Wastewater treatment using natural adsorbent incorporated polymeric mixed matrix membrane

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Abstract

Organic pollutants like synthetic dyes are continuously discharged through industrial effluents and simultaneously contaminate the water streams. The present study focuses on the synthesis of an effective polymeric mixed matrix membrane (MMM) by incorporation of a natural adsorbent, corchorus stick powder (CSP) in polyvinyl chloride (PVC) matrix for the removal of crystal violet, a cationic dye from its aqueous solution. Three different polymer-CSP MMMs were synthesized by varying the amount of CSP (i.e. 0.5, 1.0, and 1.5 wt%) and termed as PC1, PC2, and PC3, respectively. The synthesized membranes were characterized by FTIR, XRD, TGA, SEM, and contact angle determination. The influence of operating pressure, feed concentration, and operating time on the water flux, permeate flux, and percent rejection were thoroughly investigated. Among these three MMMs, PC2 was found to show best result in terms of percent dye rejection.

Keywords: Synthetic dye; polymer; natural adsorbent; mixed matrix membrane; wastewater treatment.

1. Introduction

The majority of the products that are utilized to meet our daily necessities are coloured. Synthetic dyes are used to improve their aesthetic appeal, general attractiveness, and acceptability for the end-user. The insatiable demand by modern society has stimulated the remarkable growth of the dye industry during the past 150 years [1]. Synthetic dyes are widely used in textile dyeing, colour photography, paper printing, food, pharmaceutical, cosmetic, and leather industries [2]. These hazardous pollutants are continuously discharged through industrial effluents and simultaneously contaminate the water streams. Organic dyes usually pose serious threats to the environment as well as to public health since they traverse through the entire food chain and lead to bio-magnification. They are continuously decreasing the BOD in water and killing seaweeds, molluscs, marine birds, fishes, crustaceans, and other sea organisms that serve as food for humans [3]. The separation of such harmful pollutants from industrial effluents is one of the most important environmental concerns of the 21st century. Various physical, chemical, and biological remediation technologies have been developed for the removal of toxic pollutants such as oxidation, solar photo-Fenton degradation, photo-catalytic degradation, coagulation, filtration, adsorption, membrane-based separation, photo-Fenton processes, biodegradation, electrochemical degradation, etc. [4, 5]. All these technologies have their own advantages and disadvantages. Among these different remediation, adsorption and pressure-driven separation based on synthetic polymeric membranes have proved themselves as very efficient techniques. Nowadays a wide variety of agricultural residues and by-products has been explored for wastewater treatment like bagasse, spent tea, coconut shell, straw, banana skin, etc. [6]. Incorporation of such green adsorbent into a synthetic polymeric matrix in terms of MMM membrane not only enhances the dye removal capacity and hydrophilicity of the polymer membrane but also lowers the production expenses as they are abundant in nature. Hence, the basic objective of this study is to synthesize an effective adsorbent incorporated polymeric MMM for the removal of such hazardous synthetic dyes from wastewater. In this experiment corchorus stick powder (CSP), a green adsorbent from agricultural residue has been incorporated into Polyvinyl chloride (PVC) matrix in order to investigate its ability for the removal of a synthetic dye, crystal violet from its aqueous solution.

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2. Experimental

2.1. Materials.

The natural adsorbent from agricultural residue, corchorus stick was purchased from the local market. High purity THF (analytical grade), and plasticizer dioctyl phthalate (DOP) used for this study were purchased from M/s. E. Merck (India) Ltd., Mumbai. The emulsion grade polyvinyl chloride (PVC, K value of 65) was kindly supplied by Reliance Industries, Mumbai. The stabilizer (Lead nitrate) was purchased from Loba chemical Pvt. Ltd., Mumbai. Crystal violet dye was purchased from Sigma-Aldrich (Bangalore, India). Deionized water, having a conductivity of 20 mS/cm, was produced in the laboratory itself from a RO module using polyamide reverse osmosis (RO) membrane, and it was used for experiments.

