0.016	0.001
493.200	6.876	6.878	6.877	6.877	0.001	0.015	0.001
Ce CTAB-Ben	Qe1	Qe2	Qe3	Mean	Standard deviation	Relative standard deviation	Standard error
0.359	0.641	0.644	0.642	0.642	0.002	0.238	0.001
13.624	6.376	6.377	6.378	6.377	0.001	0.016	0.001
41.890	8.110	8.12	8.14	8.123	0.015	0.188	0.009
85.300	14.700	14.74	14.72	14.720	0.020	0.136	0.012
189.000	31.000	31.2	31.3	31.167	0.153	0.490	0.088
258.900	41.100	41.2	41.3	41.200	0.100	0.243	0.058
327.000	73.000	73.2	73.3	73.167	0.153	0.209	0.088
426.100	73.9	74	74.2	74.033	0.153	0.206	0.088
Ce CPB-Ben	Qe1	Qe2	Qe3	mean	Standard deviation	Relative standard deviation	Standard error
0.571	0.429	0.43	0.432	0.430	0.002	0.355	0.001
13.623	1.377	1.378	1.379	1.378	0.001	0.073	0.001
46.251	3.749	3.75	3.76	3.753	0.006	0.162	0.004
65.000	18.000	18.1	18.2	18.100	0.100	0.552	0.058
189.000	35.000	35.2	35.4	35.200	0.200	0.568	0.115
265.000	45.000	45.3	45.2	45.167	0.153	0.338	0.088
341.000	59.000	59.2	59.1	59.100	0.100	0.169	0.058
493.000	59.7	59.8	60	59.833	0.153	0.255	0.088
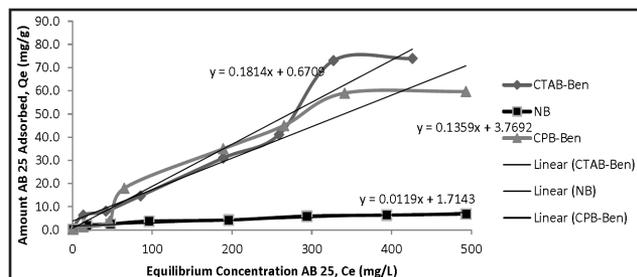
Figure 7: Equilibrium concentrations on the adsorption of AB 25 on CTAB-Ben, CPB-Ben and NB.
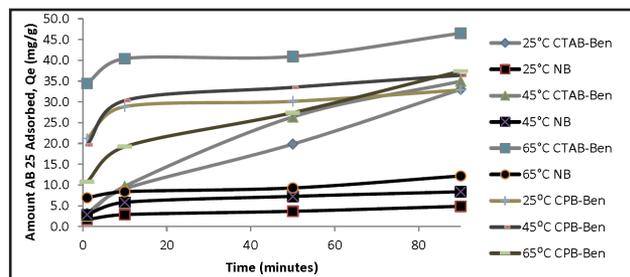
Figure 8: Test effects of temperature and time on the adsorption of AB 25 on CTAB-Ben, CPB-Ben and NB.

Table 6: Sample replication statistical results for temperature and time effects.

