# Measurement of pH of the Compacted Bentonite under the Reducing Condition

by

Syeda Afsarun NESSA[*], Kazuya IDEMITSU[**], Yosuke YAMASAKI[***],
Yaohiro INAGAKI[****] and Tatsumi ARIMA[*****]

**Abstract**

Compacted bentonite and carbon steel have been considered as the good buffer and over-pack materials in the repositories of high-level radioactive waste disposal. Sodium bentonite, Kunipia-F contains approximately 95wt% of montmorillonite. It has a high cation-exchange capacity and a high specific surface area, and its properties determine the behavior of bentonite. The pH of the pore water in compacted bentonite is an extremely important parameter because of its influence on radionuclide solubility, migration and sorption, and as well as repository safety studies. In this study, the pH of pore water in compacted bentonite was measured with a paper pH indicator wrapped with semi-permeable membrane of fresh egg under reducing conditions. On 30 days, the paper of pH indicator in the experimental apparatus indicated that the pH of pore water in compacted bentonite had been around 9~10 before electromigration. During electromigration the pH of bentonite was decreased and it reached 6~7 on 7 days. The concentration of iron and sodium showed nearly complementary distribution in the bentonite specimen after electromigartion. It is expected that iron ion could migrate as ferrous ion through the interlayer of montmorillonite replacing exchangeable sodium ions in the interlayer. Egg shell membrane does not affect the color of pH test paper during the experiment.

**Keywords:** Bentonite, Carbon steel, pH, Pore water, Montmorillonite, Reducing condition and Egg shell membrane

## 1. Introduction

Radioactive waste management is presently one of the major technical and scientific in the industrialized countries for protecting the human health, environment, beyond national borders and future generation. Bentonite and carbon steel have been considered as the good buffer and over-pack materials in the repositories of high-level radioactive waste disposal[1]. Bentonite's prominent properties of high swelling, sealing ability and cation exchange capacity provide retardation against the transport of radio nuclides from the waste into the surrounding rocks in the repository. However, as a porous media, it is possible that radionuclides migrate through the buffer into the geosphere by diffusion process[2]. Physico-chemical properties of the buffer play an important role in the solubility of nuclides in the pore-water of montmorillonite[3]. Solubility of radionuclides in an oxidized state is affected by pH of bentonite[4].

| | |
|---|---|
| * | Graduate Student of Doctor Course, Department of Applied Quantum Physics and Nuclear Engineering |
| ** | Professor, Department of Applied Quantum Physics and Nuclear Engineering |
| *** | Master Course Student, Department of Applied Quantum Physics and Nuclear Engineering |
| **** | Associate Professor, Department of Applied Quantum Physics and Nuclear Engineering |
| ***** | Research Associate, Department of Applied Quantum Physics and Nuclear Engineering |

　　　Bentonite changes the chemical characteristics of infiltrating ground water by means of mineral water chemical interactions. The interactions controlling pore-water chemistry include ion-exhange reactions of smectite, protonation/deprotonation reactions due to surface hydroxyl group of smectite, as well as dissolution/precipitation reaction and redox reactions of accessory minerals, and dissolution of soluble impurities. The protonation/deprotonation reactions of the smectite tend to decrease pH under initially slightly alkaline conditions and this reaction causes a certain dependence of pH on solid/liquid ratio in bentonite-water systems under anaerobic conditions. Wieland et al. suggested that the pore-water chemistry was affected by deprotonation of surface OH groups in montmorillonite[5]. According to their study, the deprotonation of OH groups would cause a drop of pore water's pH, which is expected to be remarkable in highly compacted bentonite. One of the important factors which affect the passive behavior of carbon steel may be the pH of the pore water in the compacted bentonite[6]. Therefore, the pH of pore water in bentonite is important to express the passivation of carbon steel in compacted bentonite. Although efforts to accumulate the theoretical modeling evidence and thermodynamic data have been accomplished so far, direct measurements of the pH of pore water in saturated bentonite have not been reported yet.

　　　The purpose of the present study is to measure the pH of compacted bentonite under the reducing condition. The pH of compacted bentonite was measured with a paper pH indicator wrapped with semi-permeable membrane of fresh egg.