2.2. Preparation of the adsorbent-polymer mixed matrix membranes

2.2.1. Preparation of the natural adsorbent

Corchorus stick purchased from the market was chopped in small pieces and washed with water and ethanol mixture. It was then washed with hot water several times to make it free from dirt, oil, and other impurities. Dried at 105°C and then cooled at room temperature. The final material was then crushed, sieved, and stored for further use.

2.2.2. Preparation of the MMM membrane

The MMM membranes were prepared by the phase inversion method. The PVC powder was first dissolved in THF (5 wt%) by stirring with a magnetic stirrer to obtain a clear viscous solution followed by the addition of lead nitrate (stabilizer, 2 wt% of PVC) DOP (plasticizer, 25 wt% of PVC) with continuous stirring for 6 h at 30°C. Then required amount of the prepared natural adsorbent powder (as given in Table 1) was added into the polymer solution and ultrasonicated for 1 h and then stirred with a magnetic stirrer for 8 h at 30°C to get the adsorbent incorporated stable polymer dispersion. The final solution was cast on a clean and smooth glass plate at ambient temperature using an applicator. Finally, the cast film was immediately immersed into deionized water (coagulation bath) after partial evaporation of THF for 2 h. The cast film samples were then kept in freshwater for 24 h so that the phase inversion process can be completed. [7, 8].

2.3. Preparation of dye solution

Stock solution (1000 mg/L) of crystal violet dye was prepared using deionized water. The dye solutions of desired concentration were prepared by diluting the stock solution. The calibration curve was prepared by measuring the absorbance of dye solutions of different concentrations at 590 nm (λmax) using UV–vis spectrophotometer (Varian, 50 Bio). The dye concentration in the permeate was evaluated from the calibration curves.

2.4. Characterization

The ATR-FTIR spectra of the adsorbent, virgin PVC, and PC2 membranes were recorded in a Bruker (AlphaII) spectrophotometer. Thermogravimetric analysis (TGA) was carried out in a Perkin Elmer instrument in a nitrogen atmosphere at a scanning rate of 10°C /min in the temperature range of 30–600°C. Wide angle x-ray diffraction profile was studied at room temperature with a diffractometer (model: X'Pert PRO, PANalytical B.V., The Netherlands) using Ni-filtered Cu Kα radiation (λ= 1.5418 Å) and a scanning rate of 2 deg (2θ)/s). The morphological study of PVC and PC2 membranes was done by Scanning Electron Microscope (SEM, S-4800, Hitachi). The static contact angle of water was measured using a Goniometer (Aapex Instrument Co. Pvt. Ltd., ACAMNSC 30). Dye concentration was measured in a UV–vis spectrophotometer (Varian, 50 Bio).

2.5. Pure water flux and permeate flux determination

Pure water flux, as well as dye removal experiments, were carried out in a dead-end filtration system of 22 cm^2 effective membrane area. Pure water flux and permeate flux were obtained by measuring the time required to collect 5 ml permeate volume. For each run, the cell was filled with 300 ml of dye feed solution. The pressure was maintained using nitrogen gas. To minimize compaction effects, the membranes were compacted at 220 kPa for 4h. After compaction, the membranes were subjected to pure water flux estimation at different trans-membrane pressure from.0 to 206.8 kPa. The flux (J, lm^{-2}h^{-1}) was obtained from the following equation [9].

$$J = Q/(\Delta t \ x \ A)$$

where Q is the amount of permeate collected (l), Δt is the filtration time (h) and A is the effective membrane area (m^2).

2.6. Dye removal experiment

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The separation experiments were conducted using a sample dye, crystal violet dye by varying the feed concentrations (5, 10, 20, 50, and 100 mg/L, respectively) and the percent rejection (%R) was calculated from the following equation [4]

$$R\ (\%) = 1 - C_P/C_F \times 100 \quad (2)$$

C_p and C_F are dye concentrations in the permeate and feed, respectively.