Material	Temperature (°c)	Time	Qe1	Qe2	Qe3	Mean	Standard deviation	Relative standard deviation	Standard error
NB	25	1	1.650	1.67	1.68	1.667	0.015	0.917	0.009
		10	2.870	2.88	2.89	2.880	0.010	0.347	0.006
		50	3.670	3.68	3.69	3.680	0.010	0.272	0.006
		90	4.870	4.88	4.89	4.880	0.010	0.205	0.006
	45	1	2.860	2.88	2.89	2.877	0.015	0.531	0.009
		10	5.826	5.828	5.829	5.828	0.002	0.026	0.001
		50	7.260	7.28	7.29	7.277	0.015	0.210	0.009
		90	8.370	8.38	8.4	8.383	0.015	0.182	0.009
	65	1	6.930	6.94	6.95	6.940	0.010	0.144	0.006
		10	8.390	8.4	8.41	8.400	0.010	0.119	0.006
		50	9.287	9.29	9.3	9.292	0.007	0.073	0.004
		90	12.170	12.18	12.19	12.180	0.010	0.082	0.006
CTAB-Ben	25	1	3.161	3.162	3.165	3.163	0.002	0.066	0.001
		10	9.072	9.073	9.074	9.073	0.001	0.011	0.001
		50	19.826	19.828	19.83	19.828	0.002	0.010	0.001
		90	33.013	33.015	33.01	33.014	0.001	0.003	0.001
	45	1	2.510	2.52	2.54	2.523	0.015	0.605	0.009
		10	9.690	9.7	9.72	9.703	0.015	0.157	0.009
		50	26.369	26.37	26.38	26.373	0.006	0.023	0.004
		90	34.960	34.98	34.99	34.977	0.015	0.044	0.009
	65	1	34.400	34.5	34.6	34.500	0.100	0.290	0.058
		10	40.400	40.5	40.6	40.500	0.100	0.247	0.058
		50	40.900	40.93	40.95	40.927	0.025	0.061	0.015
		90	46.500	46.6	46.55	46.550	0.050	0.107	0.029
CPB-Ben	25	1	21.168	21.17	21.18	21.173	0.006	0.030	0.004
		10	28.852	28.855	28.6	28.769	0.146	0.509	0.085
		50	30.120	30.15	30.2	30.157	0.040	0.134	0.023
		90	32.860	32.88	32.9	32.880	0.020	0.061	0.012
	45	1	29.000	29.2	29.4	29.200	0.200	0.407	0.115
		10	30.300	30.5	30.6	30.467	0.153	0.501	0.088
		50	33.500	33.7	34	33.733	0.252	0.746	0.145
		90	36.400	37	36.6	36.667	0.306	0.833	0.176
	65	1	10.732	10.735	10.74	10.735	0.003	0.028	0.002
		10	19.200	19.22	19.24	19.220	0.020	0.104	0.012
		50	27.400	27.42	27.44	27.420	0.020	0.073	0.012
		90	37.400	37.42	37.44	37.420	0.020	0.053	0.012

adsorption Q_{max} of CTAB-Ben and CPB-Ben was high (22.8 mg/g) compared to the Q_0 of NB (6.8 mg/g) which constitutes to a low value for Ce/Qe of CTAB-Ben (13.78) and CPB-Ben (8.27) compared to NB (72.5) (Table 8). Langmuir equilibrium constants b, were 0.13, 0.01 and 0.03 L/mg for CTAB-Ben, CPB-Ben and NB respectively have showed the drop in adsorption for CPB-Ben compared to NB. Comparison of the correlation coefficients showed that the Langmuir equation ($R^2 = 0.96$ and 0.93) fit the

adsorption of AB 25 on CTAB-Ben and CPB-Ben better than the Freundlich equation ($R^2 = 0.89$ and 0.92). Jaynes & Boyd (1991) proposed that the adsorption conformed to the Langmuir and Freundlich models (Figure 9 and Figure 10) when the value of correlation coefficient (R^2) was greater than 0.89. As a result, the indications were that CTAB-Ben, CPB-Ben and NB were suitable adsorbents for the removal of AB 25 from aqueous solution. From linear plots of the Freundlich isotherm, K_f and n were

Table 7: Isothermal equation parameters of the adsorption of AB 25 on CTAB-Ben, CPB-Ben and NB.

Adsorbent	Langmuir			Freundlich		
	q_{max} (mg/g)	b (L/mg)	R^2	K_f (mg/g)	n	R^2
Bentonite	6.8	0.03	0.94	51.29	10	0.89
CTAB-Ben	73.9	0.13	0.96	4677	5.56	0.96
CPB-Ben	59.7	0.01	0.93	3981	7.14	0.92

Table 8: Sample replication results for Langmuir isotherm values.

Ce NB	Ce/Qe1	Ce/Qe2	Ce/Qe3	Mean	Standard deviation	Relative standard deviation	Standard error
0.755	3.082	3.085	3.09	3.086	0.004	0.131	0.002
18.010	9.063	9.068	9.06	9.064	0.004	0.045	0.002
47.500	18.68	18.7	18.72	18.700	0.020	0.107	0.012
96.200	25.39	25.4	25.42	25.403	0.015	0.060	0.009
195.710	45.65	45.7	45.64	45.663	0.032	0.070	0.019
294.000	49.3	49	49.5	49.267	0.252	0.511	0.145
393.600	61.6	62	61.5	61.700	0.265	0.429	0.153
493.200	72.73	72.6	72.5	72.610	0.115	0.159	0.067
Ce CTAB-Ben	Ce/Qe1	Ce/Qe2	Ce/Qe3	Mean	Standard deviation	Relative standard deviation	Standard error
0.359	0.56	0.58	0.57	0.570	0.010	1.754	0.006
13.624	2.14	2.17	2.16	2.157	0.015	0.708	0.009
41.890	5.17	5.18	5.16	5.170	0.010	0.193	0.006
85.300	5.8	6	5.9	5.900	0.100	1.695	0.058
189.000	8.1	8	8.2	8.100	0.100	1.235	0.058
258.900	9.3	9.5	9.4	9.400	0.100	1.064	0.058
327.000	12.67	12.68	12.66	12.670	0.010	0.079	0.006
426.100	13.77	13.78	13.79	13.780	0.010	0.073	0.006
Ce CPB-Ben	Ce/Qe1	Ce/Qe2	Ce/Qe3	Mean	Standard deviation	Relative standard deviation	Standard error
0.571	1.33	1.35	1.34	1.34	0.010	0.746	0.006
13.623	1.89	1.9	2	1.93	0.061	3.152	0.035
46.251	2.34	2.35	2.36	2.35	0.010	0.426	0.006
65.000	3.61	3.6	3.62	3.61	0.010	0.277	0.006
189.000	5.4	5.5	5.6	5.5	0.100	1.818	0.058
265.000	5.89	5.9	5.88	5.89	0.010	0.170	0.006
341.000	5.78	5.8	5.79	5.79	0.010	0.173	0.006
493.000	8.26	8.28	8.27	8.27	0.010	0.121	0.006

