ISSN 2229-5518

Synthesis and characterization of novel friendly biosorbents and it uses for removal of crystal violet dye from wastewater

Elhossein A. Moawed*, Hala A. Kiwaan, Amira A.A. Elbaraay

Chemistry Department, Faculty of Science, Damietta University, Damietta, Egypt

***Corresponding author**: E-mail eamoawed@yahoo.com; Phone: 00201028921272; Fax: 0020572403868; P.O. Box: 34517- Damietta; Egypt

Abstract

The methodology of this work preparing of low cost and environmental friendliness biosorbents and used for the treatment of industrial wastewater by removing dyes from its effluent. The cellulose and lignin biosorbents were getting from the camphor tree using acidic and alkaline treatments. There are characterized using ultraviolet, visible and infrared spectra surfaces functional groups and pH zero point charge. The cellulose and lignin biosorbents were applied for removing of crystal violet from wastewater. The effect of intial pH solutions, shacking time, crystal violet concentration, and solution temperature on the removal of dye were test The cellulose and lignin biosorbents has a high efficiency for completely removing (95–100%) of Cr.V at pH 5-7 within a period from 2 to 5 min. The pseudo-second-order model was best described by kinetics process with R^2 values (1.0). The negative values of ΔG (-3.1 and -9.2 kJ/mol) for removing of Cr.V using cellulose and lignin biosorbents showed that the feasibility of the removing process and its spontaneous nature. The lower relative standard deviation (RSD% 1.32-3.39) for five replicating procedures (n=5).

Keywords: Removal; Basic dyes; Crystal violet; Cellulose; Lignin

1. Introduction

Adsorption technique is one of the most efficient procedures used for the removel of crystal violet dye from wastewater [1-3]. A variety of biosorbents were applied for the removing of organic and inorganic polluted using adsorption technique [4-6]. Cellulose and lignin were the most abundant material on the tree and comprises 80-90% of the dry weight of woody tree [7-9]. The leaching of solulble components from the tree matrix in the acidic and alkaline medium were the main problem for used it as a biosorbents. The different composition of camphor tree were used for different applications and also oil extract of camphor tree can be used for antifungal activity and also [9-12]. Many cities have planted a camphor tree in main roads, parks, and schools. In this work, the cellulose and lignin of camphor tree were used as a stable biosorbents for removing of crystal violet from wasteater.

Crystal violet dye was highly used in biological stain, dermatological agent and to prevent the formation of parasites and fungus [13-15]. Also, the crystal violet dye was soluble in water, therefore, the effluents of this dye have a negative impact on the environment [16-18]. This is causing irritation of the gastrointestinal tract; symptoms include nausea, vomiting and, diarrhea, therefore, the removing of this dye from the effluent before its discharge into the environment were a very important process [19-21]. Adsorption method was available used to overcome this problem [22, 23]. The aim of this study, we prepared the cellulose and lignin of camphor as new biosorbents by NaOH and H_2SO_4 solutions. The importance of these biosorbents has been increased due to low cost, easy handling, and storage. The highly acidic and basic characters of cellulose and lignin make it suitable for removing crystal violet from wastewater. The sorption capacities of cellulose and lignin were investigated with various parameters like pH, contact time, initial dye concentration and solution temperature.

2. Experimental

2.1. Apparatus

All spectrophotometric measurements were performed on a JASCO (V-630UV-VIS Spectrophotometer, Japan). The pH measurements were carried out using a Jenway 3510 pH-meter (Beacon Road, Stone, Staffordshire, ST15 OSA, UK). IR spectra were carried out using KBr disc on a JASCO FTIR-410 spectrometer in the 4000–400 cm^{-1} region.

2.2. Reagents and materials

Cellulose of camphor**:** 100 g of Camphor sticks were socked in 250 mL of 3M NaOH at 24 h then washed with distilled water and methanol followed by dried at 105˚C and blended in a food-processing blender.

Lignin of camphor**:** 100 g of Camphor sticks were socked in 250 mL of H_2SO_4 (1:1) at 24 h then washed with distilled water and methanol followed by dried at 105˚C and blended in a food-processing blender.

Stock solution of crystal violet ($C_{25}N_3H_{30}Cl$, 407.9 g/mol) dye was prepared by dissolving 0.1 g of pure dye in 100 mL of distilled water.

2.3. Recommended procedures

Removing processes were carried out by agitating 0.1 g of cellulose and lignin with 25 mL of Br.G or Cr.V dye solutions of a desired concentration. Br.G or Cr.V dye concentrations were estimated spectrophotometrically by monitoring the absorbance at 590 nm. The removal percentage and capacities of cellulose and lignin (Q, mmol/g) were calculated using the following relationship:

$$\%E = \left(\frac{C_o - C}{C_o}\right) \times 100$$

$$Q = \frac{C_o E V}{W}$$

Where Co and C are the initial and final concentrations of dye in solution, respectively and V (mL) is the volume of the solution and *W* (g) is the weight of biosorbents.