## 2. Experimental

### 2.1 Materials

　　　Typical Japanese sodium bentonite, Kunipia-F was used in this experiment. It contains approximately 95wt% of montmorillonite. Mineral composition and chemical composition of Kunipia-F are shown in **Tables 1** and **2**. The chemical formula of Kunipia-F is estimated from the chemical composition shown in **Table 2** as $(Na_{0.4}Ca_{0.03}K_{0.01})(Al_{1.6}Mg_{0.3}Fe_{0.1})Si_4O_{10}(OH)_2$. Approximately 372 of the molecular weight and ca. 1 eq/kg of cation exchange capacity are estimated from the chemical composition. Bentonite powder was compacted into cylinders of 10 mm in diameter and 10 mm in height with the dry density of 1.4 $Mg/m^3$. The compacted bentonite was inserted in an acrylic resin cylinder with a paper pH indicator of 4 mm in length, which was wrapped with fresh egg shell membrane and soaked in NaCl aqueous solution of 0.01M for one month.

　　　Carbon steel, JIS SM41B, was used in this study. Carbon steel was cut into cylindrical coupons of 18 mm in diameter and 3 mm in thickness. The surface of the coupon was wet-polished with a # 1500 emery paper.

**Table1** Mineral composition of Kunipia-F.

| Mineral | Weight (%) |
|---|---|
| Montmorillonite | 98-99 |
| Quartz | <1 |
| Calcite | <1 |

**Table 2** Chemical composition of Kunipia-F used in this study.

| Constituents | Contents (wt%) |
|---|---|
| $SiO_2$ | 58.36 |
| $Al_2O_3$ | 20.36 |
| $Fe_2O_3$ | 1.34 |
| FeO | 0.51 |
| $TiO_2$ | 0.13 |
| MnO | <0.01 |
| $Na_2O$ | 2.93 |
| $K_2O$ | 0.09 |
| CaO | 0.42 |
| MgO | 2.97 |
| $P_2O_3$ | <0.01 |

## 2.2 pH and electromigration tests

One month after conducting the experiment, the color of a paper pH indicator in the apparatus has been changed and became bluish. After that a carbon steel coupon was assembled with water-saturated bentonite, they were put into an apparatus for conducting an electromigration experiment as shown in **Fig. 1**. There were a reference electrode of Ag/AgCl and a counter electrode of platinum foil in upper part of the apparatus with 0.01 M of NaCl aqueous solution. The carbon steel coupon was connected with potentiostat as a working electrode and was supplied electrical potential of 300 mV vs. Ag/AgCl electrode at 25 $^0$C for up to 7 days. During supplying the electrical potential, the color of a paper pH indicator in the experimental apparatus was rapidly changed. After supplying electrical potential, the bentonite specimen was taken out from the column and was sliced into thin leaves of 1~2 mm in thickness.  Iron and sodium in each slice were extracted with 1N HCl, and the concentration of iron and sodium in each extracting solution were measured with atomic absorption spectrophotometer.
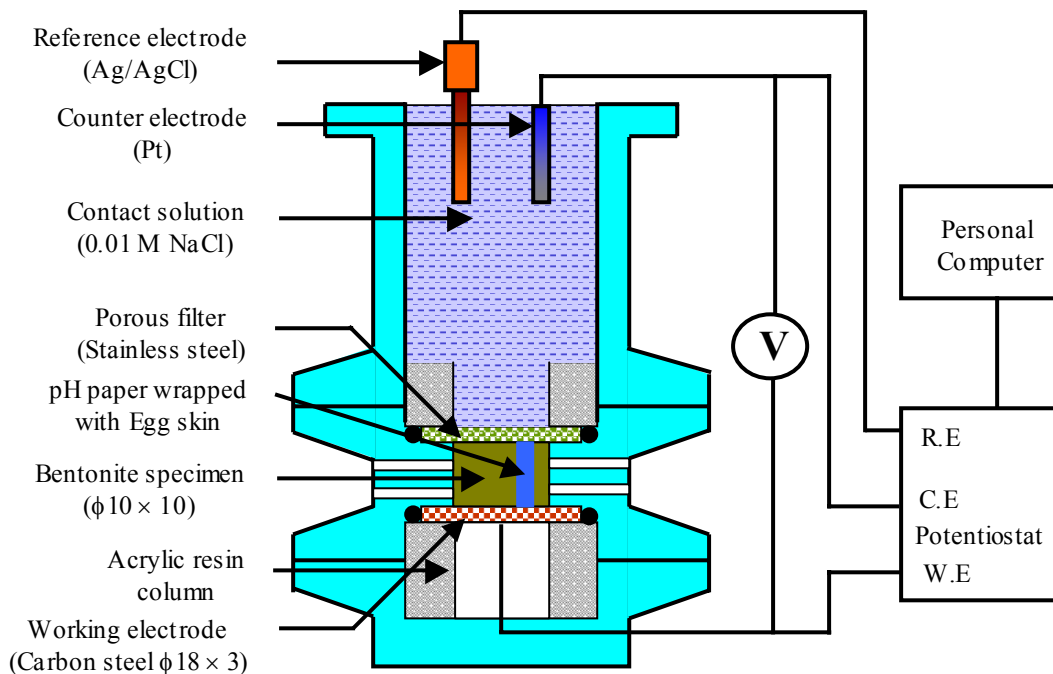


