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An assessment on the performance of activated carbon augmented by activated sludge for removing Methylene blue

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ABSTRACT

The presence of color in industrial wastewaters is a threat to the environment, so color removal from wastewaters is obligatory. In the present study, the performance of activated carbon augmented by activated sludge for removing Methylene blue from wastewater in a sequencing batch reactor (SBR) was investigated. The effects of three independent variables including: activated carbon concentration, mixed liquor suspended solids (MLSS) concentration, and aeration time on the process performance were assessed. From the results, the maximum color and chemical oxygen demand (COD) removal were achieved at 6,000 mg/L, 200 mg/L, and 6 h of MLSS concentration, activated carbon concentration and aeration time, respectively. Also, to clear the effect of activated sludge on the adsorption of the Methylene blue, two parallel SBR with two different processes including: activated carbon and activated carbon augmented by activated sludge were operated for 48 h. The outcomes showed that color and COD removal for activated carbon augmented by the activated sludge process was significantly higher compared to the activated carbon process.

Keywords: Methylene blue; Activated carbon; Activated sludge; Adsorption

1. Introduction

For years, different dyes and pigments have been widely employed in the leather, textile, pharmaceutical, food, cosmetics, paint, plastics, ceramics, porcelain, photographic, printing and paper industries. These industries ultimately result in the production of large volumes of dye-containing effluents, which are considered a major source of environmental pollution [1,2].

Environmental pollution is currently a global issue [3]. The development in industrialization and urbanization caused an increase in water demand dramatically and also a restriction on access to high-quality water. Therefore, water scarcity becomes a global threat and wastewater treatment is indeed a priority. Discharging dye-containing wastewater from the textile industry into receiving water is harmful to the aquatic environment [4–6].

Methylene blue is a heterocyclic aromatic chemical compound with the molecular formula of $C_{16}H_{18}N_3SCl$ and a molecular weight of 319.85 g/mol. Methylene blue is a functional dye that serves as an indicator oxide and changes color (blue/colorless) depending on whether it is oxidized or reduced [7]. This dye has a wide range of applications including dyeing cotton, wool, and silk. Although it is not extremely dangerous, excessive doses of Methylene blue (≥7 mg/kg) could be toxic for the human body. Inhaling this compound may cause respiratory distress. Direct exposure led to eye irritation and permanent damage to the eyes of humans and animals and also cyanosis with bluish discoloration of the skin due to deficient oxygenation of the blood.

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Further negative consequences of methylene which could be mentioned are vomiting, increased sweating, inflammation of the stomach, methemoglobinemia, jaundice, muscle weakness, and mental disorders [8–12]. Therefore, this compound needs to be removed before discharging into the environment.

Physical techniques (such as adsorption), biological approaches, chemical oxidation methods (such as ozonation), advanced oxidation methods (such as photocatalytic degradation), electrocoagulation as well as other technologies were applied to remove dyes from industrial effluents [13,14] [1].

As a fact, there are some limitations to the adoption of these technologies. The quantity of secondary waste produced by coagulation and filtration processes is considerable [15]. Membrane processes are not only expensive, but they also need skilled staff to operate [16,17]. In industry, large-scale chemical oxidation is not feasible [18]. In spite of other technologies, the adsorption method is commonly utilized for color removal in industries due to its high efficiency, ease of operation, lack of sensitivity to toxic compounds, and availability of a wide range of adsorbents [11,19].

Various low-cost adsorbents to reduce the operation cost of decolorization of wastewater have been applied like chitosan, zeolite, fly ash, coal and oxides, agricultural wastes, lignocellulosic wastes, synthetic resins, etc [20]. One of the prevalent absorbents is activated carbon which has some advantages such as high surface area, decent adsorption capability, porous structure and thermal stability [21]. Therefore, many researchers have been attracted to apply activated carbon for removing various dangerous pollutions for instance lead, cadmium, nickel, chromium, and zinc from water [22,23]. Also, wide usage of activated carbon for eliminating different dyes has been reported in the literature such as Malachite green [21], Titan yellow dye [24] Congo red dye [25] Crystal violet [26] and Methylene blue [27].