3. Results and discussion

3.1. Characteristics of cellulose and lignin biosorbents

The infrared spectra of cellulose and lignin were tested using KBr at 4000-400 cm^{-1}. The characteristic absorption peaks of cellulose were observed at 3704-2975 cm^{-1} (-OH, -CH), 1687 cm^{-1} (C=O), 1587 cm^{-1} (C=C), 1369 cm^{-1} (C–H) and 1230 cm^{-1} (C-O-C). While these bands of lignin spectrum were appeared at 3417-2447, 1704 and 1585 cm^{-1}.

Figure 1

The electronic spectra of cellulose and lignin were recorded using the Nujol mulls method. The cellulose has absorption bands at 350-354 and 369 nm wlile these bands were appeared in lignin spectra at 349, 369, 381 and 387 nm. These bands assigned to π–π^* and n–π^* transitions.

Figure 2

The pH_{ZPC} values of cellulose and lignin are the pH value when these charged surfaces are zero and the initial pHs of tested solutions equals the final pHs. The differences between initial and final pH values (ΔpH) were plotted against the initial pH (Fig. 3A). The estimated pH_{ZPC} values of cellulose and lignin were 2.8 and 8.6. The different values of pH_{ZPC} for camphor biosorbents due to change of functional groups of them. The relation between initial pH of dye solutions with the removal percentages of crystal violet was examined using the batch technique (0.1 M HCl/NaOH) and showed in figures 3B. The maximum removal percentages of crystal violet using cellulose and lignin were achieved at pH ranges 3-11 and 3-13, respectively. The wide ranges of pH values are best appropriate for removing dyes from real samples,

Figure 3

The iodine adsorption capacity (Q) was determined from the adsorbed iodine/unit mass of the adsorbent at the residual iodine concentration. The sorption capacity of biosorbent for iodine was estimated to be 1.7 and 1.6 mmol/g for cellulose and lignin, respectively. The cellulose and lignin were also characterized by estimation of methylene blue value (cation exchange capacity). The estimated values of methylene blue were 0.24 and 0.26 mmol/g, these values indicate that the surface of biosorbents contain mesopores and mesopores.

The values of electrical conductivity (σ) of cellulose and lignin were 5.1×10^{-5} and 3.6×10^{-5} Ω^{-1} m^{-1}, respectively (Table 1). The results obtained suggest that the proportional relationship between the values of conductivities and amounts of acidic sites.

Table 1

The carboxylic and phenolic sites of cellulose were 0.05 and 0.13 mmol/g, while the amounts of these sites in the lignin of camphor were 0.50 and 0.20 mmol/g, respectively. The total acidic sites of lignin (0.85 mmol/g) are greater than those of cellulose (0.28 mmol/g). While the basic sites of cellulose (0.85 mmol/g) are greater than those in lignin (0.20 mmol/g).

3.2. Optimum conditions for the removal of crystal violet

The effect of solution temperatures (25–90 ˚C) on the removal of crystal violet using cellulose and lignin was studied (Fig. 4). The removal crystal violet percentages were slightly affected by increasing temperature; this indicates that the removal process of crystal violet from wastewater is independent on the temperature.

Figure 4

The thermodynamic parameters of removing process for crystal violet using biosorbents were estimated ($\ln K = \Delta H/RT + \Delta S/R$ and $\Delta G = \Delta H - T\Delta S$). The average values of ΔH was -6.8 kJ/mol for removing of crystal violet, this value show that removing process is the exothermic. The values of ΔG for removing crystal violet by using cellulose and lignin were -3.1 and -9.2 kJ/mol. The negative values of ΔG for the removing of crystal violet onto cellulose and lignin was attributed to the spontaneous nature of the sorption process. The values of ΔS were 0.02 and -0.01 kJ/mol.

Table 2

The effect of shaking time (1–60 min) on the removal percentages of crystal violet using cellulose and lignin were tested using batch mode (Figs. 5). The maximum removal percentages of crystal violet using cellulose and lignin were found to be 1-3 min. It was noticed that the initial removal rate of dye is very rapid, where about 75% of crystal violet dye was removed from the solutions in the first 30 seconds.

Figure 5

The kinetic parameters for removing of crystal violet using cellulose and lignin were estimated by pseudo first-order [$\log(Q_e - Q_t) = Log\ Q_e - \frac{k_1 t}{2.303}$] and pseudo second-order models [$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e}$]. The average values of R^2 for pseudo second-order sorption model (1.0) are more than those for pseudo first-order kinetic (0.659). These data show that the pseudo second order sorption is predominant.

