Removal of rhodamine 6G and crystal violet dyes from water sample using cellulose acetate-(3-aminopropyl)-triethoxysilane sorbent

Andriana Joanes Leong, Ng Nyuk-Ting, Nur Safwati Mohd. Nor, Umair Baig, Wan Aini Wan Ibrahim, Mohd. Marsin Sanagi, and Aemi Syazwani Abdul Keyon

View Online   Export Citation

ARTICLES YOU MAY BE INTERESTED IN

Removal of Rhodamine 6G and Crystal Violet Dyes From Water Sample Using Cellulose Acetate-(3-Aminopropyl)-Triethoxysilane Sorbent

Andriana Joanes Leong[1,a)], Ng Nyuk-Ting[1,b)], Nur Safwati Mohd. Nor[2,c)], Umair Baig[3,4,d)], Wan Aini Wan Ibrahim[1,5,e)], Mohd. Marsin Sanagi[1,5,f)] and Aemi Syazwani Abdul Keyon[1,5,g)]

[1]*Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310, Johor Bahru, Malaysia.*
[2]*Department of Applied Mechanics and Design, School of Mechanical Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia.*
[3]*Center of Excellence for Desalination and Water Treatment, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia.*
[4]*Laser Research Group, Physics Department and Center of Excellence in Nanotechnology (CENT), King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia.*
[5]*Centre for Sustainable Nanomaterials, Ibnu Sina Institute for Scientific and industrial Research, Universiti Teknologi Malaysia, Johor Bahru, 81310, Johor, Malaysia.*

[g)]Corresponding author: aemi@kimia.fs.utm.my
[a)]adrianajoanes@gmail.com
[b)]aliciachristine92@gmail.com
[c)]safwati@mail.fkm.utm.my
[d)]umair.alig@gmail.com
[e)]wanaini@kimia.fs.utm.my
[f)]marsin@kimia.fs.utm.my

Abstract. In this work, cellulose acetate-(3-aminopropyl)triethoxysilane (CA-APTES) was evaluated for the first time as adsorbent for the removal of rhodamine 6G (R6G) and crystal violet (CV) in water. The sorbent was first synthesized then characterized using attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR). The presence of C=O amide at 1740.17 cm^{-1} and N-H amide around 3451.98 cm^{-1} confirmed that the sorbent has been successfully synthesized. The removal efficiency was determined using ultraviolet-visible (UV-Vis) spectrophotometry, where the optimum conditions were found to be at 2 ppm initial dyes concentration, sample solution of pH 7, 50 mg of sorbent, and 2 hours of shaking time. Kinetic studies for the sorbents were carried out using both pseudo-first-order and pseudo-second-order models, where the R^2 values for removal R6G and CV were 0.0064 and 0.0523 respectively for the former, and R^2 0.75 and 0.87 respectively for the latter. The kinetic study was best described using pseudo-second-order model. The optimized method was adopted for the dyes removal in real batik textile wastewater, whereby removal efficiencies of 61.81 % for CV and 48.62 % for R6G were obtained.

INTRODUCTION

Textile industry is one of the contributors to the water pollution as large volume of water is used in the dyeing process. In Malaysia, batik textile industry is a type of textile industry that used massive amounts of dyes that cause water pollution [1]. Textile industries' wastewater from dyeing process contains chemical pollutants such as salts and

surfactants which have to be treated upon discharge to the environment [2]. There are several conventional methods for dyes treatment in wastewater, but the focus on adsorption using newly synthesized materials received notable attention among researchers. The conventional methods involve a number of processes including chemical oxidation, foam flotation, electrolysis, biodegradation, adsorption, chemical coagulation and photocatalysis [3]. These techniques however, have limitations such as high cost and require an extensive period of time. Adsorption techniques are widely used in dyes removal as it is relatively cost- effective [4]. Generally, the term "adsorption" is best referred to as a process of transferring liquid to solid, resulting in either physical or chemical interaction [5]. The wastewater treatment by sorption process becomes an alternative, since the sorbent used is cheap, readily available and does not require any additional pre-treatment step before being used [6]. The abilities of the adsorption process in removing and recovering organic compounds have made it preferable to other modern electrochemical and photochemical methods [7].

