Poll Res. 42 (1) : 80-87 (2023)

ISSN 0257–8050

DOI No.: http://doi.org/10.53550/PR.2023.v42i01.013

OPTIMIZATION OF PROCESS PARAMETERS FOR DYE REMOVAL THROUGH CHITINOUS WASTE BY RESPONSE SURFACE METHODOLOGY

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(Received 9 July, 2022; Accepted 28 September, 2022)

ABSTRACT

Color present in water itself first contaminant and dyes which are harmful for human is a vast problem. Chitinous waste a problem for environment can be an alternative approach for removal of dyes from water. Nanoparticles made up of chitinous waste are used in this study. Chitosan-tripolyphosphate (CS-TPP) nanoparticles showed prominent result in removal of reactive blue 19 and reactive blue 198 dyes. Both the dyes were totally (100%) removed by the use of CS-TPP. Statistical analysis though Response Surface Methodology (RSM) and Box Behnken Design (BBD) to optimize pH and concentration were also carried out. After optimization it was evaluated that pH 6.5 and higher Chitosan-TPP concentration showed the highest removal of dyes.

KEY WORDS : Chitinous waste, Reactive blue, CS-TPP, RSM, BBD, Optimization

INTRODUCTION

Water is an essential requirement for every living being and we cannot imagine life on earth without water (Santos *et al.*, 2019). It is high time to save water for future because in upcoming decades water scarcity adversely affects the earth in many ways. Even though earth is almost surrounded by water, but sea water approximately 70% of all water present on earth is not potable for drinking (Gou *et al.*, 2009).

Excessive use of potable water in industries leads to water crisis and this industrial waste water are the most prominent source of water pollution. Several industries such as Leather, Paper, Pharmaceutical, Cosmetic and Dyeing (Nandi and Patel, 2014) use lots of water for processing and finishing of a product but among all dyeing industries are known worldwide for its polluting effluent (Rahi *et al.*, 2018) Effluent discharged from dyeing industries is a complex mixture of several harmful chemical and colors used for fabric dyeing (Sudamalla *et al.*, 2012).

Treatment of effluent containing dyes are essential before discharging it into nearby water bodies otherwise it will adversely affect the water flora and fauna (Eng *et al.*, 2014). Several techniques have already been introduced for removal of dyes from wastewater such as physical and chemical (Rahi and Gupta, 2021). All these techniques have their own adverse effects such high cost, time consuming and harmful byproduct production (Taheri *et al.*, 2012). Thus a cost effective and nature friendly technique is required to remove dyes form waste water like adsorption. Activated carbon is the highly prescribed absorbent for these types of industries but for wider application its cost restricted the use of activated carbon (Alver *et al.*, 2017). So therefore use of bio-sorbent is increased in last decades as they are giving promising result in dye removal from waste water (Khataee *et al.*, 2009).

Chitin is the second most abundant organic material on earth. Chitin is a major component of crustaceans, mollusks, insects and several fungi (Jawad and Abdulhameed, 2020). Chitinous waste can be useful in removal of dyes from waste water as it has the prominent absorbed properties. It provides an eco friendly approached as one waste is used to treat another waste (Pandey *et al,* 2007). Optimization of conditions for dye removal by chitinous waste is also required as optimization enhance the rate of dye removal (Babakhani and Sartaj, 2020). For optimization purpose statistical tool Response surface methodology (RSM) was used for this study with the combination of Box behnken Design. The Main advantage of RSM is that it reduces the number of experimental trial and provided sufficient data for statistically valid outcome (Pujari and Chandra, 2000).

This study is aimed to optimize two reactive dyes (reactive blue 19 and reactive blue 198) by chitinous waste through response surface methodology.

MATERIALS AND METHODS

Collection of chitinous wastes

The chitinous wastes of fresh water crustaceans were collected from the river bank areas of fresh water river, from Doiwala region, Dehradun, Uttarakhand, India. The waste was washed properly in order to remove the sand debris present on the surfaces. Then waste was air dried and crushed to obtain powder which is further used in the experiment.