found to be 4677 and 3981, 5.56 and 7.14 respectively for CTAB-Ben, CPB-Ben and 51.29 and 10 g/L for NB, respectively. If a value for n was equal to unity, this implied that adsorption process was chemical, but a value for n was above to unity, adsorption was favorable a physical process. Since the Freundlich constant n was greater than 1, this indicated that adsorption was favorable physical process under the studied conditions. The obtained n value was assigned to the heterogeneous nature of adsorbent surface with an exponential distribution of the adsorption energy sites (Granados-Correa & Becerril, 2009). The Langmuir and Freundlich constants both suggested that CTAB-Ben and CPB-Ben have a higher adsorptive capacity than that of NB for removing AB 25 from aqueous solution. The applicability of the two isotherm models to the all investigated systems implied that both monolayer
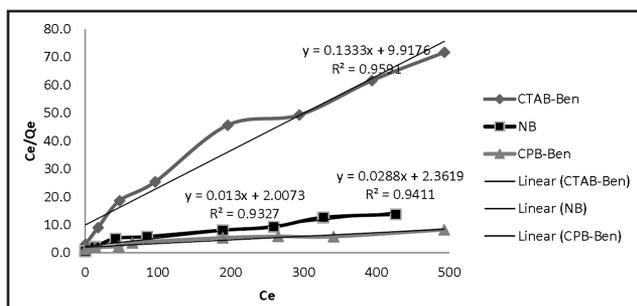
Figure 9: Langmuir isotherm graph for NB, CTAB-Ben and CPB-Ben.

Figure 10: Freundlich isotherm graph for NB, CTAB-Ben and CPB-Ben.

adsorption (i.e., only a limited number of surface sites are adsorbing sites) and heterogeneous surface conditions existed under the experimental conditions studied. Organically modified clays were much more efficient adsorbents of AB 25 than the unmodified NB.

CONCLUSION

The modification of natural Bentonite with CTAB and CPB have increased the CEC significantly, but decreased the specific surface area as the surfactant took over active sites along with the surface space of NB and as a result, CTAB and CPB can be used to remove AB 25 from aqueous solution. The amount of AB 25 adsorbed on CTAB and CPB compared to NB was 6 times higher (83%) in temperature and time tests, 5 times higher (80%) in pH changes from 5.0 to 11.0, and 9 times (88%) higher in maximum equilibrium concentration adsorption. FTIR and XRD analysis showed that CTAB and CPB adsorbed on the surface of the Bentonite were responsible for the AB 25 adsorption. The Langmuir equation ($R^2 = 0.96$) was the best fit for the adsorption of AB 25 on CTAB and CPB showed that the adsorption of AB 25 occurred on the surface of CTAB and CPB. The test effects results showed CTAB-Ben was the better modified component but there were some exceptions on results in the early parts of the temperature and time batch tests that slightly favored CPB-Ben. Overall, these results showed that little amount of surfactant modified Bentonite was very efficient and cost effective in removing AB 25 dye from the water systems.

ACKNOWLEDGEMENTS

REFERENCES

Armagan, B., Ozdemir, O., Turan, M. & Celik, M.S., 2003. The removal of reactive azodyes by natural and modified Zeolites. J. Chem. Technol. Biotechnol., 78, 725–732.

Baskaralingam, P., Pulikesi, M., Elango D., Ramamurthy, V. & Sivanesan, S., 2006. Adsorption of acid dye onto organo Bentonite. J. Hazard. Mater., 128, 138–144.