3. Results and discussion

3.1. Characterization

3.1.1. FTIR analysis

FTIR spectra of adsorbent, virgin PVC, and PC2 membranes are shown in figure1.(a). For pristine CSP the peaks at around 3343 cm^{-1}, 2898 cm^{-1}, and 1736 cm^{-1} are due to the H-bonded –OH group, the C–H stretching of the –CH$_2$ groups, and carboxyl acid groups, respectively. Besides these, two weak bands were found near 1598 cm^{-1} and 1509 cm^{-1} are due to stretching modes of the benzene ring of lignin [10-11]. For virgin PVC and PC2 membrane, the strong absorption band at around 1075 cm^{-1} and 1720 cm^{-1} corresponding to ester groups and carbonyl stretching, respectively. Peaks near 614 cm^{-1}, 957 cm^{-1}, 1258 cm^{-1}, 1426 cm^{-1}, and 2924 cm^{-1} corresponding to C–Cl stretching, C–C stretching of PVC backbone, C–H bending near Cl, C–H aliphatic bending, and C–H stretching, respectively. [7]. Besides these, the PC2 membrane was found to show a prominent band near 3428cm-1 due to the H-bonded –OH group of CSP.

3.1.2. Thermo gravimetric Analysis (TGA)

Figure 1.(b) depicts the TGA curves of pristine CSP, virgin PVC, and PC2 membranes. As shown in the figure CSP has three distinct stages of decomposition. At the first stage, a minimal weight loss occurs at a temperature range from 60 to 120°C due to the evaporation of adsorbed water. The significant weight loss begins with an increase in temperature from 200 to 300 ^{O}C due to thermal degradation of hemicelluloses and 300 to 440 ^{O}C for degradation of α-cellulose, respectively [12, 13]. PVC membrane was found to show thermal degradation in three different steps, viz., in the temperature range of 215–350°C, 350–450°C, and 450–550°C. The first weight loss is due to the loss of HCl by a free radical mechanism which leads to the formation of a polyene along with a crosslinked structure [7]. The second and third steps of the degradation correspond to the parallel reactions that lead to the formation of the monocyclic, and polycyclic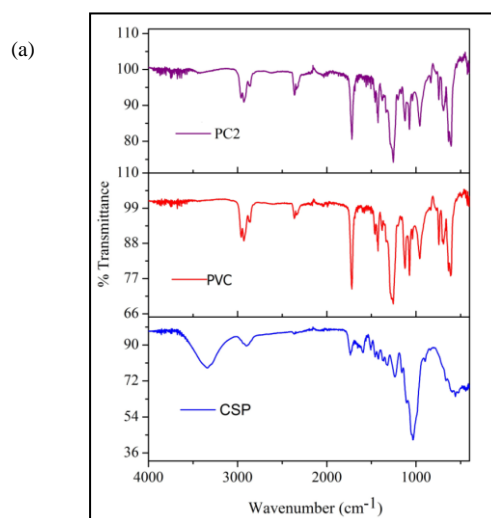 aromatic structures like benzene, toluene, and naphthalene from the conjugated polyenes [14]. For the PC2 membrane these three thermograms were shifted towards higher temperature regions, viz., 250-400 ^{O}C, 400-500 ^{O}C, and 500-600 ^{O}C, respectively indicating enhanced thermal stability of the MMM due to incorporation of the adsorbent.

3.1.3. XRD analysis

The X-ray diffraction patterns of pristine CSP, virgin PVC, and PC2 membranes are illustrated in figure 1.(c). CSP is showing three well-defined peaks at 2θ values of around 16.5^o, 22.1^o, and 34.6^o which are due to the presence of crystalline cellulose in the green adsorbent. [13, 15]. PVC membrane was found to show XRD peaks at 2θ values of around 17.9^o, 24°, and 40.6^o due to the multiphase structure of PVC, i.e. a major amorphous phase along with a weak crystalline phase [7, 16]. For the mixed matrix membrane, PC2 XRD peaks are obtained at 2θ values of around 16,8^o, 18.3^o, 22.8^o, 24.3^o, 34.9^o, and 38.1^o as shown in the figure. Presence of all characteristics peaks of CSP and PVC in the PC2 membrane indicating the presence of both components in the final MMM. A very small deviation in the 2θ values is due to their mutual interaction.

