Adsorptive Removal of Cs(I) from Water by Using Persimmon Tannin Impregnated Zeolite

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Abstract

In the present work, the presence of exchangeable cation in zeolite and polyhydroxy groups in persimmon tannin were utilized for the adsorption of Cs(I) using persimmon tannin impregnated zeolite abbreviated hereafter as PTIZ. Batch experiments were conducted to determine the binding ability of PTIZ for the Cs(I) ion. The best Cs(I) removal results was obtained when pH of the solution was adjusted higher than 5. The rate of Cs(I) uptake by PTIZ was fast at the beginning and reached adsorption equilibrium within 1h. Maximum uptake capacity and Langmuir equilibrium constant were found to be 1.24 mmol/g and 3.34 L/mmoL, respectively. The removal Cs(I) by PTIZ is inferred to be ion exchange as well as chelation mechanism. The complete or 100% removal of Cs(I) from water was successfully achieved by using small amount of PTIZ. Thus, the PTIZ can be expected to be a promising adsorbent for the treatment of effluent containing trace amount of Cs(I) from water.

Key words: *Zeolite, Persimmon tannin, Impregnation, Radionuclide, Adsorption, Cs(I) removal*

Introduction

The radioactive materials are extensively used in various industrial and research activities for medical, military, energy production and in various other areas. During the production and application of these materials, radioactive contamination could be brought about due to abundant un-reacted nuclides in the radioactive effluents[1]. The treatments of such radioactive effluents require concentration of the dissolved metal ions followed by recovery and secure disposal. The Cs(I) is the rarest of the alkali metals has little economic value and no essential biological role. However, nuclear technology has resulted in the release of large amount of radioactive isotopes (^{137}Cs and ^{134}Cs) of Cs(I) into the environment[2]. The ^{137}Cs is most important radionuclide present in large volumes in liquid radioactive wastes[3]. ^{137}Cs has been a matter of serious concern because of its relatively long radioactive half-life ($t_{1/2}$ = ~30 year), highly penetrating power and higher water solubility[4, 5]. Thus, hazardous quantities of ^{137}Cs will remain in the environment for centuries. The living organisms easily absorb ^{137}Cs and replacing it for harmless K(I) or Na(I) ion. Thus, the nuclear industry is currently faced with increasing concern and anxiety over the radiological hazards to the human beings[6]. In this regard, an effective treatment system is required for the removal of Cs(I) from aqueous radiotoxic nuclides. This type of liquid wastes could be treated using solid adsorbents, like zeolites, clay minerals and synthetic inorganic ion exchangers, concentrating the radionuclides in small volumes of solid wastes [5,7].

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Chemical precipitation, evaporation and ion exchange are some of the processes used for the removal of Cs(I) from aqueous solutions of low and intermediate level before being discharged to the environment. Among these processes, ion exchange appears to be the most effective to control radioactive wastes[8]. Ion exchange is a relatively simple technology used to remove hazardous ions from aqueous solutions which has high affinity for the ion to be removed[9]. This process has been widely studied for the removal of radioactive elements from alkaline wastes and sometimes from acid radioactive wastes. The nature of non radioactive isotopes of Cs(I) is similar to the radioactive isotopes. They exist as monovalent cesium in aqueous solution and possess similar chemical properties so that non radioactive isotope of Cs(I) was study in this case and expected to be employed for the treatment of water contaminated with radioactive cesium from water.

In the recent years, the use of natural zeolites for the treatment of radioactive waste has increased because they are considered as potential adsorbents due to their high cation exchange capacities and low cost. The commercial ion exchange resin containing phenolic moieties are popular for the removal of Cs(I) ion from aqueous solution[10, 11]. The persimmon waste containing polyphenolic compounds like tannin is very effective for the removal of radioactive metals such as uranium and thorium[12]. From the literature, the polyphenol rich waste material such as persimmon waste, persimmon tannin, waste tea leaves were demonstrated to be effective for the removal of Cs(I) from aqueous solution[13 - 15]. Direct use of radioactive cesium is prohibited in our laboratory therefore the non radioactive form of Cs(I) was used and expected to be employed also in the treatment of effluent containing radioactive Cs(I). Therefore in the present study PTIZ was used as an adsorbent for the removal of Cs(I) from water. The adsorption behaviors of Cs(I) was investigated by means of pH effect, adsorption kinetics, adsorption isotherms and adsorbent dosage from modeled solution.

