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Photocatalytic Degradation of Methylene Blue Dye Using Chitosan Silica Composite

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The ability of chitosan silica composite for the degradation of methylene blue dye from aqueous solution is studied by direct sunlight irradiation. Batch mode adsorption experiments are carried out to know the degradation capacity of the composite. Maximum removal efficiency 89.05 % of methylene blue is achieved at pH 10 with composite dosage of 0.1 g. Langmuir and Freundlich adsorption isotherm models are used to fit the obtained adsorption data. The maximum adsorption capacity is found to be 11.467 mg/g for the adsorption of methylene blue. The kinetic data is well fitted with pseudo first order kinetics. Degradation ability of methylene blue is confirmed by UV spectra studies.

Keywords: Degradation, Chitosan silica composite, Adsorption isotherms, Methylene blue.

INTRODUCTION

Among all the industrial wastewater the textile water is one of the most polluted water and it cause many unfavourable effects to the living environment [1]. Methylene blue is a thiazine (monovalent cationic) dye most commonly employed in dyeing cotton, silk, leather and cellulosic fibers. Methylene blue is not a toxic dye but it causes adverse effects on living beings. It causes eye burns, which could be a reason for permanent injury in the eyes of human beings and animals. Along with the eye infections vomiting and diarrhea, problem in gastrointestinal tract with symptoms of nausea and also creates dyspnoea, tachycardia, cyanosis, methemoglobinmia and convulsions are caused [2]. Methylene blue is dark green crystalline solid, water soluble and gives chloride ion and methylene blue cations in solution. In the oxidizing environment it is blue in colour and becomes colourless when it is reduced using reducing agents [3,4]. It is essential to degrade methylene blue from the industrial effluent. Commonly used conventional processes are ineffective because of the non-biodegradable nature of the textile wastewater [5]. Several methods have been employed for the decolourization of wastewater including electro chemical destruction, membrane filtration, ion exchange, adsorption, ozonation, flocculation, electro kinetic coagulation, irradiation *etc*. From the above methods irradiation by direct sunlight is considered to be a most effective method particularly for the non-degradable dyes [6,7]. It is necessary to develop eco- friendly method for the wastewater treatment. Solar energy has much potential which provides future energy for all the necessary needs and exploitation of this alternate energy resource.

Chitosan is high molecular polysaccharide and it has many useful aspects like antibacterial, biocompatibility and biodegradable properties [8]. Due to the intra and intermolecular hydrogen bonding between H^+ and $–NH_2$, chitosan dissolves only in the acidic medium. Raw chitosan enhances the degradation ability and it decreases the flocculent efficiency. Chitosan is suitable for anionic dyes degradation which can be compared to cationic dye. In order to increase the cationic dye degradation capacity of chitosan, various functional groups have been used to modify the chitosan [9]. Many attempts have already been reported for the degradation of methylene blue dye using chitosan based materials like chitosan zinc oxide hybrid composite [10], chitosan/ZnO nanocomposites [11], chitosan grafted polyaniline/Co_3O_4 nanocube nanocomposites [12], chitosan-copper oxide hybrid material [13], TiO_2-chitosan porous materials [14] using UV light irradiation.

In the present work the chitosan is modified with silica. Generally, silica is inert for most of the reactions but it is active towards dye degradation in aqueous solution [15,16]. Chitosan and silica is abundantly available and low cost, so they have great interest on wastewater treatment process. The novelty of the prepared chitosan silica composite is highly rigid, porous and surface functionality due to the presence of chitosan and silica. It has good physio-chemical properties, specific surface area and thermal stability than raw chitosan, which enhances the methylene blue dye degradation [17]. So for no report available in literature for the degradation of methylene blue dye onto chitosan silica composite (CSC) using solar irradiation. The main objective of this research to examine the degradation ability of CSC to degrade methylene blue dye. The preparation, physio-chemical and surface characterization of the CSC are already reported [18].

EXPERIMENTAL

Methylene blue dye, sodium hydroxide, hydrochloric acid are procured from Universal Scientific Company, India. The procured chemicals and reagents which are in analytical grade can be used without further purification. Double distilled water is used in the entire synthesis.