Table 3

The plot of initial crystal violet concentration against the amount of removal capacities of cellulose and lignin yields perfect linear curves with nearly zero intercepts were 5.0×10^{-4} and good correlation coefficient (R^2) 0.999 (Fig. 6). The sorption capacities of cellulose and lignin for crystal violet were estimated to be 0.41 and 0.34 mmol/g (167 and 139 mg/g). Comparisons for the capacities of cellulose and lignin with that of other sorbents [24-28] show that they have the better capacity (Table 4).

Figure 6

Table 4

The equilibrium data for removing process of crystal violet were analyzed using Freundlich ($logQ_c = logK_F + \frac{1}{n} logC_e$) and Langmuir [$\frac{C_e}{Q_c} = \frac{1}{K_L b} + \frac{C_e}{K_L}$] models. The plot of Q_c/C_e vs. C_e for the data according to the Langmuir model gives linear relationship (R^2=0.176). The plot of log Q_c vs. log Q_e of the data according to Freundlich model give a good linear relationship with crystal violet have average values of R^2 0.451. The results demonstrated that the Freundlich model provides an accurate description of the experimental data for the removal of crystal violet using tested biosorbents (Table 3).

3.3. Application

The removing process for crystal violet dye from wastewater samples using cellulose and lignin was examined. A 25 mL of washing machine wastewater samples was spiked with different amounts of crystal violet (100-500 µg) then the solutions were shacked at 30 min with 0.1 g of biosorbents (Table 5). The removal percentages of crystal violet dye from the industrial wastewater samples were found to be 80.6-87.9% and 90.6-93.4%, respectively. The relative standard deviation (RSD) for five replicating procedures (n=5) was 3.39% and 1.32%.

Table 5

Camphor biosorbents was applied for removing of crystal violet dye from different locations of wastewater samples. Over thirty wastewater samples from five different places in Damietta industrial city for the duration of seven weeks were collected. A 25 mL aliquot of the samples, adjusted to pH 7, was spiked with 100 µg of crystal violet dye. The average removal percentages of crystal violet dye from the samples were in the range of 82.7-99.8% (Table 6). The average value of RSD% was found to be 4.11 and 1.94% (n = 5), which is considered as a relevant value (less than 10%) for wastewater samples.

4. Conclusion

The aim of this work was to find the possible use of cellulose and lignin as a biosorbent for the removal of crystal violet dye from wastewater. The equilibrium, kinetic and thermodynamic models were fitting for removing of crystal violet dye from wastewater by using cellulose and lignin. In the kinetic study, the pseudo-second-order kinetic model was found to be well suited for the entire adsorption process of crystal violet onto cellulose and lignin. The thermodynamic parameters indicate that, the removal of crystal violet is spontaneous process. The equilibrium process is well described by the Frindulich model for removing of crystal violet. The overall results indicated that the camphor stem is an effective and low-cost tested biosorbents for the removal of basic dyes from wastewater.

References

[1] M. Massoudinejad, H. Rasoulzadeh, M. Ghaderpoori, Magnetic chitosan nanocomposite: Fabrication, properties, and optimization for adsorptive removal of crystal violet from aqueous solutions, Carbohydrate Polymers, 206 (2019) 844-853

[2] E.A. Moawed, M.A. El-Hagrasy, A.E.A. Senan, Application of bio-alkyd resin for the removal of crystal violet and methylene blue dyes from wastewater, International Journal of Environmental Science and Technology, (2019) https://doi.org/10.1007/s13762-019-02343-1

[3] E.A. Moawed, A.B. Abulkibash, M.F. El-Shahat, Synthesis, characterization of iodo polyurethane foam and its application in removing of aniline blue and crystal violet from laundry, Journal of Taibah University for Science, 2015, 9, 80-88

[4] M.E. Mahmoud, G.M. Nabil, M.A. Khalifa, N.M. El-Mallah, H.M. Hassouba, Effective removal of crystal violet and methylene blue dyes from water by surface functionalized zirconium silicate nanocomposite, Journal of Environmental Chemical Engineering, 7 (2019) 103009

[5] Q. Wu, H. Yang, H. Zhu, Z. Gao, Construction of CNCs-TiO2 heterojunctions with enhanced photocatalytic activity for crystal violet removal, Optik, 179 (2019) 195-206

[6] E.A. Moawed, M.A. El-ghamry, M.A. El-Hagrasy, M.F. El-Shahat, Determination of iron, cobalt and nickel ions from aqueous media using the alkali modified miswak, Journal of the Association of Arab Universities for Basic and Applied Sciences 23 (2017) 43-51

[7] A.C. Khorasani, S.A. Shojaosadati, Magnetic pectin-Chlorella vulgaris biosorbent for the adsorption of dyes, Journal of Environmental Chemical Engineering, 7 (2019) 103062

[8] E.A. Moawed, Effect of heating processes on Salvadora persica (Miswak) and its application for removal and determination of aniline blue from wastewater, Journal of Taibah University for Science, 7 (2013) 26–34