3.1.4. Morphological studies by SEM analysis

The surface morphologies of PVC and PC2 membranes were investigated using a scanning electron microscope (figure 1.(d) and 1.(e), respectively). From these figures it is found that the membranes are porous and the pores are uniformly distributed throughout the membrane surfaces. Membrane surfaces for both membranes are smooth without any visible cracks. The average pore diameter (as observed from figure 1.(d)) is about 4.02 μm. Figure 1.(e) shows that in the PC2 mixed matrix membrane, the CSP adsorbent is almost evenly distributed throughout the porous membrane surface.
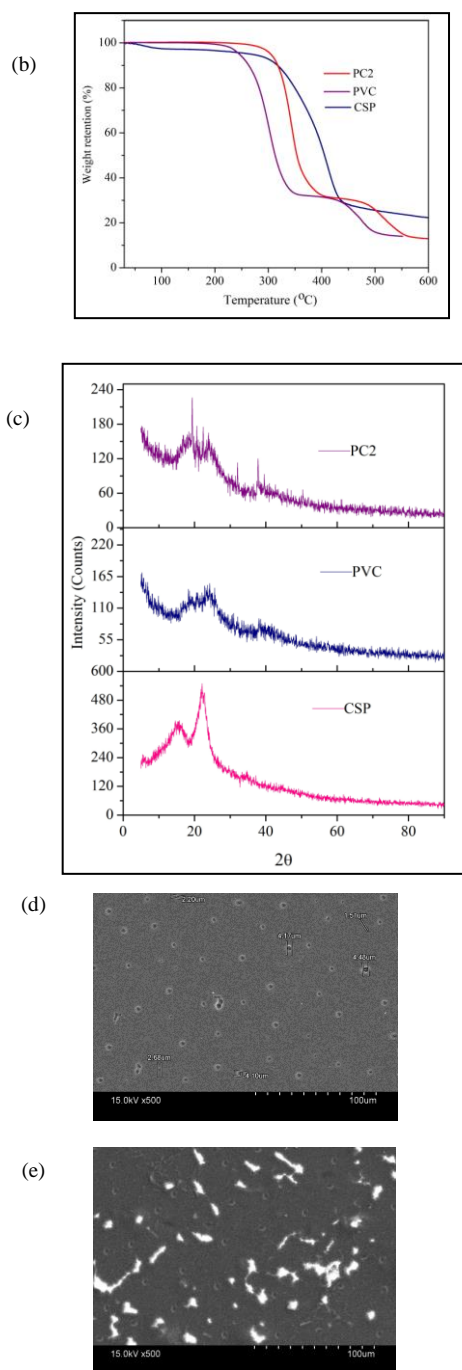

(a)

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(b)

(c)

(d)

(e)

Figure 1.(a) FTIR, (b) TGA, (c) XRD of CSP adsorbent, PVC, and PC2 membranes, (d) SEM images of PVC and (e) PC2 membranes.

3.1.5. Contact angle measurement

Contact angle with water is a popular measurement of the hydrophilicity of a surface. For contact angle measurement droplet of DI water ($\approx$ 6 μl) was dropped on the membrane surface at different positions. Table 1 is showing the average contact angles of different MMMs used for this study along with virgin PVC membrane. From the table, it is prominent that membrane contact angle decreases i.e. hydrophilicity of the prepared MMMs increases with the addition of the hydrophilic adsorbent.

Table -1 Contact angle of different MMMs

Membrane	Adsorbent (%)	Contact angle (°)
PVC	0	90.86
PC1	0.5	89.14
PC2	1	72.41
PC3	1.5	59.04

3.2. Pure water flux

3.2.1. Effect of time, Compaction

Before the pure water flux determination compaction experiment was conducted to obtain a uniform structure and steady pure water flux. Compaction was done at a pressure higher than the operating pressure to make changes in the membrane structure. In this study, the compaction test of PC1, PC2, and PC3 MMMs was conducted at 220 kPa pressure for 6h. The result is shown in figure 2.(a). All three MMMs were found to show a decrease in water flux value with time up to around 3h thereafter, a steady value was obtained during 3-6h of the experiment. It is also observed that with an increase in the adsorbent loading pure water flux also increases from PC1 to PC3. The rate of decrease in water flux values (as given in the figure) from PC2 to PC3 is higher than PC1 to PC2 which may be associated with the deviation in adhesion properties between the adsorbent and the polymer chains and surface porosity with enhanced adsorbent loading.