Demineralization of chitinous wastes

The demineralization of chitinous wastes was performed according to the method adopted by Jawad and Nawi (2012) with some modifications. The chitinous wastes were treated with 1.75 N acetic acid for about 12-15 hours at room temperature. The ratio of waste to solvent were maintained (1:15 w/v). The demineralized material obtained was recovered by filtration and rinsed with de-ionized water and forced dried in hot air oven at 65 ^{o}C temperature.

De-proteinization, removal of lipids and preparation of chitosan

The new and advanced methodology for deproteinization of proteins from demineralized chitinous wastes was designed by using deproteinization agents (Mathur *et al.*, 2011). This process were performed either by using proteolytic enzymes such as proteinase-K/Trypsin dissolved in buffer containing 0.05 M Tris-base (pH, 6.5-9.1) in a ratio 1:20 (w/v) in flasks at various temperatures in incubator-shaker for about 72 h and adding mixture of solvents (phenol: chloroform, 1:1 ratio) again and again to the residue obtained and centrifuging the mixture until the residue gives no test for the presence of protein content (Natarajan and Ponnaiah, 2017). After repeating the procedure for 3-4 times, finally the residue was treated with 2N sodium hydroxide (1:25 w/v) at 70^{0}C for 1 hour. The lipid content will get dissolved in phenol: chloroform mixture and were removed from the chitinous wastes. Greese spot test can be performed in order to determine qualitatively the presence of lipid content if any present in the residual material. The residual materials left were dried in hot air oven at 60^{o} C and percent yield of chitin extracted from crustacean waste were calculated (Jawad *et al.*, 2020). The resulting chitin was further deacetylated in 40% sodium hydroxide in 120 °C for 1-3 h. This treatment produces 70 % deacetylated chitosan.

Preparation of chitosan-tripolyphosphate (CS-TPP) nanoparticles

CS-TPP nanoparticles were prepared according to the procedure adopted with some modifications (Shahri and Niazi, 2015). Chitosan (CS), 1 mg/ml was dissolved in 1% (w/v) acetic acid and sonicated before the solution became transparent. The addition of tripolyphosphate (TPP) solution, at a concentration of 1 mg/ml, to CS solution (pH-5), with stirring at room temperature, produced the formation of CS-TPP nanoparticles by ionic gelation mechanism. The nanoparticles were separated from the solution after centrifugation at 3600 rpm for 1 hour. The residual pellet was pooled out and washed thrice with de-ionized water and freeze dried to form the powder and other analysis. The freeze-dried chitosan nanoparticles was suspended in water for characterization or directly used for other experiments.

Treatment of dyes in aqueous solutions

The treatment of dyes was followed by different treatment sets: (a) Chitosan-TPP nanoparticles solution at different concentration (viz. 10 to 100 mM/l) irradiated with ultrasonic radiations and (b) ultrasonic degradation separately. Advanced oxidation was performed in different experimental set ups for different dyes viz. using ultrasonic degradation with a frequency of 37 kHz; power (200W-500W) and in the presence of CS-TPP nanoparticles irradiated with ultrasonic radiations to remove the dyes from the aqueous solutions. The stock solution of dyes viz. reactive red 158, reactive black 5, reactive blue 19, reactive blue 5, and reactive blue 198 were prepared by dissolving 1 g of each of the dye in deionized water (1000 mg/l) and refrigerated to avoid variations in concentration (Razzaz *et al.,* 2016). The stock solutions of each of the dyes were prepared at 50 mg/l concentration and the standard method was used to determine the most appropriate wavelength for measuring the concentrations of the studied dye. Finally, the wavelength which achieved maximum absorption for the desired dye was determined using the main solution to be most appropriate. The variables pH, concentration of CS-TPP nanoparticles, initial dye concentration, and contact time were also assessed. In the first step of the process, the optimum pH was obtained such that under constant conditions, each of the dye concentration of 50 mg/l, contact time of 60 minutes, nanoparticles concentration of 1 g/l, removal efficiency rates at pH 4, 9, and 7 were assessed, and optimum pH was achieved. In the next step, the optimum nanoparticles concentration was obtained; under constant conditions, the obtained pH, dye concentration of 50 mg/l, contact time of 60 minutes, and nanoparticles concentrations of 0.5, 1, 2.5, and 3 g/l were used. The percentage of removal was further calculated. Afterwards, the effect of contact time was investigated; samples with the optimum pH, optimum nanoparticles concentration, contact times (10, 30, 60, 90, and 120 minutes), and a dye concentration of 50 mg/l were prepared and the removal percentage of each of the dye color was calculated (Dotto *et al.,* 2019)

$$\text{Dye removal ratio (\%)} = [(1-C_t/C_0) \times 100]$$

Where C_0 is the initial dye concentration and Ct is the dye concentration at contact time "T". Blanks containing no dyes were used in each series of experiments. The solutions were collected and dried for further identification by UV-VIS spectra.