[9] E.A. Moawed, Abdullah B. Abulkibash, Selective separation of Light green and Safranin O from aqueous solution using Salvadora persica (Miswak) powder as a new biosorbent, Journal of Saudi Chemical Society, 2016, 20, S178–S185

[10] L. Ramrakhiani, S. Ghosh, A.K. Mandal, S. Majumdar, Utilization of multi-metal laden spent biosorbent for removal of glyphosate herbicide from aqueous solution and its mechanism elucidation, Chemical Engineering Journal, 361 (2019) 1063-1077

[11] I.S. Bădescu, D. Bulgariu, I. Ahmad, L. Bulgariu, Valorisation possibilities of exhausted biosorbents loaded with metal ions – A review, Journal of Environmental Management, 224 (2018) 288-297

[12] J.Y. Yeo, B.L.F. Chin, J.K. Tan, Y.S. Loh, Comparative studies on the pyrolysis of cellulose, hemicellulose, and lignin based on combined kinetics, Journal of the Energy Institute, 92 (2019) 27-37

[13] Y. Wu, S. Wu, H. Zhang, R. Xiao, Cellulose-lignin interactions during catalytic pyrolysis with different zeolite catalysts, Fuel Processing Technology, 179 (2018) 436-442

[14] H. Yu, Z. Wu, G. Chen, Catalytic gasification characteristics of cellulose, hemicellulose and lignin, Renewable Energy, 121 (2018) 559-567

[15] H. Morohashi, M. Imai, T. Toyota, Construction of a chemical motor-movable frame assembly based on camphor grains using water-floating 3D-printed models, Chemical Physics Letters, 721 (2019) 104-110

[16] G. Chandra, S.S.N. Murthy, Dielectric and thermodynamic study of camphor and borneol enantiomers and their binary systems, Thermochimica Acta, 666 (2018) 241-252

[17] A.M. Ali, A.M.A. Ibrahim, Castor and camphor essential oils alter hemocyte populations and induce biochemical changes in larvae of Spodoptera littoralis (Boisduval) (Lepidoptera: Noctuidae), Journal of Asia-Pacific Entomology, 21 (2018) 631-637

[18] R.G.E. Krause, J.P.D. Goldring, Crystal violet stains proteins in SDS-PAGE gels and zymograms, Analytical Biochemistry, 566 (2019) 107-115

[19] E.A. Moawed, Y. Alqarni, Determination of azine and triphenyl methane dye in wastewater using polyurethane foam functionalized with tannic acid, Sample Preparation, 1(2013) 18-27

[20] E.A. Moawed, M.F. El-Shahat, Equilibrium, kinetic and thermodynamic studies of the removal of triphenyl methane dyes from wastewater using iodopolyurethane powder, Journal of Taibah University for Science, 10 (2016) 46–55

[21] E.A. Moawed, M.A. El-Hagrasy, A.A.M. Farhat, Application of the magnetic isothiouronium polyurethane sorbent for removal of acidic and basic dyes from wastewater, Journal of Cleaner Production, 2017, 157, 232–242

[22] E.A. Moawed, H.A. Kiwaan, M.M. Elshazly, Application of polyurethane@salvadora persica composite for detection and removal of acidic and basic dyes from wastewater, Journal of the Taiwan Institute of Chemical Engineers, 2017, 80, 894–900

[23] E.A. Moawed, A.E. Wahba, R.A. Gabr, Synthesis and application of LGB/St/Al2O3 biocomposite for sensitive detection and efficient removal of brilliant green dye from wastewater, Journal of Environmental Chemical Engineering 2018, 6, 7225–7232

[24] H.J. Kumari, P. Krishnamoorthy, T.K. Arumugam, S. Radhakrishnan, D. Vasudevan, An efficient removal of crystal violet dye from waste water by adsorption onto TLAC/Chitosan composite: A novel low cost adsorbent. Int J Biological Macromolecules, 96 (2017) 324-333.

[25] M.K. Satapathy, P. Das, Optimization of crystal violet dye removal using novel soil-silver nanocomposite as nanoadsorbent using response surface methodology. J Environ Chem Eng, 2 (2014) 708–714.