3.2.2. Effect of pressure

Pure water flux was found to vary with applied pressure as well as CSP loading. This is due to the presence of the cellulosic moieties which are responsible for the dye adsorption in the green adsorbent as evidenced from XRD as well as TGA data. Figure 2. (b) demonstrates the effect of Trans membrane pressure on pure water flux for different MMMs. It is observed from the figure that with an increase in applied pressure pure water flux also increases. Again pure water flux also increases from PC1 to PC3. As we are using a hydrophilic adsorbent, hence with an increase in adsorbent dosage pure water flux also enhances.
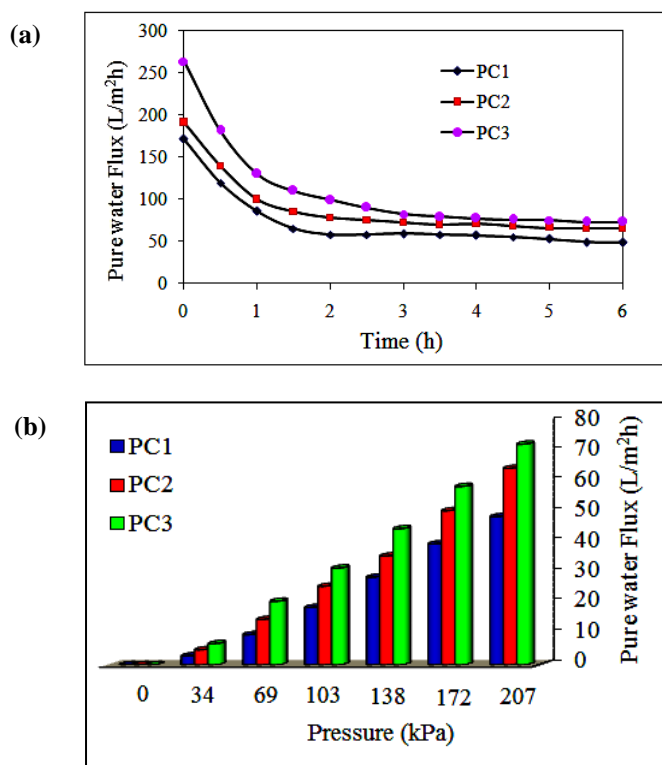
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(a)

(b)

Figure 2. Effect of (a) time and (b) pressure on pure water flux

3.3. Dye removal

The prepared MMMs were used to remove a cationic dye, crystal violet from its aqueous solution. Crystal violet is a very common dye of the triphenylmethane group which has a wide range of industrial applications and is known for its mitotic and mutagenic poisoning nature [17]. Besides being used as a textile dye, it is also used to dye paper and as a component of navy blue and black inks for printing, ball-point pens, and inkjet printers, anti-freezers, fertilizers, gram staining, antiseptic (e.g., athlete's foot and ringworm), detergents and leather industry [18]. Hence it has been chosen as sample dye for this study.

3.3.1. Effect of pressure

The permeate flux, as well as dye rejection (%R), were determined at different transmembrane pressures (34.5 to 206.8 kPa). Figure 3.(a) shows the effect of pressure on permeate flux and percent dye removal. The permeate flux was found to increase almost linearly with applied pressure for all three MMMs whereas %R is showing the opposite trend. Permeate flux is lower than the pure water flux because partial plugging of the membrane pores due to concentration polarization causes lower permeate flux in comparison to the pure water flux. From this