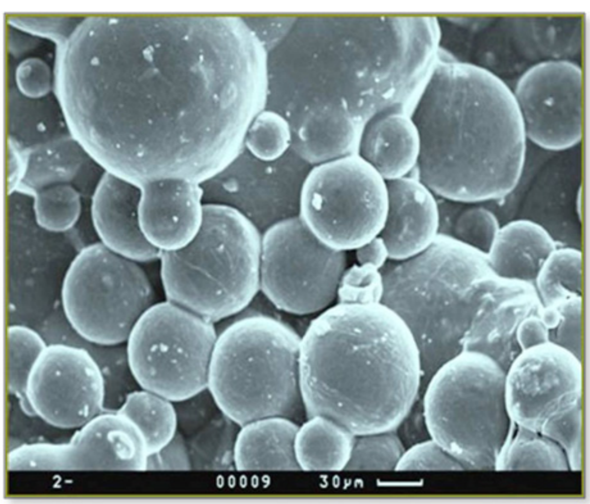
Optimization of Dye removal percentage through Response Surface Methodology (RSM)

Parameters for dye removal were optimized through BBD-RSM technique. RSM is a statistical tool which gives the exact idea about the variables interactive effect of experimental data. Expected and experimental values are check to the fit of the empirical model in Box-Behnken design. RSM analysis was performed through MINITAB software. In this study three factors were analyzed through RSM and their impact was noticed on Dye removal efficacy. Total 15 runs of time, pH and concentration were analyzed and regression equation of these runs in terms of dye removal was calculated as follows (Mohammad *et al.,* 2019):

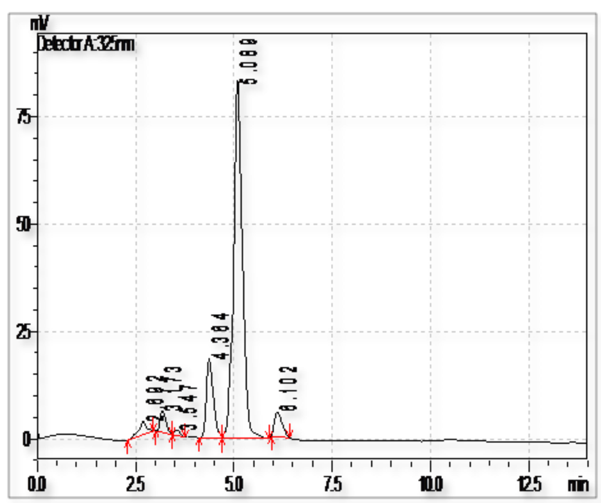
$$\text{\% Dye Removal} = -158.7 + 53.2\ \text{pH} + 0.251\ \text{Conc.} - 0.106\ \text{Time} - 4.24\ \text{pH*pH} + 0.00131\ \text{Conc.*Conc.} + 0.00049\ \text{Time*Time} + 0.0307\ \text{pH*Conc.} + 0.0271\ \text{pH*Time} + 0.00110\ \text{Conc.*Time}$$

RESULTS AND DISCUSSION

The average particle size of CS-TPP synthesized nanoparticles was found to be 30 µm (Figure 1a). The dominant peak of CS-TPP nanoparticles when purified through HPLC showed retention time of



(**A**)



(**B**)

Fig. 1. (**A**) Chitosan-TPP (CS-TPP) nanoparticles as determined by SEM, (**B**) HPLC chromatogram of Chitosan-TPP (CS-TPP) nanoparticles

5.089 minutes (Figure 1b). The removal of reactive red 158, reactive black 5, reactive blue 19, Reactive blue 5, and Reactive blue 198 dyes were determined by preparing a concentration of 50 mg/l of dye, exposing it to CS-TPP nanoparticles with ultrasonic irradiation (50 mmol/l) and ultrasonic degradation as such and sampling it at test times (10, 30, 60, 90, and 120 minutes). Results showed that, during these times, the initial dye concentration was unchanged, and ultrasonic degradation alone did not affect in dye removal; these results are in agreement with those of other studies.