Experimental Methods

Material and chemicals

The sample of persimmon tannin impregnated zeolite abbreviated hereafter PTIZ was kindly received from HiFuMi Sangyo (Hifumi industry) Co. Ltd., Gunma Prefecture, Japan. The adsorbent particle size was made <75 µm by crushing with morter and pestle and was utilized for the experimental runs. The stock solution 1000 mg/L of Cs(I) an Na(I) were prepared in deionized water using CsCl and NaCl salts (Wako Pure Chemical Industries, Ltd), respectively. From this stock solution the required concentration of Cs(I) an Na(I) solution was prepared by diluting with deionized water for fresh use.

Batch wise adsorption test

The batch adsorption tests of Cs(I) was carried out in order to observe their adsorption behavior onto persimmon tannin impregnated zeolite powder. In a typical set, 15 ml of test solution containing predetermined amount of Cs(I) was added to 15 mg of the PTIZ and the resulting mixtures were shaken in a thermo-stated shaker at 150 rpm for 24 h except kinetic study. For kinetic study, 250 mg of the PTIZ and 250 mL of 0.5 mmol/L of Cs(I) solution were stirred at 303K at pH 6.7 and sampled were collected at different time interval between 5 minute to 4 hour. After shaking, the samples were filtered and the concentration of Cs(I) ion was determined by using atomic absorption spectrometer (AAS). The pH of the Cs(I) solution was adjusted by adding some drops of either 0.1M HCl or 0.1M NaOH solution. The percentage adsorption (% A) and Cs(I) uptake capacity were determined by using equation 1 and 2, respectively.

$$\%A = \frac{C_i - C_e}{C_i} \times 100 \qquad (1)$$

$$q = \frac{C_i - C_e}{W} \times V \qquad (2)$$

Where, C_i and C_e are initial and equilibrium concentration (mmol/l) of Cs(I) respectively. W is weight of the adsorbent (g) and V is volume of solution (L).

Results and discussion

Influence of contact time

Adsorption kinetic of Cs(I) during the adsorption process is very important for the evaluation of adsorption rate and equilibrium time. **Fig. 1** shows the effect of contact time for the adsorption of Cs(I) onto PTIZ. As can be seen from the result of this figure that initially Cs(I) was rapidly adsorbed onto the adsorbent then the rate of adsorption was gradually slow down and finally approaching a constant value. It can be noticed that curve of cesium adsorption onto the present adsorbent is characterized by fast adsorption and the equilibrium was reached within 1 h of contact time. The fast adsorption rate of Cs(I) on PTIZ reflects its tremendous affinity towards Cs(I) and is attributable to the accessibility of monovalent cesium ion to the cation exchange site of PTIZ. Although equilibrium was observed to be reached within 1h at 0.5 mmol/L concentration of Cs(I), subsequent adsorption experiment were carried out for about 24 h in order to ensure complete equilibrium.

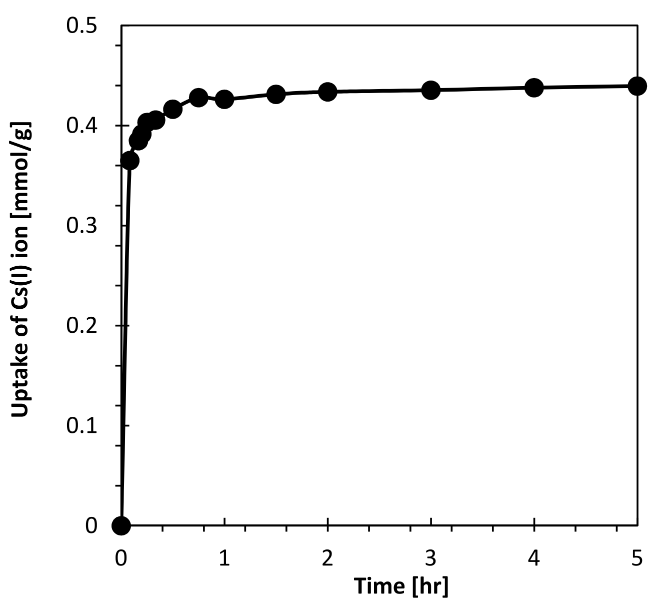


Figure 1: *Adsorption kinetics of Cs(I) onto PTIZ (**condition:** Volume of solution = 250 ml, concentration of Cs = 0.5 mM, wt of adsorbent = 250 mg, temp. = 303 K and shaking = 500 rpm).*