**Fig. 1** Schematic diagram of experimental apparatus used in the present study.

# 3. Results and Discussion

## 3.1 Profile of iron and sodium in bentonite specimens

Iron and sodium concentration profiles infiltrated in bentonite specimen are shown in **Fig. 2.** The concentration of iron and sodium showed nearly complementary distributions in deeper part as reported in the previous study[7]. In other words, iron, as a ferrous ion, migrated in bentonite with exchanging it for two sodium ions in interlayer of montmorillonite.
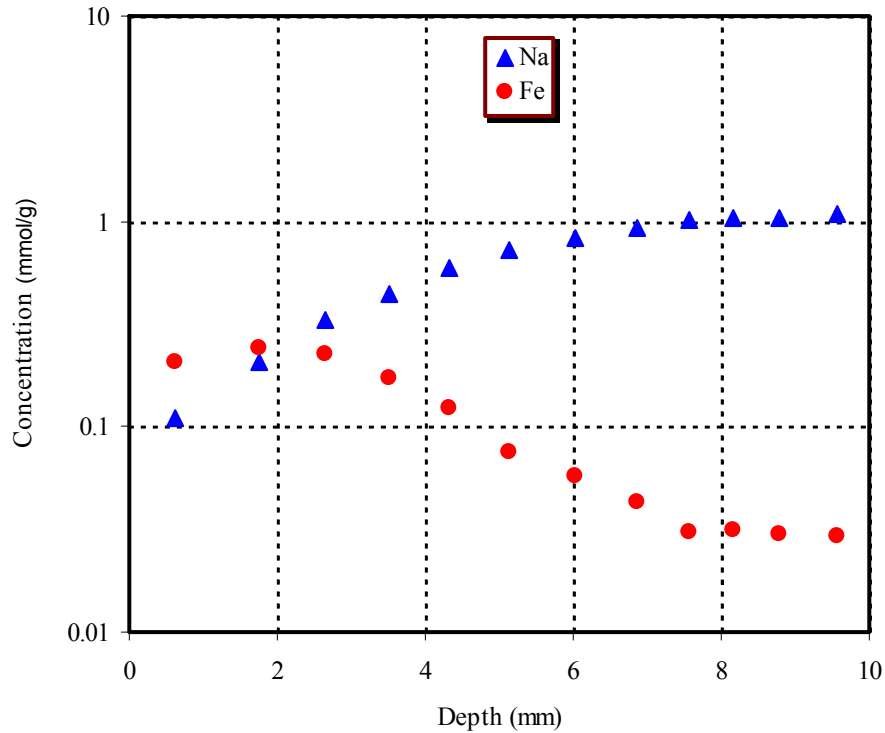
**Fig. 2** Typical penetration profiles of iron and sodium into bentonite specimen.

### 3.2 Observation

The color of a paper pH indicator wrapped with egg shell membrane attached to the surface of a bentonite specimen in the experimental apparatus became light blue on 15 days after and finally reached blue on 30 days after the start of the experiment, respectively. This blue color indicated that the pH of pore water in saturated bentonite had been around 9~10 before electromigration on 30 days after. The carbon steel coupon was connected with potentiostat as a working electrode and was supplied electrical potential of 300 mV vs. Ag/AgCl electrode for 7 days. During electromigration, the color of a paper pH indicator was changed to yellow on 7 days after which indicated that the pH of pore water in compacted bentonite had been around 6~7. Photographs (a), (b), (c), (e) and (f) in **Fig. 3** show the change of pH of pore water bentonite before electromigration and after electromigration, respectively. Photographs (a), (b) and (c) are taken at 1 hour and on 15 and 30 days after starting experiment, respectively. (d) is taken the photograph of pH indicator. Photographs (e) and (f) are taken at 2 hours and on 7 days after starting electromigration, respectively.