A stock solution of 1000 mg/L of methylene blue is prepared by dissolving 1 g of dye in the double distilled water. All experiments are carried in triplicate and the mean values are reported.

Photo degradation: Batch mode parameters such as effect of pH, effect of adsorbent dosage, effect of initial dye concentration and effect of contact time are analyzed using CSC under direct sunlight irradiation.

A methylene blue stock solution is prepared and it is further diluted for batch mode experiments. The concentration of the solution varies from 10-70 mg/L of the dye. NaOH/HCl is used to adjust the pH of the dye solutions ranges from 4-11, with CSC dosage from 0.02 to 0.1 g. 50 mL of methylene blue solutions are taken in the different set of flasks for different CSC dosage, time, concentration and pH and are stirred magnetically in dark to attain equilibrium between dye and CSC. After reaching the equilibrium condition the solutions are kept under direct solar radiation. The absorbance is measured using UV-visible spectrophotometer 119 with regular intervals ranges from 200-800 nm. The degradation efficiency (η) is calculated by the eqn. 1 as given below:

$$\eta = \frac{A_0 - A_t}{A_0} \quad (1)$$

where A_0 is the initial absorbance of the dye and A_t is the absorbance of dye after degradation [19].

RESULTS AND DISCUSSION

Batch mode studies

Effect of contact time: In the batch mode parameters contact time plays a vital role. The effect of contact time for the degradation of methylene blue on CSC is analyzed by using optimum parameters. 0.1 g of CSC, pH of the dye solution is 10 and varying the contact time of the dye solution which is carried out under sunlight irradiation. As the time increases the degradation ability also increases upto the equilibrium condition. When contact time increases the bond present in the methylene blue dye becomes weaker and the chromophores is breakdown, this indicates the colour change of the methylene blue dye [20]. The maximum degradation ability is achieved at 80 min is shown in the Fig. 1.

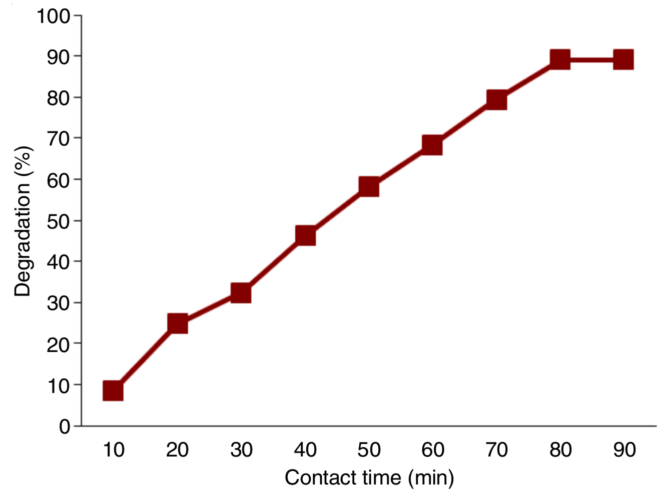

Fig. 1. Effect of contact time on the degradation of methylene blue using chitosan silica composite

Effect of composite dose: The degradation ability of methylene blue increases with increase dose of composite from 0.02 g to 0.1 g. Beyond 0.1 g of composite dose does not cause any change in degradation. It is mainly due to the excess composite dose gives a large number of active sites leading to a lower utility of the sites at a definite concentration of methylene blue dye solution [21]. So 0.1 g of CSC dose is fixed as an optimum dose for the entire process. The effect of composite dose on the degradation of methylene blue dye is shown in the Fig. 2.