[26] F. Shojaeipoor, B. Masoumi, Aminopropyl containing ionic liquid based organosilica as a novel and efficient adsorbent for removal of crystal violet from wastewaters. Chinese J Chem Eng, 25 (2017) 1294-1302

[27] U.A. Guler, M. Ersan, E. Tuncel, F. Dügenci, Mono and simultaneous removal of crystal violetand safranin dyes from aqueous solutions by HDTMA-modified Spirulina sp, Process Safety and Environmental Protection, 99 (2016) 194–206

[28] J. Liu, Y. Wang, Y. Fang, T. Mwamulima, S. Song, C. Peng, Removal of crystal violet and methylene blue from aqueous solutions using the fly ash-based adsorbent material-supported zero-valent iron. J Mol Liq, 250 (2018) 468-476

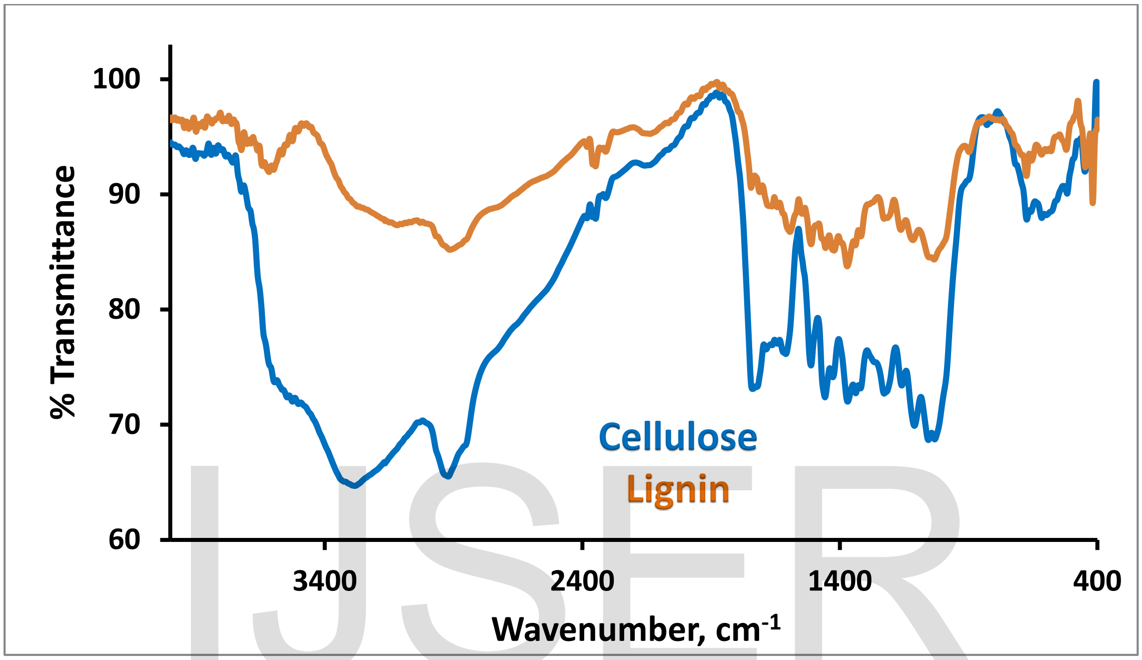


Fig. 1: Infrared spectra for cellulose and lignin

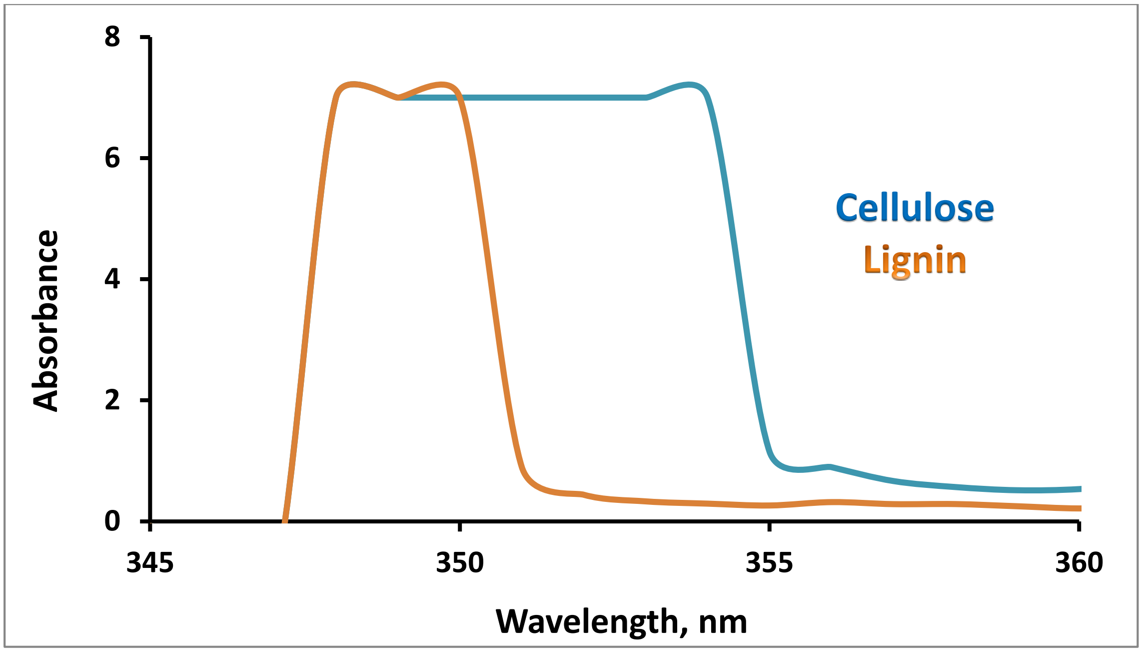
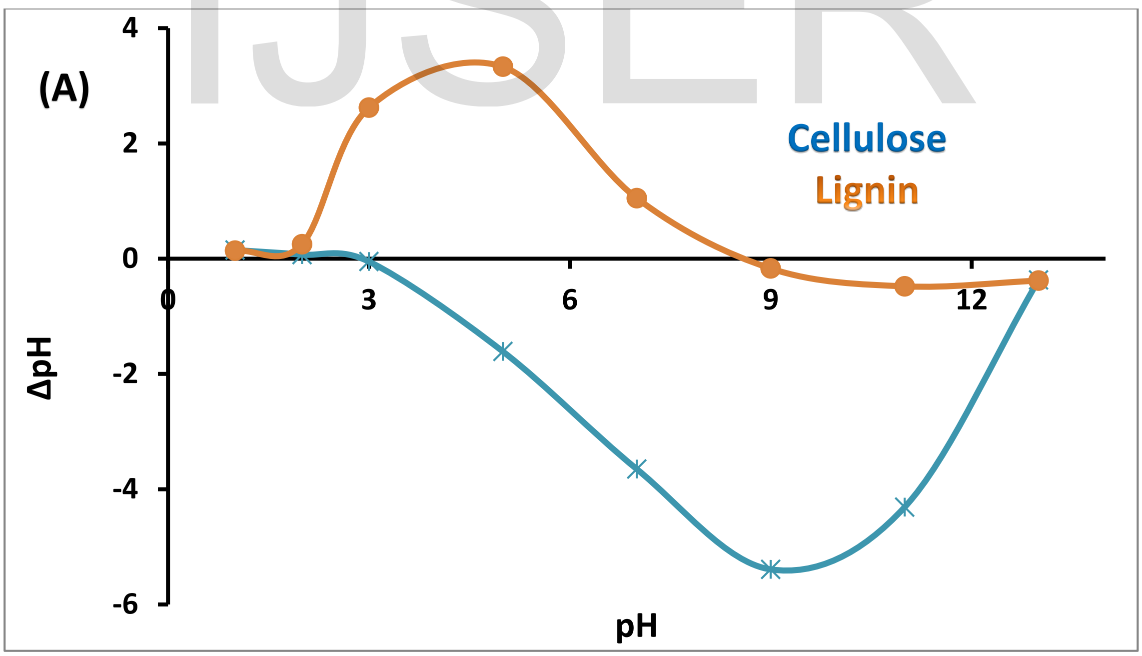


Fig. 2: Ultraviolet spectra for cellulose and lignin



ISSN 2229-5518

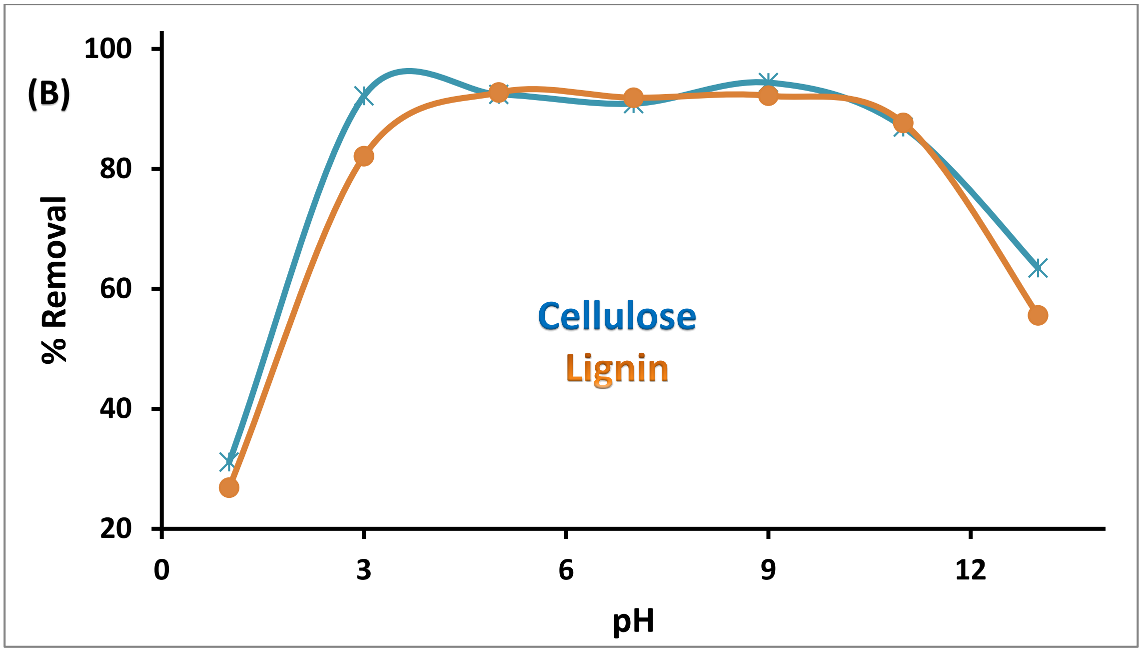


Fig. 3: The pHZPC of cellulose and lignin(A) Effect of pH on the removing of crystal violet (B)