Several types of sorbent such as fly ash, bio-gas waste slurry, chitosan, chitin, silica, banana pith and others - mostly low-cost recognized as bio-waste [8]. A type of sorbent that is chemically synthesized, known as organic-inorganic magnetic nanoparticles (MNP) has been the spotlight in dyes removal. The examples of MNPs include gold-polypyrrole, silver-polyprrole, silicon dioxide-polypyrrole and iron oxide-polypyrrole [9-12]. Polypyrrole has the characteristics of being easy to synthesize. The process involves the adsorption of dyes molecules onto the surface of the MNPs [8], and a subsequent desorption process using methanol, which later subjected for further analysis.

Cellulose is suitable for dyes removal owing to the fact that cellulose exists in abundance. It can also be chemically modified to be a semi-synthetic material. Silva *et al.* [13] have successfully modified cellulose with aminoethanethiol and was used to remove reactive red dye. The modified cellulose showed a satisfactory performance in adsorption of reactive red dye at a pH of 2 where the adsorbed dye was 78 mg/g at 45 and 55 °C. Zhao *et al.* synthesized cellulose acetate–organo-montmorillonite (CA/OMMT) to be the adsorbent for the adsorption of anionic dye from aqueous solution [14]. It was reported that the increasing amount of organo-montmorillonite in CA/OMMT from 10 wt.% to 60 wt.% had increased the adsorption capacity from 3.1 to 85.7 mg/g. Therefore, an exploration on the modification of cellulose-based adsorbent for the removal of dyes is said to have a realistic meaning altogether.

The present work investigates, for the first time, the use of cellulose acetate-(3-aminopropyl)triethoxysilane (CA-APTES) as the adsorbent for the extraction of targeted dyes, rhodamine 6G (R6G) and crystal violet (CV) from batik textile wastewater samples prior to ultraviolet-visible (UV-Vis) spectrophotometry analysis. Parameters such as initial dyes concentration, pH, mass of sorbent and the shaking time were optimized to indirectly determine the removal efficiency of dyes in batik textile wastewater. The findings showed the feasibility of the organic-inorganic adsorbent for the analysis of cationic dyes in batik textile wastewater.

EXPERIMENTAL

Chemical and Instrumentations

All reagents used were of analytical reagent grade. Standard dyes, CV and R6G were purchased from Sigma-aldrich (U.S.A). The sorbent, CA-APTES was synthesized using cellulose acetate (CA), (3-aminopropyl)triethoxysilane (APTES), toluene, and ethanol. Deionized water was used in the preparation of stock standard solution and working standard solutions. The working standard solutions were prepared daily through appropriate dilution of the stock standard solution with deionized water to the required concentration. The instruments used in this study were UV-Vis spectrophotometer (Perkin Elmer, U.S.A) for the analysis of dyes, attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR, Perkin Elmer, U.S.A.) for the characterization of the sorbent and Brunauer–Emmett–Teller (BET) instrument (3Flex Physisorption, U.S.A.).

Synthesis of Cellulose Acetate-(3-aminopropyl)triethoxysilane

CA (0.2 g) was dispersed in dry toluene (20 mL). The mixture was then sonicated for 5 mins. A solution was prepared by adding APTES (1 mL) in toluene (5 mL). The prepared solution was then added dropwise to the mixture and was stirred at 25 °C for 24 hr. Then, the sorbent was washed with dry toluene and ethanol. The sorbent was finally dried at 60 °C for 24 h, and subjected for characterizations.

The Study of Dyes Removal

CA-APTES (50 mg) sorbent was added into dyes solution (10 mL) having an initial concentration of 2 ppm. The pH was adjusted to 7 by adding sufficient volume of HCl or NaOH (1.0 M). The mixture of dyes and sorbent was then sonicated for 5 mins to agitate the particles in dyes solution and distributed the sorbent uniformly. After that, the mixture was shaken using an orbital shaker (250 rpm) for 2 hr. The mixture was then separated from the sorbent by centrifugation (4000 rpm) for 5 mins. The absorbance of the final solution was determined using UV-Vis spectrophotometry. The removal experiment and UV-Vis spectrophotometry analysis were replicated twice.

Sampling and Preparation of Batik Textile Wastewater

Wastewater sample was collected in glass sample bottles from different wells at Ilham Batik textile factory in Kota Bharu, Kelantan, Malaysia. The bottles were fully covered with aluminium foil and stored in a freezer (-4 °C) prior to analysis. As for the analysis, the wastewater sample was mixed from three different bottles collected, filtered using 0.45 μm filter paper and ready for removal procedure. Appropriate volume of treated wastewater sample was spiked with 2 ppm R6G and CV.