Effect of pH and adsorption mechanism

The pH is an important parameter to be considered in adsorption processes because it may affect both the properties of the adsorbent and the composition of the solution. As illustrated in **Fig. 2**, the percentage adsorption of Cs(I) increased with increasing the pH. The result shows that the adsorption of Cs(I) was increase from 83% to 96% by increasing the pH from 2.8 to 4.6 whereas it was found to achieved nearly 100% at pH higher than 5.5. As we know that the structure of zeolite consists of three dimensional frameworks of Si-O and Al-O tetrahedral. The aluminium ion is small enough to occupy the position in the center of the tetrahedron of four oxygen atoms and the isomorphous replacement of Si^{4+} by Al^{3+} produces a negative charge in the lattice. The net negative charge is balanced by the exchangeable cation such as Na(I) or K(I) as shown in **Scheme 1a**.These positive ions are rather loosely held and can readily be exchanged with others in a contact solution during adsorption as shown in **Scheme 2**. Persimmon tannin contain polyphenol (for example **Scheme 1b**) where adsorption of Cs(I) occurs by chelation as demonstrated in **Scheme 3**. In the case of persimmon tannin impregnated zeolite (PTIZ) powder due to the presence of both zeolite and polyphenol, the adsorption of Cs(I) occurs through both cation exchange as well as chelation mechanism therefore effective adsorption of Cs(I) onto PTIZ is possible.

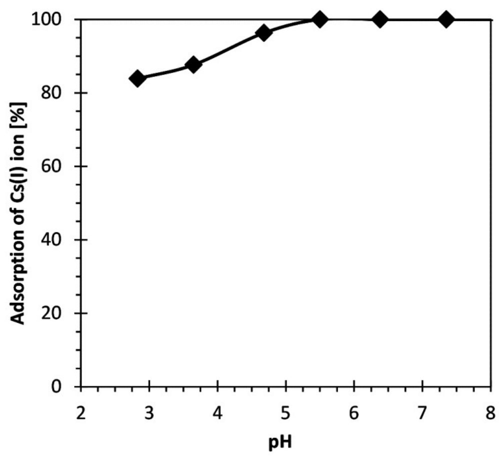
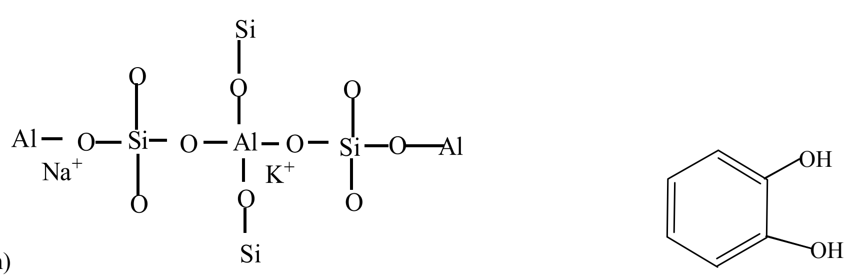


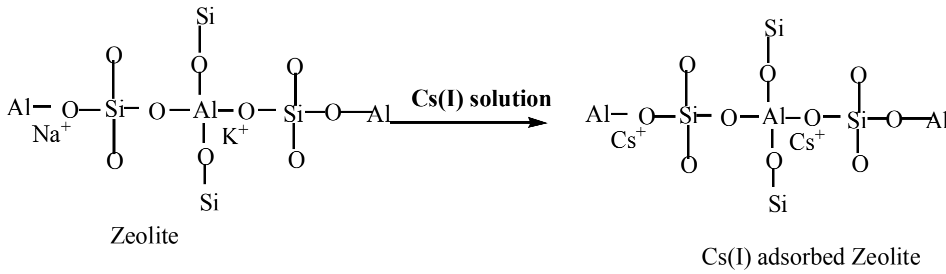
Figure 2: *Effect of pH for the removal of cesium from aqueous solution onto PTIZ (**condition**: weight of dry gel = 15 mg, volume of the solution = 10 mL, concentration of Cs^+ = 60 mg/L, temperature = 30°Cand shaking ime*



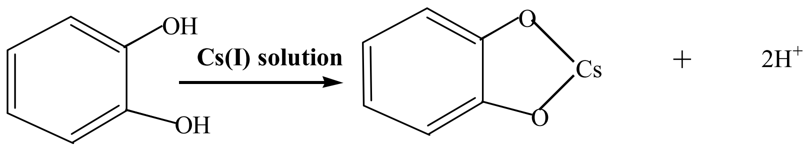
= 24 h)

(a) **(b)**

Scheme 1 (a) Structure of zeolite (b) structure of polyphenol (catecol).