figure, it is also observed that flux enhances with adsorbent loading from PC1 to PC3 throughout the pressure ranges. PC2 MMM is showing a satisfactory flux value whereas the %R value of PC2 is much higher than both PC1 and PC3. Hence from this study, we can say PC2 is giving the optimum result in terms of both flux and % dye removal. After each run, the used membrane was washed with DI water and then cleaned using sodium hydroxide (NaOH) solution followed by hydrogen peroxide solution (0.5% v/v) to remove the organic pollutants from the membrane surface. The membranes were again washed with DI water until the pH became neutral, and pure water flux was monitored again to ensure that partial plugging do not cause any deviation in flux value.
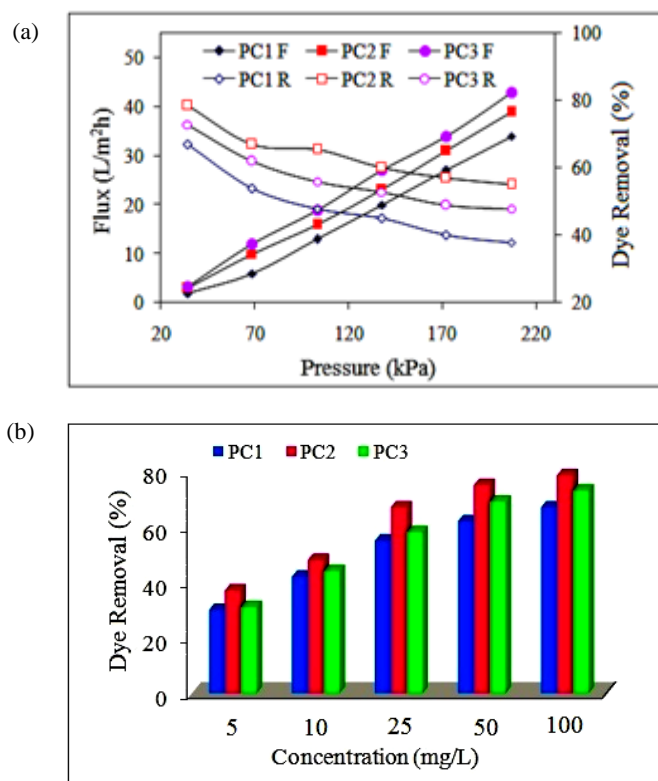
(a)

(b)

Figure 3.(a) Effect of pressure on permeate flux and %R and (b) variation of % R with feed concentration

3.3.2. Effect of feed concentration

Initial dye concentration plays a significant role in the membrane separation process. The effect of initial dye concentration in feed solution is shown in figure 3.(b). In this study, feed concentration was varied from 5 to 100 mg/l. As evidenced from the figure, %R increases with the increase in feed concentration for all three membranes. With an increase in dye concentration in feed, the

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accumulation of dye on the membrane surface increases, and as a result %R becomes higher at high feed concentrations in comparison to lower ones [19, 20]. The dye rejection capacity of the MMMs increase from PC1 to PC2 and then decreases. In PC3 there may be some agglomeration of the adsorbent in the polymer matrix and hence a decrease in %R is evidenced.

4. Conclusion

- In this study, CSP, a natural adsorbent was prepared from an agricultural residue, corchorus stick, and incorporated into PVC matrix to prepare mixed matrix membrane (MMM) for the removal of a synthetic cationic dye crystal violet.
- Three different MMMs were prepared by varying the CSP concentration.
- The synthesized CSP and mixed matrix membranes along with virgin PVC membrane were characterized by FTIR, XRD, TGA, and SEM analysis.
- Performance of the membrane was analyzed by determination of contact angle, pure water flux, permeate flux, and % dye removal.
- PC2 membrane was found to show the highest %R (76.52, at 206.8 kPa pressure for 100mg/l feed solution) among these three MMMs.

Acknowledgment

References

[1] Zhou, Q. Chemical Pollution and Transport of Organic Dyes in Water–Soil–Crop Systems of the Chinese Coast. Bull. Environ. Contam. Toxico. 2001, 66, 784.

[2] Couto, S.R. Dye removal by immobilised fungi. Biotechnol. Adv. 2009, 27, 227.

[3] Haseena, M.; Malik, M.F.; Javed, A.; Arshad, S.; Asif, N.; Zulfiar, S.; Hanif, J. Water pollution and human health. Environ. Risk. Assess. Remediat. 2017,1(3),16.

[4] Sachdeva, S.; Kumar, A. Preparation of nanoporous composite carbon membrane for separation of rhodamine B dye. J. Membr. Sci. 2009, 329, 2.

[5] Crini, G.; Lichtfouse, E. Advantages and disadvantages of techniques used for wastewater treatment. Environ. Chem. Lett. 2019,17,145.