RESULTS AND DISCUSSIONS

Characterization of CA-APTES Sorbent

The characterization of the modified CA was achieved by ATR-FTIR spectroscopy and BET techniques. The characterization was done to both CA and CA-APTES for comparison purposes. ATR-FTIR was used to characterize the functional groups present while BET was used to study their surface areas and physical properties. The spectrum of CA showed in Figure 1a indicates peaks of several functional groups that present in the material. The broad absorption band at around 3300 to 3500 cm^{-1} was attributed to the strectching frequency of hydroxyl group, -OH. A moderately intense band at 1736.66 cm^{-1} corresponded to the stretching vibration of the carbonyl group, C=O while the other two bands at 1224.36 and 1036.95 cm^{-1} embodied the C-O stretching frequencies [15]. The modified CA-APTES material also showed several peaks that represent its functional groups, as illustrated in Figure 1b. The N-H stretching for the amide group appeared as a single spike at 3452.98 cm^{-1}, while a strong sharp band at 1740.17 cm^{-1} was attributed to the carbonyl, C=O of the amide group. The sp^3 C-H stretching also present in the modified CA-APTES at around 2840 to 3000 cm^{-1}.
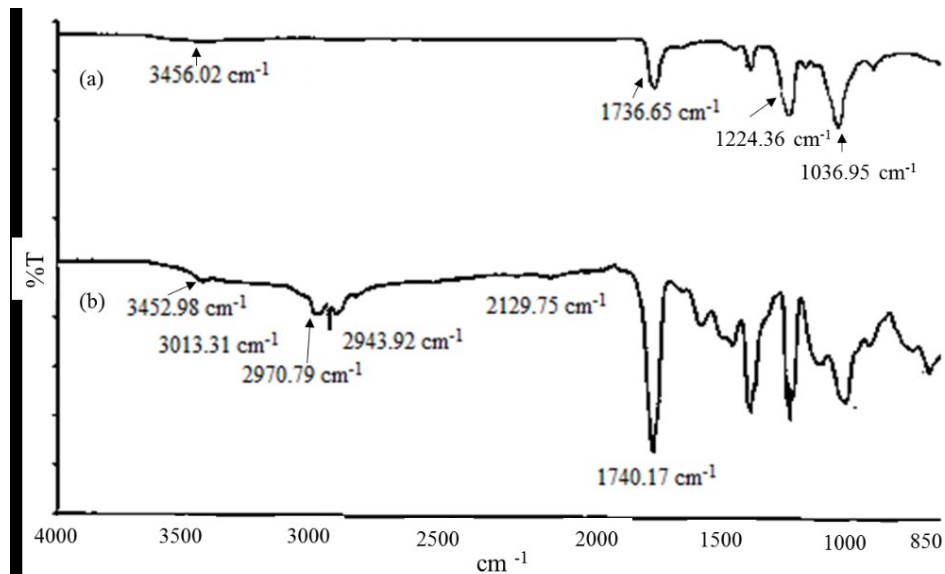

**FIGURE 1.** The ATR-FTIR spectrum of (a) CA and (b) CA-APTES.

The BET results of CA showed that the BET surface area and Langmuir surface area were 1.7726 m^2/g and 1.9661 m^2/g, respectively. The volume of pores and average pore diameter for adsorption were 0.009794 cm^3/g and 221.0130 A respectively. While for CA-APTES, the BET surface area and Langmuir surface area were 1.4576 m^2/g and 2.6935 m^2/g with corresponding volume of pores and average pore diameter of 0.001246 cm^3/g and 34.1982 A. The BET surface area for CA was found to be relatively larger as compared to the CA-APTES, contrary to their Langmuir surface areas. BET measures the surface area of the nitrogen adsorption, thus larger adsorbent size results in a superior adsorption [16]. Although the BET surface area for CA-APTES adsorbent was quite small as compared to CA, but it has the ability to remove more than 40% of the dyes. Mesoporous materials are those having pore filling in multilayer region of sorption isotherms wide pore diameter [17]. Generally, porosity can be categorized into three classes based on the pore diameters; micropores (<2 nm), mesopores (2-50 nm), and macropores (>50 nm) [18]. Based on Table 1, CA-APTES sorbent can be classified as mesopores. Mesoporous size of the sorbent may efficiently remove dyes due to its large size [19]. Its large size could trapped the dyes in its networks, so it improved the removal efficiency.