Activated sludge is a process for the biological treatment of biodegradable wastewaters. This technology could be coupled with activated carbon to enhance adsorption performance. As a fact, activated sludge provides more surface area to adsorb different pollutions, so it could improve removal efficiency. Some studies have been reported using activated carbon augmented by activated sludge for removing different pollutions like a landfill leachate, phenol, brilliant blue and acid orang [28–30]. In the current study, the performance of activated carbon augmented by activated sludge in a sequencing batch reactor (SBR) for removing Methylene blue has been investigated. Moreover, the effects of three independent variables including aeration time, mixed liquor suspended solids (MLSS) concentration, and activated carbon concentration on color removal have been assessed by response surface methodology.

2. Materials and methods

2.1. Wastewater characteristics

Paste tomato industrial wastewater was collected from a working paste tomato processing production plant, Kermanshah, Iran. Table 1 shows the characteristics of the wastewater. It should be mentioned that Methylene blue was added to paste tomato wastewater.

2.2. Bioreactor operation

A common SBR was operated with a working volume of 2 L which is presented in Fig. 1. The bioreactor was filled with 2 L of fresh wastewater over 10 min via a peristaltic pump (filling step). The bioreactor was aerated by a blower and a fine air bubble diffuser from the bottom of the column. After a certain aeration time (depending on the conditions of the experiments) aeration pump was off for 40 min and the sedimentation process occurred. After that, the treated wastewater was discharged by the effluent pump over 10 min. The operation time of influent and effluent pumps as well as the aeration pump was controlled by a time controller.

Three independent variables in three levels were investigated including: MLSS concentration (2,000; 4,000 and 6,000 mg/L), activated carbon (200, 400 and 600 mg/L), and aeration time (2, 4 and 6 h). Experimental conditions were designed by Design-Expert Software (version 13.0). Also, chemical oxygen demand (COD) removal, effluent absorbance of Methylene blue, and sludge volume index (SVI (were reported as responses. The range and levels of the variables and also the values of responses are given in Table 2.

2.3. Analytical methods

For COD, a colorimetric method with a closed reflux method was developed. A spectrophotometer (DR 5000, HACH, JENWAY, USA) at 600 nm was used to measure the absorbance of COD samples. Also, the effluent absorbance of Methylene blue was measured by spectrophotometer at 660 nm. SVI was determined according to standard methods [31].

2.4. Statistical analysis

In the present research, three responses were selected to evaluate the system performance (COD removal, effluent absorbance and SVI) which their attained data were modeled by Design-Expert software and the obtained equations are reported in Table 3. The analysis of variance (ANOVA) results for SVI, COD removal, and effluent absorbance of Methylene blue were presented in Table 3. According to Table 3, probability values of the used models were very low (<0.0001) verifying the significance of the used models. The square of correlation coefficient (R^2) for three responses was in the range of 0.83–0.9.

3. Results and discussion

3.1. Process performance

3.1.1. Effluent absorbance

The main focus of the present research was to remove Methylene blue from wastewater, so effluent absorbance was measured as a key response. Effluent absorbance data were modeled by a reduced quadratic model which the ANOVA results are presented in Table 3. *A* (Aeration time) and *B* (MLSS concentration) are the significant model terms. Moreover, the 3D plots of effluent absorbance variation as a function of MLSS concentration and aeration time at different levels of activated carbon concentration (200, 400 and

600 mg/L) are shown in Fig. 2a–c. The effluent absorbance was decreased from 1.7 to 1 with increasing activated carbon concentration from 200 to 600 mg/L. This outcome verified that higher activated carbon concentration led to an improvement in adsorption and color removal efficiency. Also, MLSS concentration showed a positive effect on color removal, so that, the effluent absorbance was reduced with increasing MLSS concentration at activated carbon concentrations of 200, 400, and 600 mg/L. As a fact, this result is a sign of the ability to activate sludge to purvey surface area and adsorb color. Aeration time is another effective parameter for color removal. The effluent absorbance presented a decreasing trend with increasing aeration time from 2 to 6 h, indicating that a higher aeration time is required to obtain high absorption efficiency. However, at an activated carbon concentration of 600 ppm, the effluent absorbance was increased with increasing aeration time from 4 to 6 h. As an elucidation, the required aeration time for high levels of activated carbon concentration is relatively low.