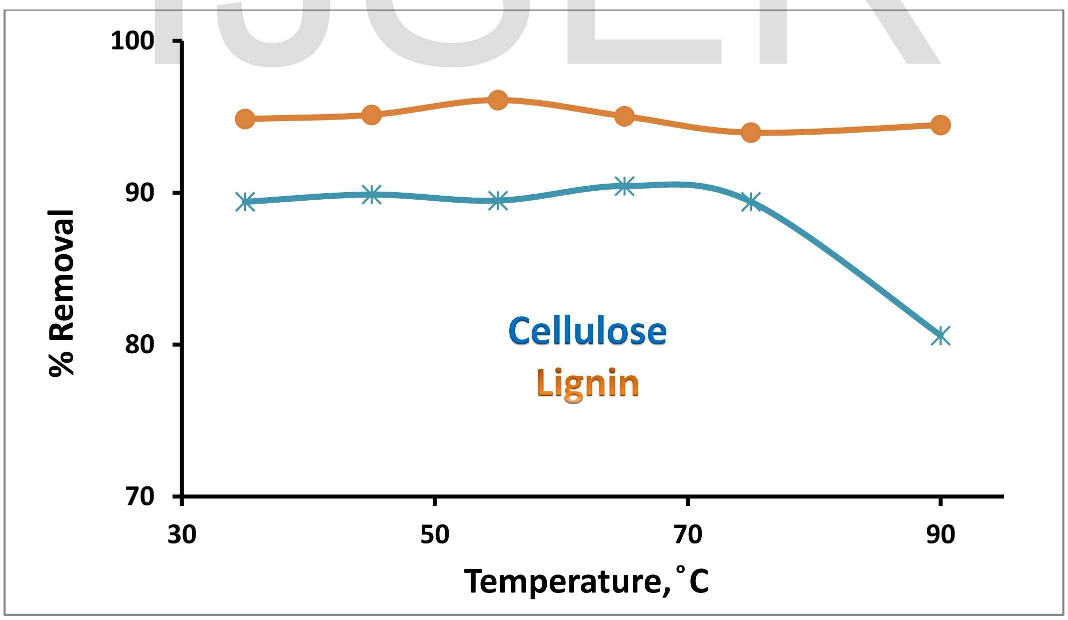


Fig. 4: Effect of temperature on the removing of crystal violet

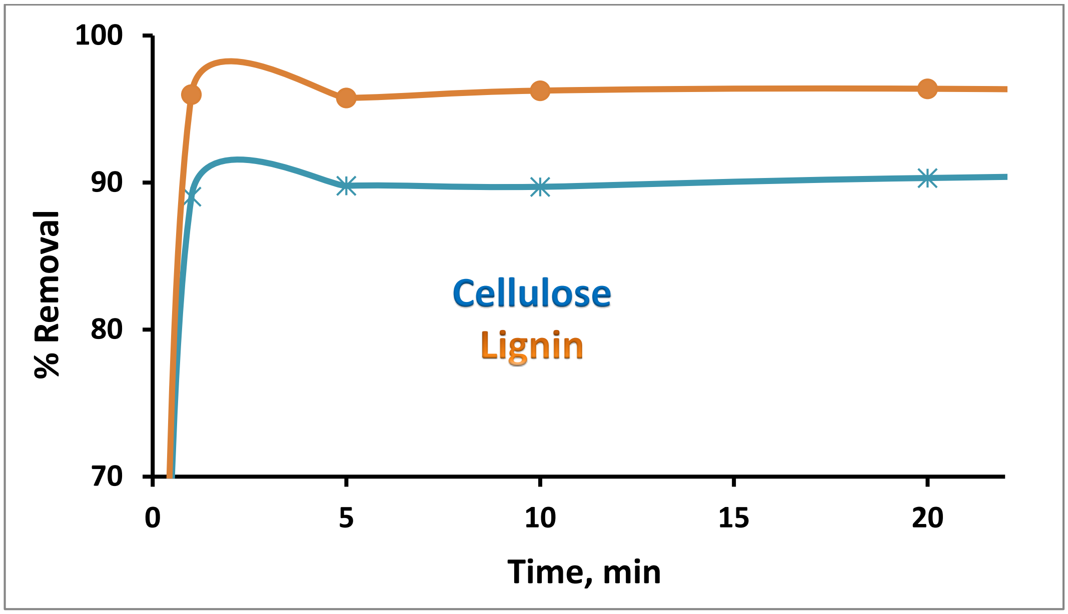


Fig. 5: Effect of time on the removing of crystal violet

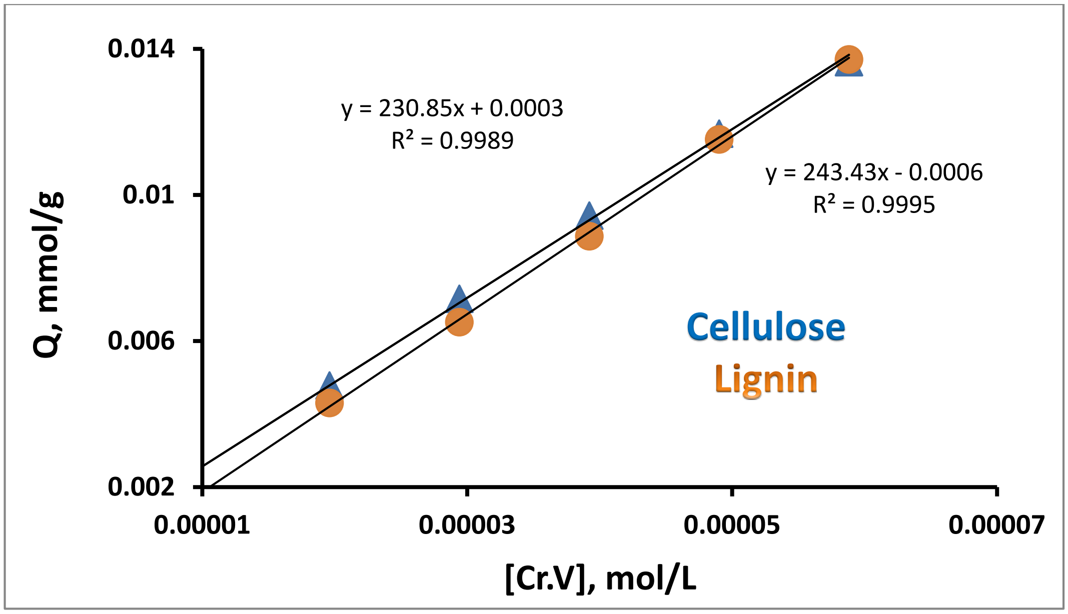


Fig. 6: Effect of dye concentration on the removing of crystal violet

Table 1

Physical and chemical properties of camphor biosorbents

Property	Cellulose	Lignin
IR spectra; $\upsilon_{OH, CH, CO}$ (cm^{-1})	3704-2975, 1687	3417-2447, 1704
UV-Vis spectra (nm)	350-354, 369	349, 369, 381, 387
pH_{ZCP}	2.8	8.6
Iodine value (mmol/g)	1.7	1.6

Methylene blue index (mmol/g)	0.2	0.3
Conductivity×10^{-5} (Ω^{-1} cm^{-1})	5.1	3.6
Acidic sites (mmol/g)	0.9	0.3
Basic sites (mmol/g)	0.2	0.9

Table 2
Thermodynamic parameters of removing process for Cr.V dye

Parameter	Cellulose	Lignin
ΔG (kJ/mol)	-3.1	-9.2
ΔH (kJ/mol)	-6.0	-7.6
ΔS (kJ/mol)	0.02	-0.01

Table 3

Comparison of R^2 values between kinetics and equilibrium models