Bentonite is known to buffer the pH in a neutral or mildly alkaline region by exchanging with the ion[8]. The composition of the water in contact with bentonite seems to affect the pH reaction of the bentonite water. Consequently, the compositions of the bentonite pore water slowly change with time. Bentonite contains large quantities of montmorillonite, therefore its properties are largely determined by this clay mineral. Amphoteric surface site exists on the edges of the montmorillonite structure units. The initial pH is fixed by the high buffering capacity afforded by this amphoteric $\equiv SOH$ sites. The pH of the pore water of compacted bentonite depends directly on the specification of these sites i.e. the proportions of sites present as $\equiv SOH$, $\equiv SOH_2^+$ and $\equiv SO^-$. In this investigation, the pH of pore water in compacted bentonite reached 9~10 due to presence of these highly functional groups.

The surface of montmorillonite clay platelets carry a permanent negative charge arising from isomophous substitution of lattice cations by those with a lower valency. Charge neutrality is maintained by the presence of an excess amount of cations in solution. Since the areas within the interlayer space are predominant, the compensating cations reside mainly there. The eletrostatically

bound cations, which form the electrical double layer, can undergo stoichiometric exchange with the cations in solution[9)-10)]. When the carbon steel specimen came into contact with the bentonite specimen and applying electrical potential, the corrosion was occurred. Corrosion reaction can be written as follows:

$$Fe = Fe^{2+} + 2e, \qquad E^0 = -440 \text{ mV (vs. NHE)} \qquad (1)$$
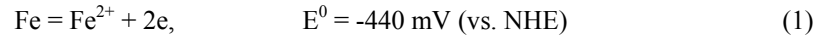
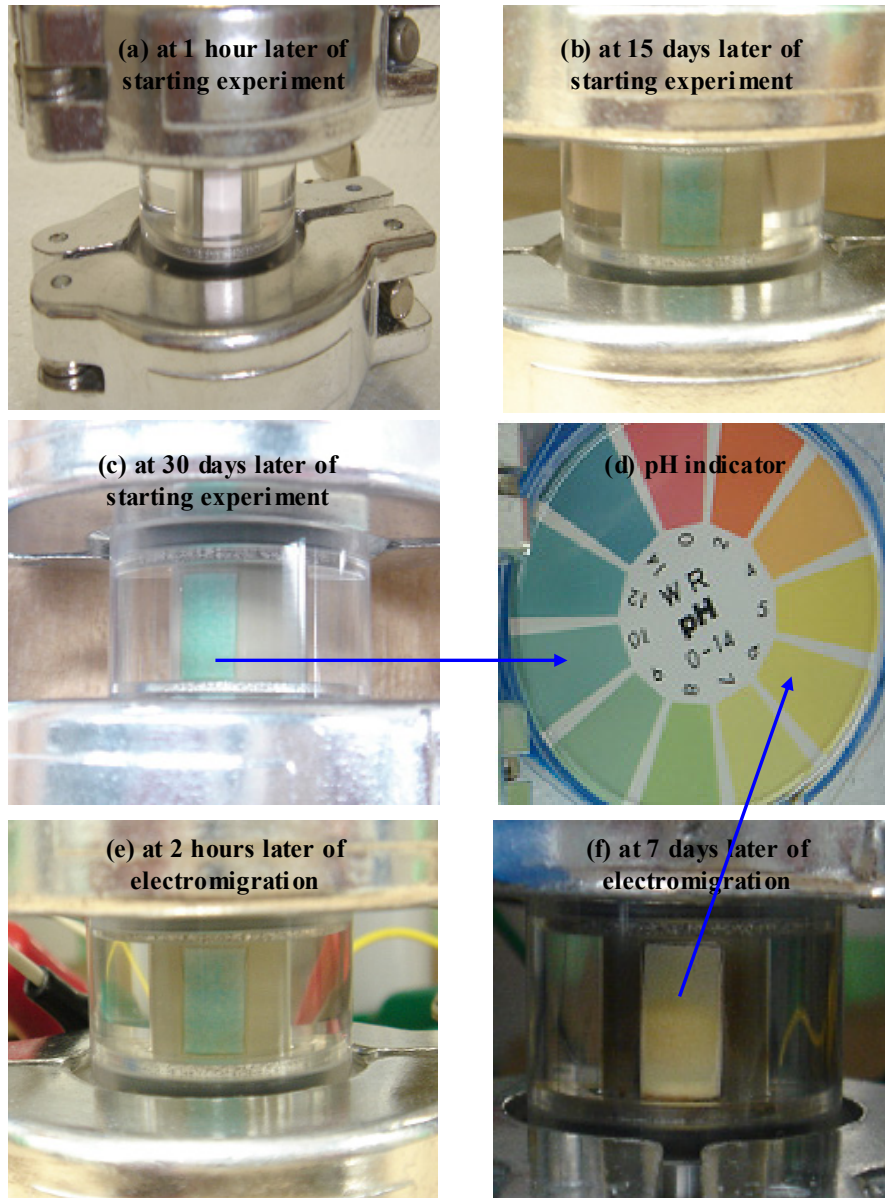$$E \text{ (mV)} = E^0 + \frac{59.1}{2} \log a_{Fe}^{2+} . \qquad (2)$$