Scheme 2 Cs(I) adsorption mechanism by using zeolite *via.* cation exchange



Scheme 3 Mechanism Cs(I) adsorption by chelation with polyphenolic group of persimmon tannin.

Influence of Cs(I) concentration

The influence of Cs(I) concentration during adsorption was tested in order to evaluate the maximum uptake capacity of persimmon tannin impregnated zeolite towards Cs(I). **Fig. 3a** shows the adsorption isotherm of persimmon tannin impregnated zeolite for Cs(I) at pH 6.7. As revealed by this figure, the amount of Cs(I) adsorbed on to the adsorbents increased with increasing Cs(I) concentration at lower concentration region where as it approached a constant values at higher concentration exhibiting typical Langmuir type monolayer adsortion. The experimental data was modeled by using well known Langmuir and Freundlich isotherm equations as depicted by equation 3 and 4 respectively. Langmuir isotherm can be expressed in the form of following equation (Eq. 3) as[16]

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \quad (3)$$

where, C_e (mmol/L) and q_e (mmol /g) are equilibrium concentration and amount of adsorption, respectively, while q_{max} is the maximum loading capacity and b is the ratio of adsorption/desorption rate related to energy of adsorption. The q_{max} and b were calculated from the slope and intercept of the linear plot of C_e/ q_e versus C_e (**Fig. 3b**) and presented in **Table 1**. Similarly, Freundlich isotherm can be expressed in its linear form as[17]

$$\log q_e = \log K_F + (1/n) \log C_e \quad (4)$$

where K_F and n are Freundlich constants related to the adsorption capacity and adsorption intensity, which can be calculated from the intercept and slope of the linear Freundlich plot of log q_e *versus* log C_e (**Fig. 3c**). The evaluated values of K_F and n are also listed in **Table 1**. The value of correlation regression coefficient in case of Langmuir isotherm model (R^2 value higher than 0.99) is comparatively higher than that obtained from Freunlich isotherm model (where R^2 value less than 0.93) which strongly suggest that the experimental data is better fitted with the Langmuir isotherm, which strongly suggest the formation of monolayer Cs(I) on the surface of PTIZ. The maximum adsorption capacity and Langmuir equilibrium constant evaluated using Langmuir isotherm model was found to be 1. 24 mmol/g, and 3.34 L/mmol, respectively.

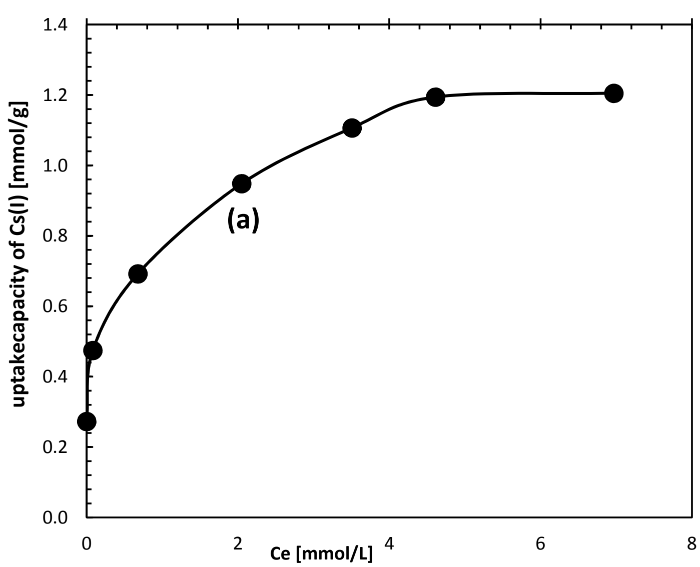
The Langmuir equilibrium constant b can be utilized to investigate the suitability of adsorption process by calculating a dimensionless separation factor (R_L) according to the equation as[18]

$$R_L = \frac{1}{1+bC_i} \qquad (4)$$

where b and C_i are Langmuir equilibrium constant, initial concentration of Cs(I) ion, respectively. The value of R_L determines the nature of adsorption process. Zero value of R_L indicates irreversible nature of adsorption whereas if it is equals to one then the adsorption process is linear. In the case if the value of R_L is greater than one indicating unfavorable nature of adsorption and the value of R_L in between 0 and 1 showing favorable nature of adsorption process[16]. It was found that the value of R_L at different initial concentration tested in this study were in between 0 and 1 i.e.$0 < R_L < 1$, which strongly suggest that the adsorption of Cs(I) onto PTIZ is favorable

Table 1 Freundlich and Langmuir parameters for the adsorption of Cs(I) onto PTIZ at = 30°C.