In order to obtain the best concentration of CS-TPP nanoparticles (optimum concentration), solution concentrations of 10, 15, 20, 50, and 100 mMol/l were prepared irradiated with ultrasonic radiation (200 W) and placed in contact with 50 mg/l concentrations of each of the dyes for 60 minute and 120 minutes respectively. For the prepared nanoparticles concentrations, removal efficiency rates were variable and it was found that maximum percent color reduction of each of the dyes solution treated occurs at 100 mMol/l concentration (Table 1; Figure 3).

Further, the treatment sets were compared with ultrasonic radiation as such at power 200-500 W. The results showed that at high power, maximum color reduction occurs but not much in comparison to the chitosan-TPP nanoparticles treated with ultrasonic irradiation (Table 2; Figure 4). After treatment Reactive blue 198 were showed prominent in comparison of reactive blue 19 dye. Figure 5 and **6** showed the result of dye removal.

After analyzing the result statistically it was observed that all three parameters such as pH, Concentration and Time play a significant role in dye removal. Box-Behnken design evaluated total 15 different combination of these three parameters and it was evaluated that at ph 6.5, 100 mMol/L concentrations in 120 minute highest dye removal (94.91%) can be observed. Both the predicated value and experimental value for the same combination showed the highest removal of dye (100%). Table 3 showed the all 15 combination of predicated valued evaluated by the RSM-BBD design.

Normal Probability plot (Figure 7) showed that

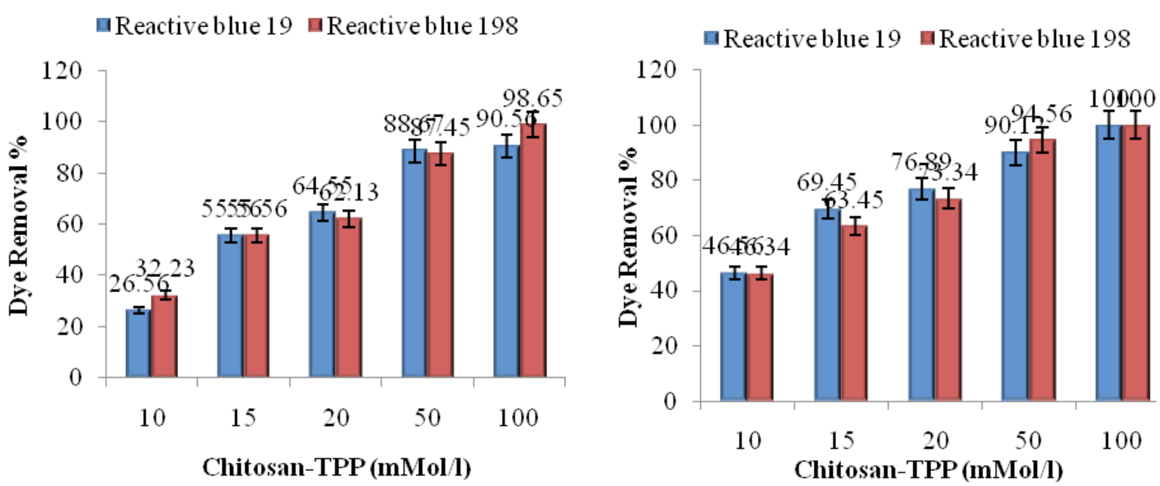


Fig. 3. Graphical representation of Chitosan-TPP irradiated nanoparticles treatment on Reactive blue 19 and Reactive blue 198 dyes after 60 and 120 minutes

Table 1. Chitosan-TPP irradiated nanoparticles treatment on different dyes after 60 and 120 minutes