**Fig. 3** Typical photographs illustrating the changes in color of a paper pH indicator, which is attached to compacted bentonite in the experimental apparatus before and after supplied electrical potential.

The experimental results shown in **Fig. 2** indicated that ferrous ion migrated in bentonite by exchanging it for two sodium ions in interlayer of montmorillonite. In the case of ferrous ion hydrate;

$$Fe^{2+} + H_2O = Fe\,(OH)_2 + 2H^+, \tag{3}$$

where the pH of compacted bentonite decreases and reaches 6~7.

### 3.3 Effect of Eggshell membrane on pH change

Egg shell membrane was used to wrap a paper pH indicator in order to protect the disappearance of the color of the paper of pH indicator in this study. Egg shell membrane is composed of protein fibers that are arranged so as to show a semi permeable functionality[11]. The surface of this membrane doesn't react with the pore water of compacted bentonite. However, this membrane has the capacity to allow the migration of the pore water from compacted bentonite to the pH test paper. Moreover, three experiment were carried out at different pH standard solutions of 4.01, 6.86 and 9.18 with the paper pH indicator wrapped with egg shell membrane, wrapped with collodion sheet, and in addition unwrapped a paper pH indicator to examine the effect of egg shell membrane on the pH of the specimen.
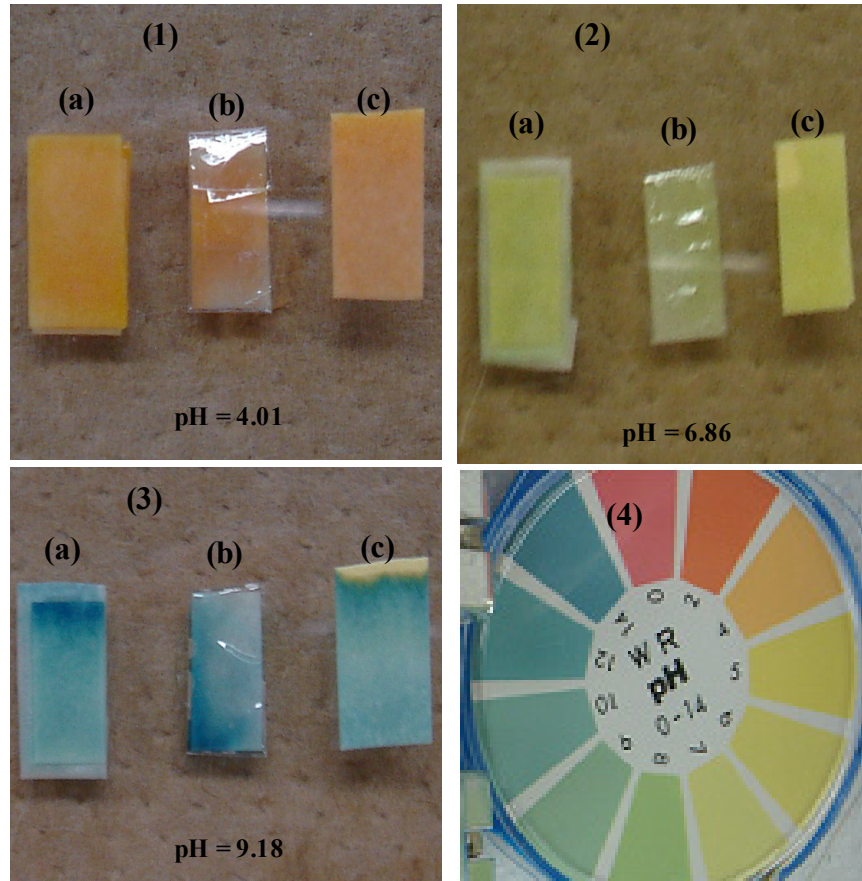