TABLE 1. Physical properties of CA and CA-APTES.

Properties	CA	CA-APTES
BET surface area (m^2/g)	1.7726	1.4576
Langmuir surface area (m^2/g)	1.9661	2.6935
Adsorption total pore volume of pores (cm^3/g)	0.0098	0.0012
Adsorption average pore diameter (A)	221.0130	34.1982
Total volume in pores (cm^3/g)	0.0120	0.0014
Total area in pores (m^2/g)	0.4090	0.5420

Optimization of Removal Efficiency

The percentage removal of R6G and CV at 2 ppm were 45.59 % and 75.77%, respectively. The sorbents have the maximum capacity to adsorb certain amount of dyes was most probably due to their surface areas. Based on the trend shown in Figure 2a, there was an increase in the percentage removal from 1 ppm to 2 ppm and the value started to gradually decreased from 2 ppm to 3 ppm. Therefore, the initial concentration was considered as a crucial parameter for the adsorption as the percentage of removal increased until it reached an equilibrium point. The reason behind the latter trend (decreased % removal starting at 2 to 3 ppm) was most likely due to the repulsive forces that occured from the vacant site that have been filled up with dyes molecules [20].
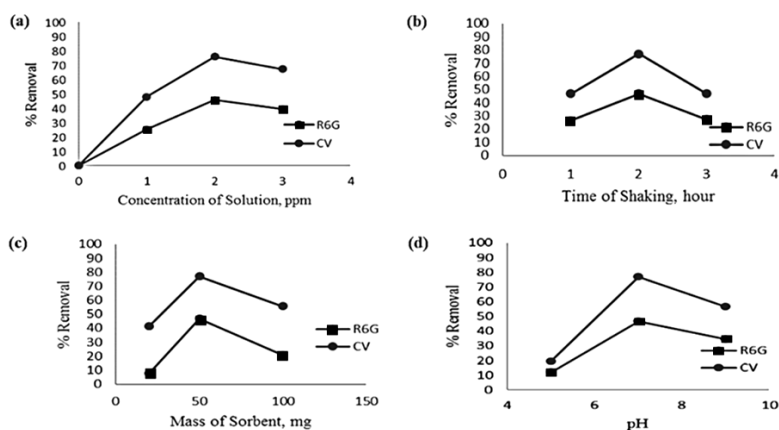
FIGURE 2. (a) The removal percentage of dyes at different initial dyes concentration at 25 °C, sample solution of pH 7, 50 mg adsorbent, 10 mL solution, and 2 hours of shaking at 250 rpm. (b) The removal percentage at different shaking time; conditions of 2 ppm sample solution and pH 7. (c) The removal percentage at different mass of sorbent; conditions of 2 hr shaking time, 2 ppm sample solution at pH 7. (d) The removal percentage at different sample pH, conditions of 2 hr shaking time and 2 ppm sample solution.

Figure 2b shows the result of the dyes removal at different shaking time at pH 7, concentration of 2 ppm, 10 mL solution and 50 mg sorbent. The optimum removal of dyes was at 2 hr shaking time by which 46.80 % of R6G and 77.03 % of CV had been removed. The removal of dyes based on the shaking time may be affected by the adsorption processes such as diffusion, particle diffusion, mass transfer and chemical reaction [21]. At 2 hr of shaking, the adsorption process might have reached its equilibrium by which the removal dyes will no longer increase beyond this point. This concludes that the maximum time of shaking removing 2 ppm of dyes from aqueous solution was 2 hr.

The mass of sorbent might be another factor affecting the percentage of dyes removal. The optimization was done within the range of 20 - 100 mg. The results as illustrated in Figure 2c, shows that the highest percentage of dyes removal; 46% for R6G and 77% for CV could be achieved when 50 mg of sorbent was used. Therefore, 50 mg mass of sorbent was used throughout the experiment. The increment trend shows that the contact surface of the adsorbent played an important role [22]. However, the maximum contact surface between the adsorbent and the dyes molecules can only be achieved when 50 mg of adsorbent was used.

The pH value affecting the removal of dyes might due to the sorbent surface charge, speciation of the sorbent, and the degree of the ionization [21]. Figure 2d shows the high percentage removal of both R6G and CV in a pH 7 medium. Removal of CV was much higher as compared to R6G with the optimum percentage removal of 77.03% and 46.77%, respectively. This might be due to the higher interaction of the sorbent itself with CV than with R6G.