Model	Cellulose	Lignin
Pseudo first order	0.489	0.829
Pseudo second order	1.000	1.000

Freundlich	0.534	0.368
Langmuir	0.290	0.062

Table 4

Sorption capacities of various sorbents for crystal violet dye

Sorbents	Q (mg/g)	Reference
TLAC/Chitosan composite	0.3	[24]
Soil-Silver nanocomposite	2.0	[25]
ILOS-NH_2	20.6	[26]
Surfactant modified Spirulina sp	101.9	[27]
ZVI-GAM	172.4	[28]
Cellulose	167.2	This work
Lignin	138.7	

Table 5

Removal of different amounts crystal violet dye from wastewater using cellulose and lignin

Amount added	Cellulose		Lignin	
µg	Removal%	RSD%	Removal%	RSD%
100	87.9	3.39	93.4	1.32
200	85.9		93.0	

ISSN 2229-5518

300	85.2		91.9	
400	82.7		91.1	
500	80.6		90.6	

Table 6

Removal percentages of crystal violet dye from different location of wastewater samples using cellulose and lignin

Location	Cellulose	Lignin
1	88.7	90.7
2	89.1	87.4
3	90.4	90.2
4	88.8	91.9
5	80.4	91.3
Average %	87.5	90.3
RSD%	4.11	1.94