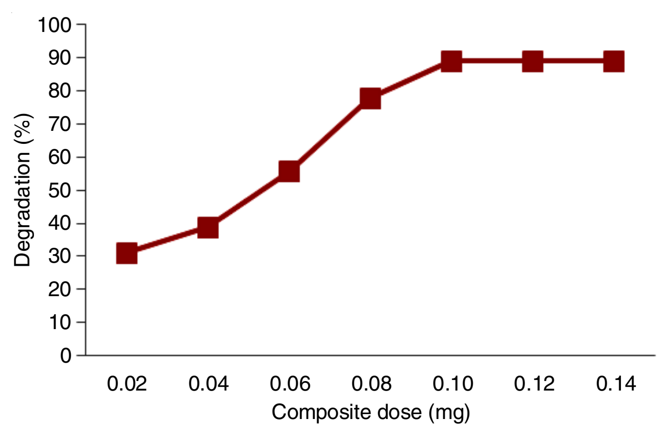

Fig. 2. Effect of composite dosage on the degradation of methylene blue using chitosan silica composite

Effect of pH: The pH of the dye solution plays an important role in the degradation process. The pH influences the surface charge of the composite, dissociation of the functional groups on the active sites of the composite and the degree of ionization of the material present in the solution. The effect of pH for the degradation of methylene blue on CSC is studied in the range of pH from 4-11. The CSC surface is negatively charged because the solution pH is greater than the zpc (7.8), which enhances the degradation of methylene blue dye [22]. The optimum pH for batch mode studies is stetted as 10. The uptake of dye increases with increasing pH. At high pH the surface of the composite is negatively charged which increases the positively charged methylene blue cations through electrostatic attraction [23]. The effect of pH on methylene blue dye degradation is shown in Fig. 3.

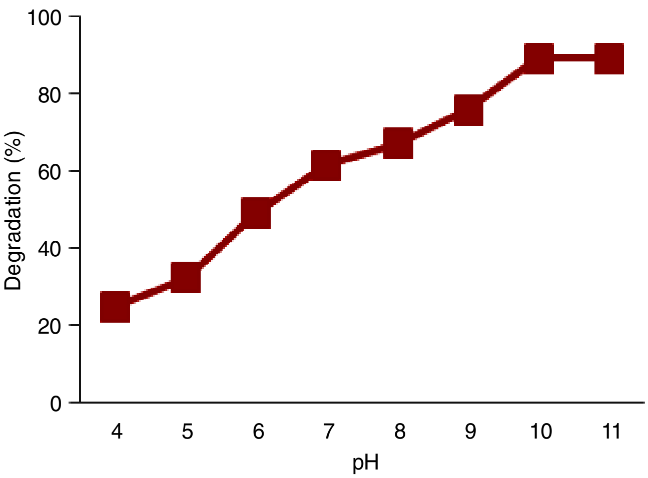

Fig. 3. Effect of pH on the degradation of methylene blue using chitosan silica composite

Effect of Initial dye concentration: The degradation ability of the composite for methylene blue is decreased by increasing initial dye concentration. There is complete degradation of methylene blue at lower concentration, when the concentration of the dye solution increases the degradation efficiency is reduced up to 70 mg/L. It is clearly explained on the basis of the variation in optical density for the various concentration of methylene blue dye solution. The concentration of methylene blue solution increases, the density of the dye molecules in the solution is also increases which retard the penetration of the light into the solution [24]. When methylene blue is at higher concentration there is a decrease in energy of CSC is the main cause for poor degradation. The relationship between initial dye concentration and % of degradation is given in Fig. 4.

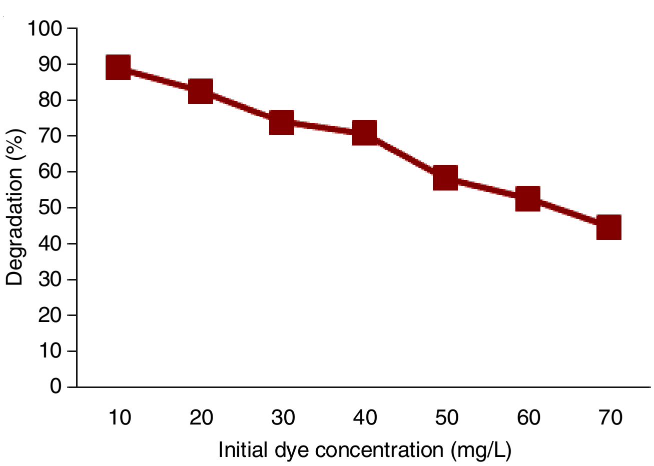

Fig. 4. Effect of initial dye concentration on the degradation of methylene blue using chitosan silica composite