Freundlich parameters	Isotherms parameters	Calculated value
	K_F (mmol/g)	0.97
	1/n	0.23
	R^2	0.92
Langmuir parameters	$q_{max..}$ (mmol/g)	1.24
	b (L/mmoL)	3.34
	b (L/mmoL)	3.34
	R^2	0.99



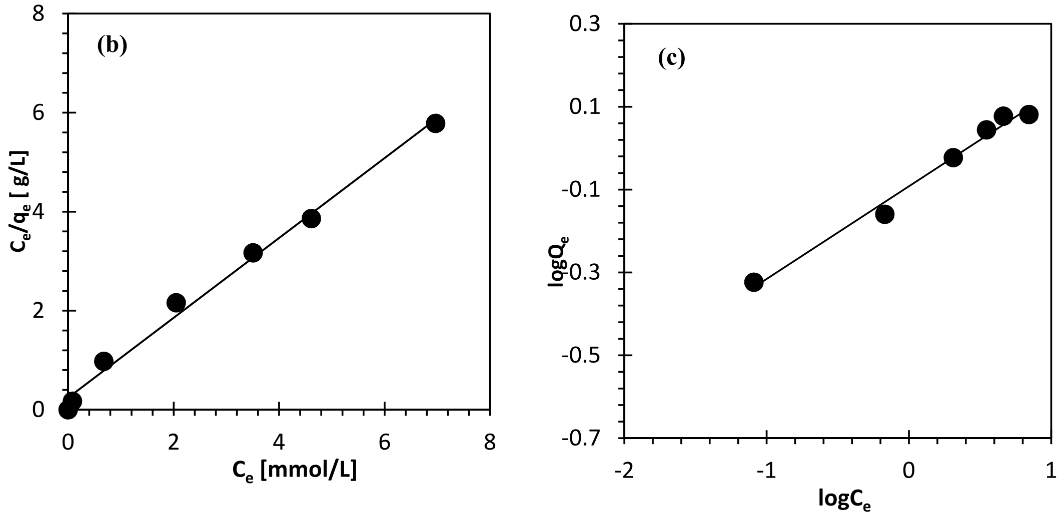


Figure 3: *Adsorption isotherms of Cs(I) onto persimmon tannin impregnated zeolite from aqueous solution (a) experimental isotherm plot, (b) Langmuir plot, and (c) Freundlich plot (**conditions:** Volume of solution = 10 ml, wt of gel = 15 mg, temp = 30°C, shaking time = 48 h, and shaking speed = 150 rpm).*

Effect of adsorbent dose

In order to optimize the dosage of the adsorbent to the Cs(I) adsorption, the experiment was conducted by using 8.7 mg/L of Cs(I) solution prepared at deionized water. The result is shown in **Fig.4**, which presents the plot of residual Cs(I) concentration as a function of solid-liquid ratio. The results clearly suggests that the concentration of Cs(I) was decreased from 8.7 mg/L to 0.53 mg/L by using 0.5 g/L of PTIZ whereas it was found to achieved at zero or 100% removal by using 1 g/L or higher dosage. From this result, the PTIZ is effective for the complete removal of trace concentration of Cs(I) polluted.