Dantas, T.N.D.C., Beltrame, L.T.C., Neto, A.A.D. & Moura, M.C.P.A., 2004. Use of microemulsions for removal of color and dyes from textile wastewater. J. Chem. Technol. Biotechnol., 79, 645–650.
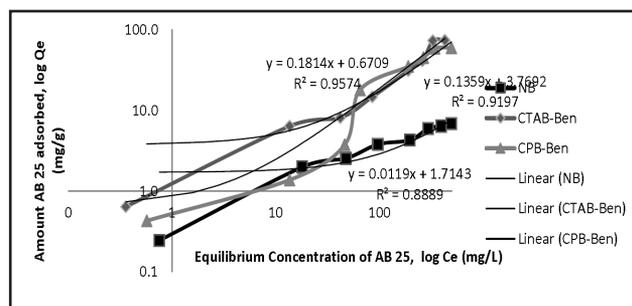
Granados-Correa, J.F. & Becerril, J., 2009. Chromium (VI) adsorption on boehmite. Applied Clay Science, 35, 250–257.

Ijagbemi, C.O., Baek, M.H. & Kim, D.S., 2009. Montmorillonite surface properties and sorption characteristics for heavy metal removal from aqueous solutions. J. Hazard. Mater., 166, 538–546.

Jaynes, W.F. & Boyd, S.A., 1991. Hydrrophobicity of siloxane surfaces in Smectites as revealed by aromatic hydrocarbon adsorption from water. Clays and Clay Miner., 39(4), 428-436.

Jin, X., Jiang, M., Du, J. & Chen, Z., 2013. Removal of Cr(VI) from aqueous solution by surfactant-modified kaolinite. Ind. Eng. Chem. Res., 20, 3025–3032.

Kiransan, M., Reza, D.C.S., Hassani, A. & Khataee, A., 2014. Preparation of cetyltrimethylammonium bromide modified montmorillonite nanomaterial for adsorption of a textile dye. J. Taiwan Inst. Chem. Eng., 45(5), 2565-2577.

Lazarevic, S., Jankovic-Castvan, I., Jovanovic, D. & Petrovic, R., 2007. Adsorption of Pb^{2+} Cd^{2+} and Sr^{2+} ions onto natural and acid-activated Sepiolites. Appl. Clay Sci., 73, 47–57.

Li, Z. & Bowman, R.S., 1997. Counter ion effects on the sorption of cationic surfactant and chromate on natural clinoptiloite. Environ. Sci. Techonol., 31, 2407–2412.

Ma, J., Cui, B., Dai, J. & Li, D., 2011. Mechanism of adsorption of anionic dye from aqueous solutions onto organobentonite. J. Hazard Mater., 186, 1758-1765.

Ogawa, M., Kawai, R. & Kuroda, K., 1996. Adsorption and aggregation of a cationic cyanine dye on Smectites. J. Phys. Chem. (US), 100, 16218–16221.

Ozcan, A. & Erdem, B., 2004. Adsorption of Acid Blue 193 from aqueous solutions onto Na–Bentonite and DTMA–Bentonite. J. Colloid Interf. Sci., 280, 44–54.

Ozcan, A. & Oncu, E.M., 2006. Kinetics, isotherm and thermodynamic studies of adsorption of Acid Blue 193 from aqueous solutions onto natural Sepiolite. Colloids Surf. A: Physicochem. Eng. Aspects, 277, 90–97.

Pereira, L. & Alves, M., 2012. Dyes-Environmental Impact and Remediation. In: A. Malik, E. Grohmann (Eds.), Environmental Protection Strategies for Sustainable Development, Springer, New York, 111–162.

Shen, Y.-H., 2001. Preparation of organo Bentonite using non-ionic surfactants. Chemosphere, 44, 989–995.

Unuabonah, E.I., Adebowale, K.O., Olu-Owolabi, B.I. & Kong, L.X., 2008. Adsorption of Pb (II) and Cd (II) from aqueous solutions onto sodium tetraborate-modified Kaolinite clay: Equilibrium and thermodynamic studies. Hydrometallurgy, 93(1–2), 1-9.

Wang, C.-C., Juang, L.-C., Hsu, T.-C. & Huang, F.-C., 2004. Adsorption of basic dyes onto Montmorillonite. J. Colloid Interf. Sci., 273, 80–86.

Won, S.W., Choi, S.B. & Yun, Y.-S., 2006. Performance and mechanism in binding of Reactive Orange 16 to various types of sludge. Biochem. Eng. J., 28, 208–214.