Conformation studies for the degradation of methylene blue dye degradation

UV spectra of methylene blue onto chitosan silica composite (CSC): The relation between wavelength and absorbance is shown in Fig. 5. The amount of degradation is measured at the wavelength 663 nm of methylene blue onto CSC. When the irradiation time increases the absorbance

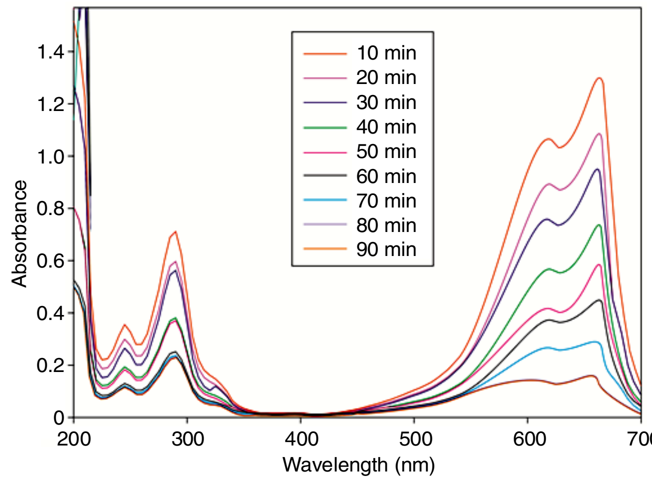

Fig. 5. UV spectra of methylene blue onto chitosan silica composite

decreases gradually in the presence of sunlight irradiation. Before the degradation the absorbance of methylene blue dye is 1.303 mol/L and after the degradation the absorbance is 0.156 mol/L. It indicates that the dye has been degraded.

The degradation of methylene blue is analyzed quantitatively by using optimum pH, contact time, concentration and CSC dose. The maximum degradation of methylene blue onto CSC is 89.05 % and achieved at 90 min

Proposed mechanism for degradation of methylene blue using chitosan silica composite (CSC): The proposed mechanism for the formation of chitosan silica composite involves two steps. In the first step chitosan and silica are dispersed in acetic acid solution, where silica dissolves immediately and forms coordination bonds with –OH and NH_2 groups of chitosan chain [25]. In the second step pH of the solution is increased by the drop wise addition of NH_4OH. The formed precipitate is filtered and heated at 55 °C for 5 h.

The mechanism and the charge transfer process happen in the present silica composite. During the degradation process the used dye molecules has been transferred and adsorbed in silica by the organized orientation *via* π-π loading between the skeleton of dye and aromatic groups of carbon chain. When sunlight irradiation is used to irradiate the prepared composite, the fast shift of obtianed photo excited electrons to the surface of silica composite and it eliminates few adsorbed O_2 molecules to form O_2^{2-} and O_2^{-}. In this condition the composite has more electrons and more pores are the main reason for the easy and fast degradation of dye molecules [26] is shown in Fig. 6.

Adsorption isotherms: Langmuir and Freundlich are the two equilibrium isotherm models are employed to fit the experimental data for the adsorption of methylene blue dye in CSC. The linear form of Langmuir and Freundlich isotherm is given below:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}} b + \frac{C_e}{q_{max}} \quad (2)$$

hence C_e is the concentration of methylene blue dye solution (mg/L), q_e is the methylene blue dye concentration in CSC (mg/g), q_{max} is the maximum degradation capacity (mg/g) and b is the Langmuir equilibrium constant [27].