**Fig. 4** Typical photographs illustrating the color of pH test paper at different pH standard solutions, where (a): pH test paper wrapped with egg shell membrane, (b): pH test paper wrapped with collodion and (c): unwrapped pH paper indicator.

Photographs (1), (2), and (3), in **Fig. 4** show the pH is of different standard solutions which are Phthalate pH Standard Solution, Phosphate pH Standard Equimolar Solution and Teteaborate pH Standard Solution, respectively. (4) shows the photograph of pH indicator. Each photograph contains three pH test papers (a), (b), and (c), which are pH test papers wrapped with egg shell membrane, and collodion sheet, and unwrapped one, respectively. The pH paper indicators in Figs. 4 (a), (b), and (c) show almost the same color. Therefore, egg shell membrane does not affect the color of pH test paper.

## 4. Conclusions

The pH of pore water in compacted bentonite was measured with pH test paper wrapped with egg shell membrane under reducing conditions. The following facts were obtained from the result of this study.
(1) The pH in compacted bentonite can be measured by the pH test paper wrapped with egg shell membrane.
(2) The pH of the pore water of compacted bentonite reached 9~10 on 30 days after starting the experiment by the high buffering capacity afforded by the amphoteric $\equiv$SOH sites.
(3) After electromigration, the pH of pore water reached 6~7 on 7 days after due to the replacement of sodium ion by ferrous ion as well as hydration ferrous ion to produce proton in the pore water solution.

## References

1) F. Bucher, M. Miiller-Vonmoos, Butonite as a containment barrier for the disposal of highly radioactive waste, Applied Clay Science, 4, 157 (1989).
2) Japan Nuclear Cycle Development Institute (JNC), JNC/TN 1410, 2000-001 (2000).
3) Y. Torikai, S. Sato and H. Ohashi, Thermodynamic properties of water in compacted sodium montmorillonite. Nuclear Technology, 115, 73 (1996).
4) K. Idemitsu, H. Furuya, Y. Tachi and Y. Inagaki, Diffusion of uranium in compacted bentonite in the presence of carbon steel, Scientific Basis for Nuclear Waste Management XVII, edited by A, Barkatt and R. A. Van Konynenburg (Mater, . Res. Soc. Proc. 333, Pittsburgh, PA, 1994) 939-946.
5) E. Wieland, H. Wanner, Y. Albinsson, P. Wersin and O. Karnland, SKB Technical Report, 94-26 (1994).
6)    G. P. Marsh, I. W. Blend, J. A. Desport, C. Naish, C. Westcott and K. J. Taylor, European App. Res. Rept.-Nucl. Sci. Techno., 5.2, 223 (1983).
7) K. Idemitsu, S. Yano, X. Xia, Y, Kikuchi, Y. Inagaki, T. Arima, Migration behavior of iron in compacted bentonite under reducing condition by using electromigration, Scientific Basis for Nuclear Waste Management XXVI, edited by R. J. Finch and D. B. Bullen (Mater. Res. Soc. Proc. 757, Pittsburgh, PA, 2003) 657-664.
8) M. Sneliman, H. Uotila and J. Rantanen, Scientific Basis for Nuclear Waste Management X, edited by J. K. Bates and W. B. Seefeldt (Mater. Res. Soc. Proc. 84, Pittsburgh, PA, 1987) 781-790.
9) R. E. Grim, Clay Mineralogy, Mc Graw Hill (1953).
10) H. Van Olphen, An introduction to clay colloid chemistry, Interscience Publishers, J. Wiley and Sons (1963).
11) W. T. Tsai, J. M. Yang, C. W. Lai, Y. H. Cheng, C. C. Lin and C. W. Yeh, Characterization and adsorption properties of eggshells and eggshell membrane, Bioresource Technology, 97, 488 (2006).