Kinetic Study

To study the adsorption kinetics of the dyes on CA-APTES adsorbents, two kinetic models: pseudo-first order and pseudo-second order models were used to fit the kinetic data obtained from the adsorption of the dyes. The R^2 for the pseudo-first-order were 0.0064 and 0.0523 for R6G and CV, respectively (data not shown). There was no correlation observed between pseudo-first order with the removal efficiency as the R^2 values were not even closed to 1. Figure 3a and b show the plots of pseudo-second order kinetic with R^2 values of 0.75 and 0.87 for the removal of R6G and CV, respectively. R^2 value that was close to 1 indicated a perfect fit to the pseudo-second-order model. Therefore, both R6G and CV were concluded to be best fitted to the pseudo-second-order model rather than to the pseudo-first-order. Although their R^2 values were not as close as to one but it was still considered better as compared to the pseudo-first-order. Since they fit to the latter model, the removal of dyes was said to solely influence by chemical sorption, without the involvement of mass transfer process [23]. Therefore, the removal of dyes using CA-APTES sorbent might due to the chemical sorption as the R^2 was nearing 1.
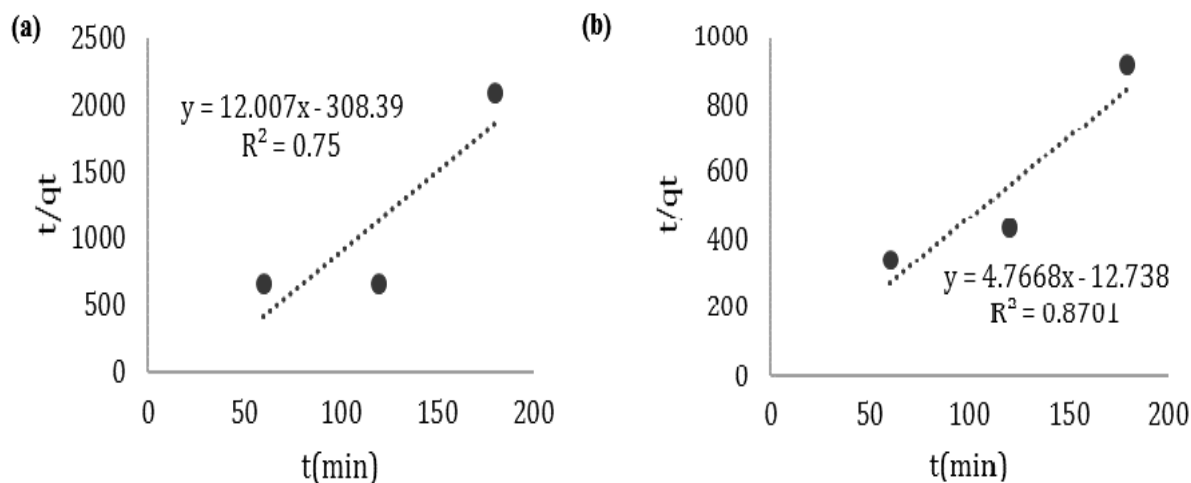
FIGURE 3. (a) Pseudo-second order kinetic for R6G at 25 °C, batch volume, 10 mL (b) Pseudo-second order kinetic for CV at 25 °C, batch volume of 10 mL.

Application of CA-APTES Removal Method For Batik Textile Wastewater Sample

The optimized removal process using CA-APTES sorbent was then adapted for the removal of dyes in batik textile wastewater sample in order to investigate its applicability to complex sample matrix. The wastewater was obtained from a factory and spiked with 2 ppm of R6G and CV. The removal efficiency for CV (61.81 %) was far superior as compared to R6G (48.62 %). This suggested that the sorbent can be used to remove dyes in solution.

CONCLUSION

Cellulose acetate (3-aminopropyl)-triethoxysilane (CA-APTES) sorbent was successfully synthesized. This was supported by ATR-FTIR results showing the presence of C=O of amide at 1740.17 cm^{-1} and N-H stretching frequency around 3452.98 cm^{-1}. BET study showed that the surface area of the sorbent was 1.4576 m^2/g. The removal of R6G and CV was optimized at an initial dye concentration of 2 ppm at pH 7, 50 mg mass sorbent and at 2 hours of shaking time. The optimized method was able to remove 61.81% of CV and 48.62% of R6G from batik textile wastewater. The kinetic studies of the sorbents using pseudo-first order gave corresponding R^2 values of 0.0064 and 0.0523 for R6G and CV, and R^2 of 0.75 and 0.87, for the pseudo-second order. Based on R^2 values from the two kinetic studies, the adsorption of both dyes molecules were concluded to be best described using pseudo-second-order than using pseudo-first-order model.