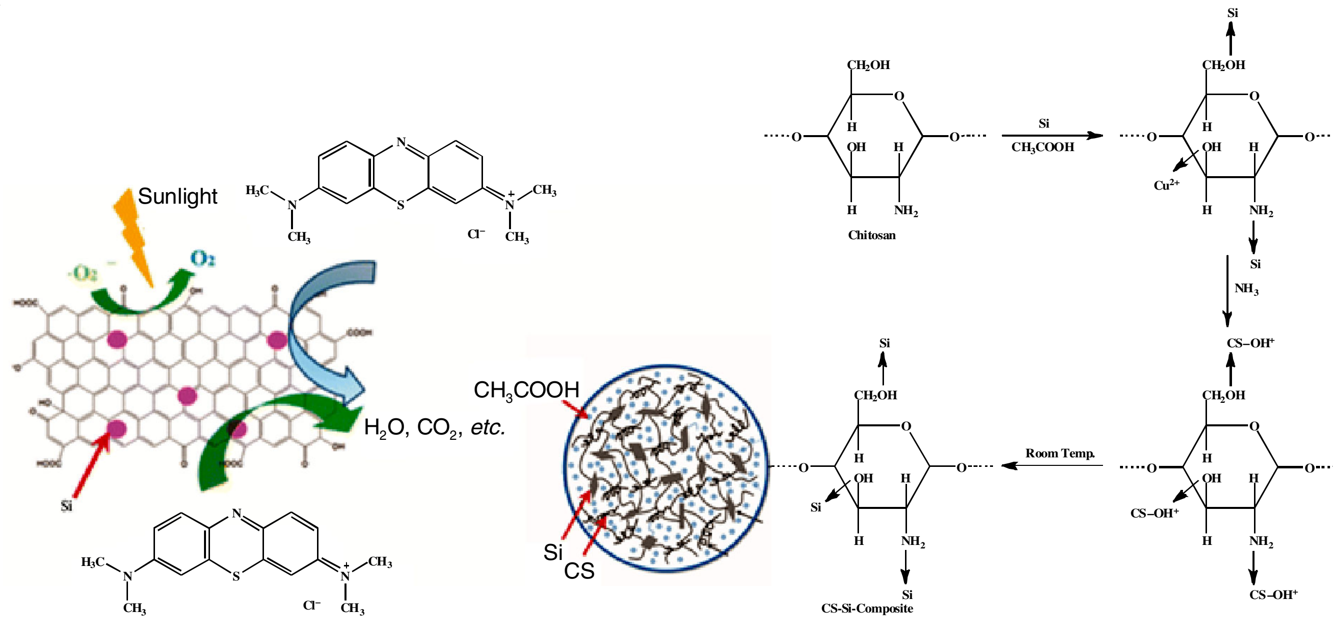

Fig. 6. Proposed scheme of photodegradation of methylene blue dye solution by chitosan silica composite

$$\log q_e = \frac{1}{n}\log(C_e) + \log K_f \quad (3)$$

where K_f is the Freundlich constant (mg/g), n is the Freundlich exponent [28].

The Langmuir and Freundlich isotherms are fitted to the experimental data is indicated by correlation coefficients. The multilayer adsorption of methylene blue on CSC shows the heterogeneity surface of CSC.

The Langmuir Isotherm equation is well fitted with experimental data and it shows CSC has a homogeneous surface for the adsorption of dyes. The R^2 values of Langmuir model (0.9976) are closer to the Freundlich Isotherm model (0.9362) for CSC on methylene blue dye. The Langmuir and Freundlich isotherm parameters for the degradation of methylene blue onto chitosan silica composite is given in Table-1.

TABLE-1
LANGMUIR AND FREUNDLICH ISOTHERM PARAMETERS FOR THE DEGRADATION OF METHYLENE BLUE USING CHITOSAN SILICA COMPOSITE

Isotherm model	Parameters	Chitosan silica composite
Langmuir Isotherm	Q_m (mg/g)	11.467
	b (L/mg)	3.311
	R^2	0.9976
Freundlich Isotherm	1/n	2.807
	K_F (mg/g)	3.287
	R^2	0.9362

Comparative analysis of methylene blue dye degradation using chitosan based materials: Table-2 represents the comparative analysis of degradation capacity and reaction time of methylene blue dye by present study with other chitosan based materials. From the table it is clear that the photocatalytic degradation of methylene blue is carried out using UV light radiation by many researchers. Even though the previous works give better efficiency with less reaction time, the use of UV light is expensive and harmful to human health. So, the current work emphasizes the utilization of solar energy (naturally occurring energy) for the photocatalytic degradation of methylene blue dye. Chitosan silica composite shows better result than other chitosan based material by is degradation efficiency and reaction time in solar irradiation.