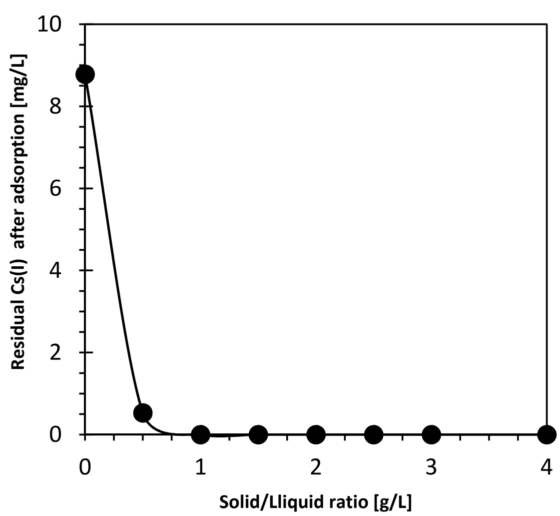


Figure 4: *Effect of adsorbent dose for the removal of Cs(I) onto persimmon tannin impregnated zeolite (**conditions**: volume of the solution used = 10 ml, Cs(I) concentration = 8.72 mg/L, solution pH = 5.76, shaking time = 24 h, shaking speed = 150 rpm and temperature = 30 °C).*

Conclusions

The feasibility of using PTIZ for the rapid removal of Cs(I) from water was studied in the present work and following conclusions could be drawn from this study:

- Efficient and rapid adsorption of Cs(I) took place within only 1 h contact time.
- Batch adsorption studies showed approximately 100% removal of Cs(I) at 30°C from mixed solution containing trace concentration of Cs(I) ion which suggest high selectivity of PTIZ for Cs(I) ion.
- Isotherm study proved Langmuir type monolayer adsorption of Cs(I) on the surface of PTIZ.
- Therefore, the PTIZ investigated in this study can be offer to be a promising candidate for the treatment of water or waste water contaminated with Cs(I) ion.

References

1. H. Paudyal, B. Pangeni, K. Inoue, K. Ohto, H. Kawakita, K.N. Ghimire, H. Harada and S. Alam, *Sep. Sci. Technol (2014)*, **49,** 1244-1250.
2. A.E. Osmanliouglu, *J. Hazard. Mater.* 2006, **137**, 332-335.
3. D. Ding, Y. Zhao, S. Yang, W. Shi, Z. Zhang, Z. Lei, Y. Yang, *Water Res*. 2013, **47,** 2563-2571.
4. R.J. Rad, H. Ghafourian, Y. Asef, S.T.Dalir, M.H. Sahafipour and B.M. Gharanjik, *J. Hazard. Mater*. 2004, **B116,** 125-134.
5. T. Sangvanich, V. Sukwarotwat, R.J. Wiacek, R.M. Grudzien, G.E. Fryxell, R.S. Addleman, C. Timchalk, W. Yantasee, *J. Hazard. Mater.* 2010, **182**, 225-231.
6. K.C. Song, H.K. Lee, H. Moon, K.J. Lee, *Sep. Purif. Technol*. 1997, **12**, 215-217.
7. A.M. EI-Kamash, *J. Hazard. Mater.* 2008, **151**,432-445.
8. S. Hasan, T.K.Ghos, D.S. Viswanath, S.K. Loyalka, B. Sengupta, *Sep. Sci. Technol. 2007,* **42,** 717-738.
9. H. Paudyal, B.a Pangeni, K. Inoue, H. Kawakita, K. Ohto, K.N. Ghimire and S. Alam, *Biores. Technol.* 148, 221-227.
10. S.K. Samanta and M. Ramaswamy, Sep. Sci. Technol. 1992, **27,** 255 -267.
11. T. Sakaguchi, A. Nakajima, Recovery, *Sep. Sci. Technol.* 1987, **22,** 1609-1623.
12. K. Inoue, H. Kawakita, K. Ohto, T. Oshima, H. Murakami, *J. Radioanal. Nucl. Chem*. 2006, **267,** 435-442.
13. B. Pangeni, H. Paudyal, K. Inoue, H. Kawakita, K. Ohto, S. Alam, Chem. Eng. J. 2014, **242,** 109-116.
14. B. Pangeni, H. Paudyal, K. Inoue, K. Ohto, M. Gurung, H. Kawakita, S. Alam, *Waste and Biomass Valorization* 2014*,* **5(6),** 1019-1028.
15. M. Gurung, B.B. Adhikari, S. Alam, H. Kawakita, K. Ohto, K. Inoue, H. Harada, *Chem. Eng. J.* 2013, **231**, 113-120.
16. I. Langmuir, *J. Am. Chem. Soc.* 1916, **38,** 2221- 2295.
17. H. Freundlich, *J. Phys. Chem.* 1906, **57**, 385 – 470.
18. C.L. Xia, Y. Jing, Y.Z. Jia, D.Y. Yue, J. Ma and X.J.Yin, *Desalination* 2011, **265,** 81- 87.