S. No.	Chitosan-TPP (mMol/l) irradiated with ultrasound irradiation	Percent removal of dyes (50 mg/l) in first 60 minutes		Percent removal of dyes (50 mg/l) in first 120 minutes	
		Reactive blue 19	Reactive blue 198	Reactive blue 19	Reactive blue 198
1	10	26.56	32.23	46.56	46.34
2	15	55.56	55.56	69.45	63.45
3	20	64.55	62.13	76.89	73.34
4	50	88.67	87.45	90.12	94.56
5	100	90.56	98.65	100	100

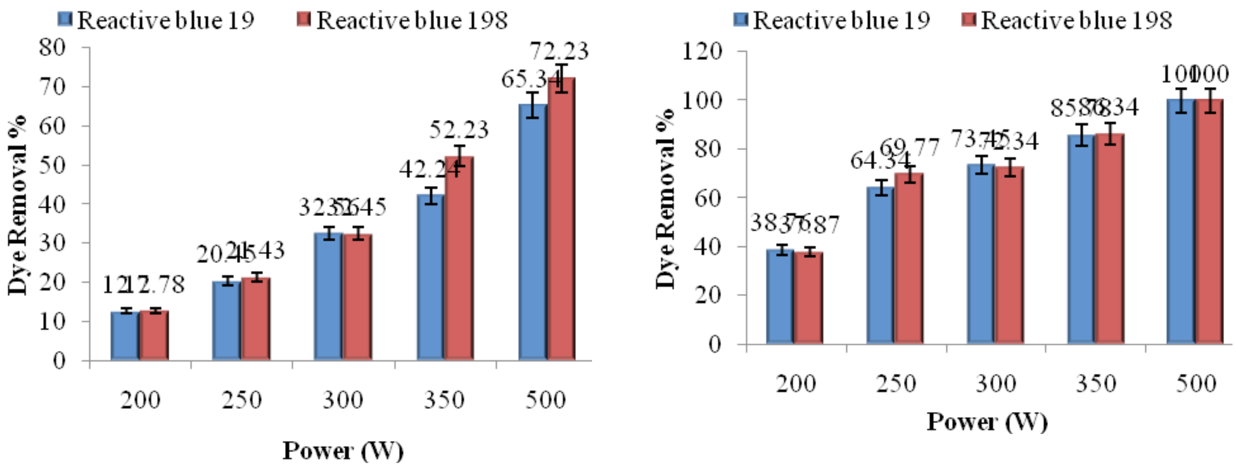


Fig. 4. Graphical representation of ultrasonic treatment of Reactive blue 19 and Reactive blue 198 dyes after 60 and 120 minutes

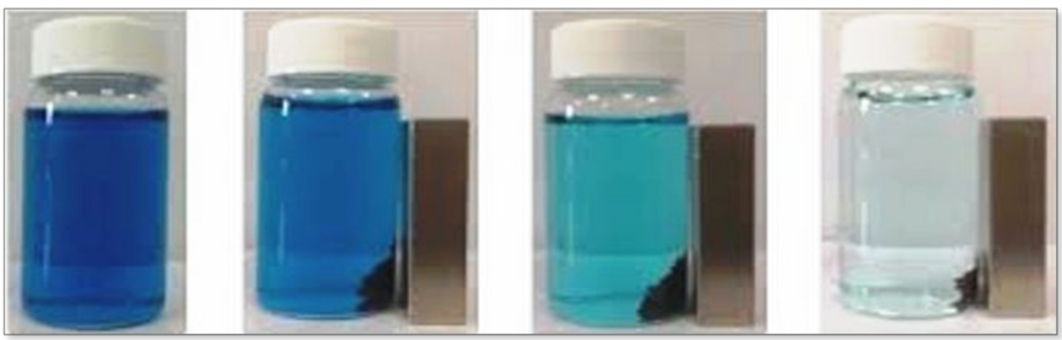


Fig. 5. Reactive blue 19 treated with ultrasonic irradiations

Fig. 6. Reactive blue 198 treated with chitosan nanoparticles irradiated with ultrasonic irradiations

Table 2. Ultrasonic radiation treatment on different dyes after 60 amd120 minutes

S. No.	Power (W)	Percent removal of dyes (50 mg/l) in first 60 minutes		Percent removal of dyes (50 mg/l) in first 120 minutes	
		Reactive blue 19	Reactive blue 198	Reactive blue 19	Reactive blue 198
1	200	12.70	12.78	38.76	37.87
2	250	20.45	21.43	64.34	69.77
3	300	32.56	32.45	73.45	72.34
4	350	42.24	52.23	85.78	86.34
5	500	65.34	72.23	100	100