Kinetic studies

Pseudo first order kinetics: Kinetic models are employed to investigate the mechanism of adsorption. To examine the adsorption kinetics of methylene blue on CSC pseudo first order kinetics is applied.

The expression for the pseudo first order kinetic model is given below:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

where q_e (mg/g) is the amount of methylene blue dye is adsorbed at the equilibrium phase, qt (mg/g) is the amount of dye adsorbed at time t and k_1 (min^{-1}) is the rate constant of the pseudo-first-

TABLE-2
COMPARISON OF DEGRADATION EFFICIENCY OF VARIOUS CHITOSAN BASED ADSORBENTS

Composite used	Degradation (%)	Reaction time (min)	Light source	Ref.
Chitosan zinc oxide hybrid composite	64.00	180	UV light irradiation	[10]
Chitosan/ZnO nanocomposites	80.00	240	UV light irradiation	[11]
Chitosan grafted polyaniline/Co_3O_4 nanocube nanocomposites	88.00	180	UV light irradiation	[12]
Chitosan-copper oxide hybrid material	84.00	30	UV light irradiation	[13]
TiO_2-Chitosan porous materials	91.00	180	UV light irradiation	[14]
Chitosan silica composite	89.05	80	Solar irradiation	Present study

order adsorption model [29,30]. The methylene blue adsorption data is well fitted with the pseudo first order equation. The rate constant for CSC is 0.1013. The linear regression coefficient value R^2 is equal to 0.9953. This indicates the adsorption of methylene blue on CSC follows pseudo first order kinetics.

Conclusion

• The present study shows that chitosan silica composite (CSC) can be used as an effective composite for the degradation methylene blue from aqueous solution.

• The amount of dye adsorbed is found to vary with initial pH, composite dose, methylene blue concentration and contact time.

• The adsorption data are found to fit with Langmuir and Freundlich adsorption isotherm.

• Pseudo first order kinetic model can be used to predict the adsorption kinetics.