ACKNOWLEDGMENTS

The authors have declared no conflict of interest.

REFERENCES

1. P.M. Birgani, N. Ranjbar, R.C. Abdullah, K.T. Wong, G. Lee, S. Ibrahum, C. Park, Y. Yoon and M. Jang, J. Environ Manage, **184**, 229-239 (2016).
2. W.F. Khalik, L.N. Ho, S.A. Ong, Y.S Wong, N.A. Yusoff and F. Ridwan, Sains Malaysiana, **44**(4), 607-612 (2015).
3. M.P. Shah, Adv Recycling Waste Manag, **2**(1), 1-11 (2016).
4. S.N.A Abas. M.H.S. Ismail, M. L Kamal and S. Izhar, World Appl. Sci. J, **28**(11), 1518-1530 (2013).
5. S. Babel and T.A. Kurniawan, "Various Treatment Technologies to Remove Arsenic and Mercury from Contaminated Groundwater: An Overview", in *The First International Symposium on Southeast Asian Water Environment*, edited by O. Shinichiro et al (IWA Publishing, London, 2006). pp. 433-440.
6. M.F. Attallah, I.M Ahmed and M.M. Hamed, Environ Sci Pollut Res Int, **20**(2), 1106-16 (2013).
7. K.A. Adegoke and O.S. Bello, Water Resource and Industry, **12**, 8-24 (2015).
8. C. Namasivayam and D. Kavitha, Dyes Pigm, **54**(1), 47-58 (2002).
9. W. Wang, W. L, R. Zhang and J. Wang, Synth Met, **160**(21–22), 2255-2259 (2010).
10. A.A. Asgharinezhad, S. Karami, H. Ebrahimzadeh, N. Shekari and N. Jalilian., Int J App Pharm, **494**(1), 102-112 (2015).
11. E.A. Dil, M. Ghaedi, A. Asfaram and A.A. Bazrafshan, Ultrason Sonochem, **46**, 99-105 (2018).
12. Y.Y. Dong, S. Li, Y.J. Liu, L.Y. Meng and M.G. Ma, J. Mater. Sci., **52**(13), 8219–8230 (2017).
13. L.S Silva, L.C. Lima, F.C. Silva, J.M.E. Matos, M.R.M.C. Santos, L.S. Santos Junior, K.S. Sousa and E.S Silva Filho, Chem. Eng. Sci., **218**, 89-98 (2013).
14. C. H. Zhou, D. Zhang, D.S. Tong, L.M. Wu, W.H. Yu and S. Ismadji, Chem. Eng. Sci., **209**, 223-234 (2012).
15. D. Zavastin, I. Cretescu, M. Bezdadea, M. Bourceanu, M. Dragan, G. Lisa, I. Mangalagiu, V. Vasic and J.Z Savic, Colloid Surf A Physicochem Eng Asp, **370**(1-3), 120-128 (2010).
16. K. Hammes, R.J Smernik, J.O. Skjemstad, M.W. I. Schmidt, Appl Geochem, **23**(8), 2113-2122 (2008).

17. S. Lowell. J.E. Shields, M.A. Thomas and T. Maththias, *Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density* (Springer Science+Business Media, New York, 2004), pp. 11-19.
18. J.B. Condon, *Surface Area and Porosity Determinations by Physisorption: Measurements and Theory*. (Elsevier, Amsterdam, 2006), pp. 1-23.
19. N.H. Wu, H. Wei and L. Zhang, Environ. Sci. Technol., **46**(1), 419-425 (2012).
20. S. Banerjee and M.C. Chattopadhyaya, Arab J Chem, **10**(S2), S1629-S1638 (2017).
21. S. Hokkanen, E. Repo, T. Suopajarvi, H. Liimatainen, J. Niinimaa and M. Sillanpaa, Cellulose, **21**(3), 1471-1487 (2014).
22. B. Benguella and H. Benaissa, Water Res, **36**(10), 2463-2474 (2002).
23. M. Monier, D.M. Ayad, Y. Wei and A.A Sarhan, React Funct Polymer, **70**, 257-266 (2010).