Table: 3 RSM-BBD predicated value and experimental value

Run Order	pH	Conc. (mMol/l)	Time (Minute)	% Dye Removal	
				Predicted Values	Observed Values
1	4	10	65	6.89	5.71
2	6.5	10	120	29.53	10.11
3	9	55	10	11.79	4.97
4	4	100	65	46.12	34.21
5	9	100	65	60.82	48.22
6	6.5	55	65	47.34	52.42
7	9	10	65	6.01	5.90
8	6.5	100	10	67.99	87.42
9	6.5	55	65	47.34	52.21
10	6.5	10	10	13.52	8.43
11	6.5	55	65	47.34	37.41
12	4	55	10	11.45	3.94
13	4	55	120	25.46	32.29
14	9	55	120	40.70	48.22
15	6.5	100	120	94.91	100

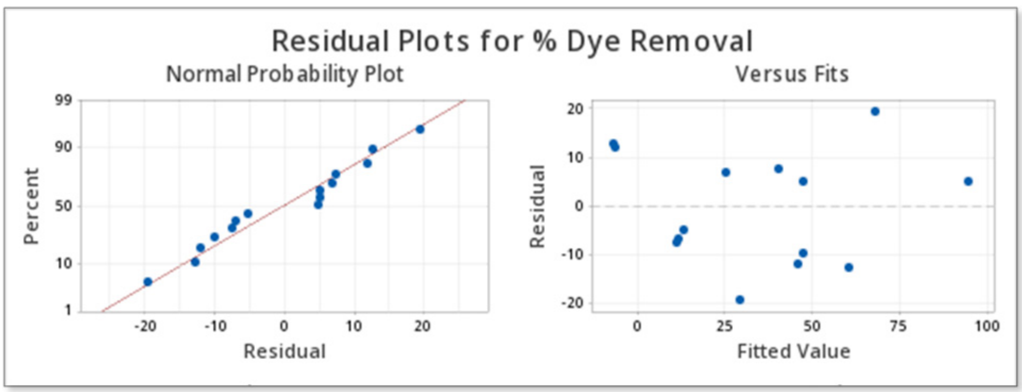


Fig. 7. Normal Probability Plot and residual against fitted value graph

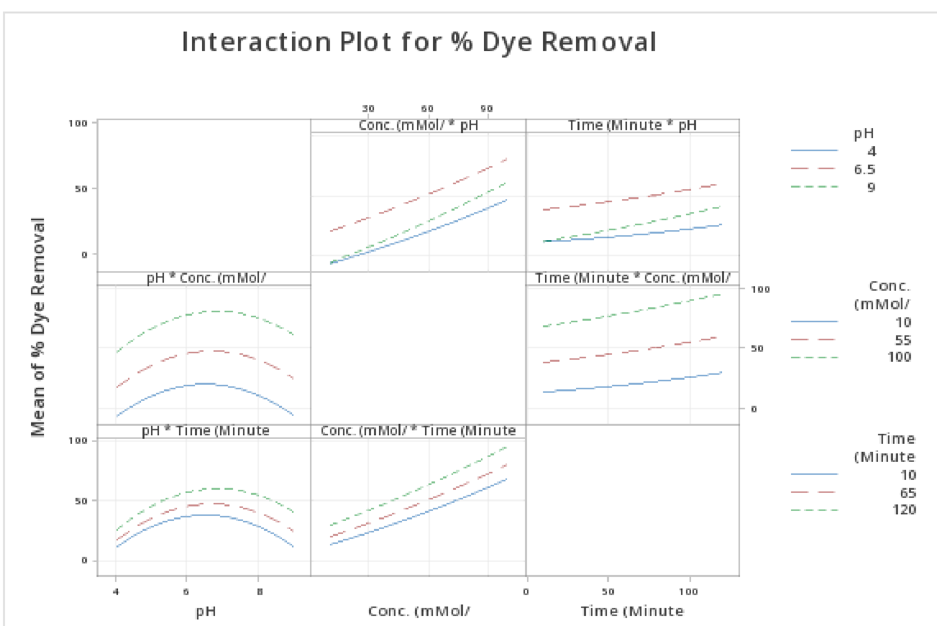


Fig. 8. Mean of dye removal against pH, Concentration and Time

actual values are very near to the predicated values and are near to straight line create a linear relationship between predicated value and experimental value. This shows the significance of the data collected during the experimental work.