[6] Dai, Y.; Sun, Q.; Wang, W.; Lu, L.; Liu, M.; Li, J.; Yang, S.; Sun, Y.; Zhang, K.; Xu, J.; Zheng, W.; Hu, Z.; Yang, Y.; Gao, Y.; Chen, Y.; Zhang, X.; Gao, F.; Zhang, Y. Utilizations of agricultural waste as adsorbent for the removal of contaminants: A review. Chemosphere. 2018, 211, 235.

[7] Das, P.; Ray, S.K. Pervaporative recovery of tetrahydrofuran from water with plasticized and filled polyvinylchloride membranes. J. Ind. Eng. Chem. 2016, 34, 321

[8] Ghazanfari, D.; Bastani, D.; Mousavi, S.A. Preparation and characterization of poly (vinyl chloride) (PVC) based membrane for wastewater treatment. J. Water. Process. Eng. 2017, 16, 98.

[9] Sangeetha, K.; Vinodhini, P.A.; Sudha, P.N.; Faleh, A. A.; Sukumaran, A. Novel chitosan based thin sheet nanofiltration membrane for rejection of heavy metal chromium. Int. J. Biol. macromol. 2019, 132, 939.

[10] Panda, G.C.; Das, S.K.; Guha, A.K. Jute stick powder as a potential biomass for the removal of congo red and rhodamine B from their aqueous solution. J. Hazard. Mater. 2009, 164, 374.

[11] Karahan, M.; Ozkan, F.; Yildirim, K.; Karahan, N. Investigation of the Properties of Natural Fibre Woven Fabrics as a Reinforcement Materials for Green Composites. Fibres. Text. East. Eur. 2016, 24, 4(118), 98.

[12] Nitu, I.P.; Islam, Md. N.; Ashaduzzaman, Md.; Amin, Md. K.; Shams, Md. I. Optimization of processing parameters for the manufacturing of jute stick binderless particleboard. J. Wood. Sci. 2020, 66, 65.

[13] Chowdhur y, Z.Z.; Hamid, S.B. Abd.; Rahman, Md. M.; Rafique, R.F. Catalytic activation and application of microspherical carbon derived from hydrothermal carbonization of lignocellulosic biomass: statistical analysis using Box– Behnken design. RSC Adv. 2016, 6,102680.

[14] Soudais, Y.; Moga, L.; Blazek, J.; Lemort, F. Coupled DTA–TGA–FT-IR investigation of pyrolytic decomposition of EVA, PVC and cellulose. J. Anal. Appl. Pyrolysis. 2007,78, 46.

[15] Ishak, W.H.W.; Ahmad, I.; Ramli, S.; Amin, M.C.I.M. Gamma Irradiation-Assisted Synthesis of Cellulose Nanocrystal-Reinforced Gelatin Hydrogels. Nanomaterials. 2018, 8,749.

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[16] Abdelghany, A.M.; Meikhail, M.S.; Asker, N. Synthesis and structural-biological correlation of PVC\PVAc polymer blends. J.Mater. res. technol. 2019, 8(5), 3908.

[17] Roy, D.C.; Biswas, S.K.; Saha, A.K.; Sikdar, B.; Rahman, M.; Roy, A.K.; Prodhan, Z.H.; Tang, S.S.; Biodegradation of Crystal Violet dye by bacteria isolated from textile industry effluents. Peer.J. 2018, 6, e5015.

[18] Abdi, M.; Balagabri, M.; Karimi, H.; Hossini, H.; Rastegar, S.O. Degradation of crystal violet (CV) from aqueous solutions using ozone, peroxone, electroperoxone, and electrolysis processes: a comparison study. Appl. Water. Sci. 2020,10,168.

[19] He, Y.; Li, G.; Wang, H.; Zhao, J.; Su, H; Huang, Q. Effect of operating conditions on separation performance of reactive dye solution with membrane process. J. Membr. Sci. 2008, 321,183.

[20] Ghadhban, M.Y.; Majdi, H.S.; Rashid, K.T.; Alsalhy, Q.F.; Lakshmi, D.S; Salih, I. K.; Figoli, A. Removal of Dye from a Leather Tanning Factory by Flat-Sheet Blend Ultrafiltration (UF) Membrane. Membrane. 2020,10, 47.

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