REFERENCES

1. S. Madhavakrishnan, K. Manickavasagam, R. Vasanthakumar, K. Rasappan, R. Mohanraj and S. Pattabhi, *E-J. Chem.*, **6**, 1109 (2009); https://doi.org/10.1155/2009/764197.
2. K. Bhattacharyya and A. Sharma, *Dyes Pigments*, **65**, 51 (2005); https://doi.org/10.1016/j.dyepig.2004.06.016.
3. D. Ghosh and K.G. Bhattacharyya, *Appl. Clay Sci.*, **20**, 295 (2002); https://doi.org/10.1016/S0169-1317(01)00081-3.
4. H. Choi, E. Stathatos and D.D. Dionysiou, *Desalination*, **202**, 199 (2007); https://doi.org/10.1016/j.desal.2005.12.055.
5. A. Dabrowski, *Adv. Colloid Interface Sci.*, **93**, 135 (2001); https://doi.org/10.1016/S0001-8686(00)00082-8.
6. M.S. Chiou and G.S. Chuang, *Chemosphere*, **62**, 731 (2006); https://doi.org/10.1016/j.chemosphere.2005.04.068.
7. I.A. Salem and M. El-maazawi, *Chemosphere*, **41**, 1173 (2000); https://doi.org/10.1016/S0045-6535(00)00009-6.
8. O.S. Bello, M.A. Ahmad and T.T. Siang, *Trends Appl. Sci. Res.*, **6**, 794 (2011); https://doi.org/10.3923/tasr.2011.794.812.
9. G. Kyzas and D. Bikiari, *Mar. Drugs*, **13**, 312 (2015); https://doi.org/10.3390/md13010312.
10. 10.Y. Haldorai and J.-J. Shim, *Compos. Interfaces*, **20**, 365 (2013); https://doi.org/10.1080/15685543.2013.806124.
11. S. Dhanavel, E.A.K. Nivethaa, V. Narayanan and A. Stephen, *Int. J. Chemtech Res.*, **6**, 1880 (2014).
12. S. Shahabuddin, N.M. Sarih, F.H. Ismail, M.M. Shahid and N.M. Huang, *RSC Adv.*, **5**, 83857 (2015); https://doi.org/10.1039/C5RA11237K.
13. Y. Haldorai and J.-J. Shim, *Int. J. Photoenergy*, **2013**, 1 (2013); https://doi.org/10.1155/2013/245646.
14. C.E. Zubieta, P.V. Messina, C. Luengo, M. Dennehy, O. Pieroni and P.C. Schulz, *J. Hazard. Mater.*, **152**, 765 (2008); https://doi.org/10.1016/j.jhazmat.2007.07.043.
15. H. Yoshida, M.G. Chaskar, Y. Kato and T. Hattori, *J. Photochem. Photobiol. Chem.*, **160**, 47 (2003); https://doi.org/10.1016/S1010-6030(03)00220-X.
16. L. Yuliati, T. Hattori and H. Yoshida, *Phys. Chem. Chem. Phys.*, **7**, 195 (2005); https://doi.org/10.1039/b410089a.
17. T.M. Budnyak, I.V. Pylypchuk,V.A. Tertykh, E.S. Yanovska and D. Kolodynska, *Nanoscale Res. Lett.*, **10**, 87 (2015); https://doi.org/10.1186/s11671-014-0722-1.
18. P. Saraswathi and M. Makeswari, *Rasayan J. Chem.*, **10**, 759 (2017); https://doi.org/10.7324/RJC.2017.1031752.
19. N. Madhusudhana, K. Yogendra and M.K. Mahadevan, *Res. J. Chem. Sci.*, **2**, 72 (2012).
20. M.A.H. Devadi, M. Krishna, H.N.N. Murthy and B.S. Sathyanarayana, *Procedia Mater. Sci.*, **5**, 612 (2014); https://doi.org/10.1016/j.mspro.2014.07.307.
21. R. Kumar, J. Rashid and M.A. Barakat, *Colloid. Interf. Sci.Commun.*, **5**, 1 (2015); https://doi.org/10.1016/j.colcom.2015.05.001.
22. M. Makeswari and T. Santhi, *Int. J. Mod. Eng. Res. Technol.*, **3**, 3255 (2013).
23. Z. Wu, H. Zhong, X. Yuan, H. Wang, L. Wang, X. Chen, G. Zeng and Y. Wu, *Water Res.*, **67**, 330 (2014); https://doi.org/10.1016/j.watres.2014.09.026.
24. K.L. Ameta, N. Papnai and R. Ameta, *Orbital E-J. Chem.*, **6**, 14 (2014).
25. A. Higazy, M. Hashem, A. ElShafei, N. Shaker and M.A. Hady, *Carbohydr. Polym.*, **79**, 867 (2010); https://doi.org/10.1016/j.carbpol.2009.10.011.
26. Y.L. Min, K. Zhang, Y.C. Chen and Y.G. Zhang, *Sep. Purif. Technol.*, **86**, 98 (2012); https://doi.org/10.1016/j.seppur.2011.10.025.
27. I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918); https://doi.org/10.1021/ja02242a004.
28. H. Freundlich, *Z. Phys. Chem.*, **57U**, 385 (1907); https://doi.org/10.1515/zpch-1907-5723.
29. Y.S. Ho and G. McKay, *Chem. Eng. J.*, **70**, 115 (1998a); https://doi.org/10.1016/S0923-0467(98)00076-1.
30. Y.S. Ho and G. Mckay, *Process Saf. Environ. Prot.*, **76**, 183 (1998); https://doi.org/10.1205/095758298529326.