Figure 7 showed the all combination and predicated that highest removal of dyes can be observed at 6.5 pH while least was observed at pH 4. Time and concentration showed the best result as they gradually increase. By increasing the nanoparticles concentration in the solution, the hydroxyl radicals that play the main role in decomposition of dye and other contaminants were increased; the collision probability of these very active radicals with the target contaminants were also increased, and decomposi-tion and removal were conducted. The results are in correlation with the previous findings reported.

CONCLUSION

This study concludes that chitosan-tripolyphosphate (CS-TPP) nanoparticles are prominent in Reactive blue dye removal. Both the dyes were successfully removed. Through UV-Vis spectra analysis and HPLC analysis it was confirmed that intermediate product were formed during the treatment of dyes. Peak positions in spectral analysis confirmed the degradation of dyes which is due to chemical change of a particular substance. Optimization studies were also carried out through RSM statistical tool which is useful to control various variables such as pH and Concentration of chitosan-tripolyphosphate (CS-TPP) nanoparticles. Highest removals of both the reactive blues dyes were obtaibed at pH 6.5 and 100% Concentration of chitosan-tripolyphosphate (CS-TPP) nanoparticles. Gradual increases in concentration gradually increase the dye removal efficiency. Predicted values in the RSM and experimental values were observed similar which sowed the accuracy of experiment. Overall chitosan-tripolyphosphate (CS-TPP) nanoparticles were showed prominent result in removing reactive blue dyes, so it can be further used in pilot scale study.

REFERENCES

Alver, E.M., Bulut, A. Ü. and Metin, H. Ç. 2017. One step effective removal of Congo Red in chitosan nanoparticles by encapsulation. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 171: 132-138.

Babakhani, J. and Sartaj, M. 2020. Removal of Cadmium (II) from aqueous solution using tripolyphosphate crosslinked chitosan. *J. Environ. Chem. Eng.* 8: 103-111.

Dotto, J., Fagundes-Klen, M. R., Veit, M. T., Palácio, S. M. and Bergamasco, R. 2019. Performance of different coagulants in the coagulation/flocculation process of textile wastewater. *J. Clean. Prod.* 208: 656-665.

Eng, J.C., Technol, A. E., Ghaly, R., Ananthashankar, M., Alhattab, V. and Ramakrishnan, V. 2014. Chemical Engineering and Process Technology Production, Characterization and Treatment of Textile Effluents: *A Critical Review*. 5(1): 1-19.

Gou M., Qu Y., Zhou J., Mab F. and Tan, L. 2009. Azo dye decolorization by a new fungal isolate *Penicillium* sp. and fungal-bacterial cocultures. *J Hazard Mater*. 170(1) : 314-319.

Jawad, A. and Nawi, M. 2012. Oxidation of crosslinked chitosan-epichlorohydrine film and itsapplication with TiO2 for phenol removal. *Carbohydr. Polym.* 90: 87-94.

Jawad, A. H., Malek, N. N., Abdulhameed, A.S. and Razuan, R. 2020. Synthesis of Magnetic Chitosan-Fly Ash/Fe3O4 Composite for Adsorption of Reactive Orange 16 Dye: Optimization by Box-Behnken Design, *J. Polym. Environ*. 28(3): 1068-1082.

Jawad, A. and Abdulhameed, A. 2020. Mesoporous Iraqi red kaolin clay as an efficient adsorbent for methylene blue dye: Adsorption kinetic, isotherm and mechanism study. *Surf. Interfac*. 18: 417-422.

Khataee, A.R., Ayazloo, M. and Pourhassan, M. 2009. Biological decolorization of C.I. Basic Green 4 solution by *Chlorella* sp.: effect of operational parameters. *Chin J Appl Environ Biol.* 15:110-114.

Li J.T., Lan R.J. and Chen B.H., 2013. Ultrasonic degradation of Fuschin in basic aqueous solution : Effects of operating parameters and additives. *Int. J. Photo Energy*. 01-07.

Mansour, G., Sohrab, G., Mohammad, A., Aliakbar, M., Azim, A., Nezam, M. and Afshin, G. 2016. Removal of blue cat 41 dye from aqueous solutions with ZnO nanoparticles in combination with US and US-H_2O_2 advanced oxidation processes. *Environmental Health Engineering & Management Journal.* 3 (2): 107-113.

Mathur, A., Rawat, A., Bhatt, G., Baweja, S., Ahmad, F., Grover, A., Madhav, K., Dhand, M., Mathur, D., Verma, S.K., Singh, S.K. and Dua, V.K. 2011. Isolation of *Bacillus* producing chitinase from soil: Production and purification of chito-oligosaccharides from chitin extracted from fresh water crustaceans and antimicrobial activity of chitinase. *Rec. Res. Sc. Tech*. 3(11) : 01-06.

Mohammad, A. T., Abdulhameed, A. S. and Jawad, A. H. 2019. Box-Behnken design to optimize the synthesis of new crosslinked chitosan-glyoxal/TiO2 nanocomposite: Methyl orange adsorption and mechanism studies. *Int. J. Biol. Macromol*. 129: 98-109.

Nandi, B. K. and Patel, S. 2014. Removal of Brilliant Green from Aqueous Solution by Electrocoagulation using Aluminum Electrodes: Experimental, Kinetics, and Modeling. *Sep. Sci. Technol.* 49(4) : 601-612.

Natarajan, E. and Ponnaiah, G.P. 2017. Optimization of process parameters for the decolorization of Reactive Blue 235 dye by barium alginate immobilized iron nanoparticles synthesized from aluminum industry waste. *Environ. Nanotechnol. Monit. Manage*. 7 : 73-88.

Pandey, A., Singh, P. and Iyengar L. 2007. Bacterial decolorization and degradation of azo dyes, *Int. Biodeter. Biodegrad*. 59: 73-84.

Pujari, V. and Chandra, T. 2000. Statistical optimization of medium components for enhanced riboflavin production by a UV-mutant of Eremothecium ashbyii. *Process Biochem.* 36(2):31-37.

Rahi, R. K. and Gupta, V. 2021. Biodegradation of Carcinogenic Reactive Azo Dyes by Indigenous Bacterial Consortium X5RC5. *Journal of Environmental Science and Management*. 24(2): 54-61.

Rahi, R. K., Prasad, R. N. and Gupta, V. 2018. Analysis of physico-chemical properties of textile effluents collected from Sanganer, Jaipur. *Int. J. Adv. Sci. Res. Manag*. 3 (7): 119-123.

Razzaz, A., Ghorban, S., Hosayni, L., Irani, M. and Aliabadi, M. 2016. Chitosan nanofibers functionalized by TiO_2 nanoparticles for the removal of heavy metal ions. *J. Taiwan Inst. Chem. Eng*. 58: 333-343.

Santos, P., Santos, J., Corrêa, J., Corio, P. and Andrade, G. 2019. Plasmonic photodegradation of textile dye Reactive Black 5 under visible light: a vibrational and electronic study. *J. Photochem. Photobiol. A Chem*. 37: 159-165.

Shahri, F.B. and Niazi, A. 2015. Synthesis of modified maghemite nanoparticles and its application for removal of acridine orange from aqueous solutions by using Box-Behnken design. *J. Magn. Magn. Mater*. 396 : 318-32

Sudamalla, P. Pichiah, S. and Manickam, M. 2012. Responses of surface modeling and optimization of Brilliant Green adsorption by adsorbent prepared from *Citrus limetta* peel. *Desalin. Water Treat*. 50(1): 367-375.

Surwase, S.N. and Jadhav, J.P. 2011. Bioconversion of L-tyrosine to L-DOPA by a novel bacterium *Bacillus* sp. *JPJ. Amino Acids*. 41(2) : 495-506.

Taheri, M., Moghaddam, M.R.A. and Arami, M. 2012. Optimization of Acid Black 172 decolorization by electrocoagulation using response surface methodology. *Iranian J. Environ. Health Sci. Eng.* 9(1): 23-29.