Table 1
Characteristics of paste tomato industrial wastewater

Parameters	Value
Soluble chemical oxygen demand	1,000–1,100 mg/L
Biological oxygen demand	890–950 mg/L
$N\text{–}NH_4^+$	50–65 mg/L
$N\text{–}NO_3^-$	1–3 mg/L
Total phosphorus	4–6 mg/L
pH	7.5–8.5

As a conclusion, the maximum color removal (the minimum effluent absorbance) was reported at 200 mg/L, 6,000 mg/L and 6 h of activated carbon concentration, MLSS concentration and aeration time, respectively.

3.1.2. COD removal

In the biological treatment process, COD removal is considered as the main response to evaluate the bioreactor performance. From Table 3, similar to effluent absorbance, *A* and *B* are the effective variables. Therefore, the changing of COD removal was plotted based on MLSS concentration and aeration time at activated carbon concentrations of 200, 400, and 600 mg/L in Fig. 3a–c. From Fig. 3a–c activated carbon concentration had no significant effect on COD removal efficiency at all levels of activated carbon concentrations. As a matter of fact, the main source of influent COD was supplied from tomato paste wastewater which biomass plays a key role to remove COD from wastewater.

As presented in Fig. 3, MLSS concentration and aeration time are two important parameters for COD removal consistent with ANOVA results. As MLSS concentration was increased from 2,000 to 6,000 mg/L, COD removal was increased at all levels of aeration time. It should be mentioned that the effect of MLSS concentration was more significant with increasing aeration time from 2 to 6 h. Generally, the value of COD removal efficiency was in the range of 75%–92%, indicating a proper performance of the bioreactor. The maximum COD removal efficiency was achieved at MLSS concentration of 6,000 mg/L and aeration time of 6 h at all three levels of activated carbon concentration.

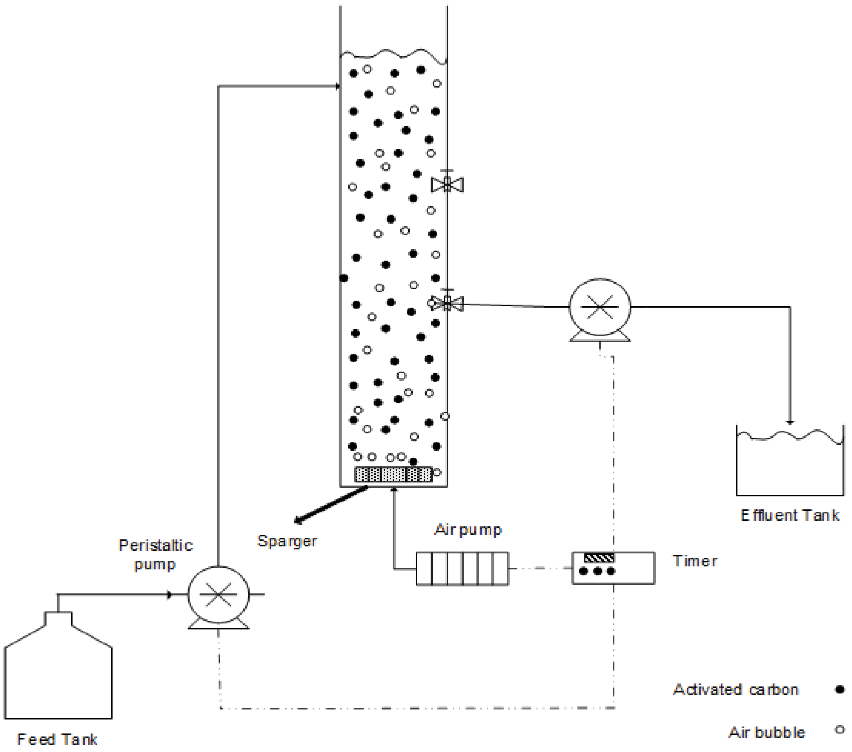


Fig. 1. Schematic of the used SBR.

Table 2
Experimental conditions and results

Run	Factors			Responses		
	A: Time (h)	*B*: Mass concentration (mg/L)	*C*: Activated carbon (mg/L)	SVI (mL/g)	COD removal (%)	Effluent Abs.
1	2	6,000	200	111.6	77.39	0.856
2	4	4,000	400	50	78.63	0.322
3	4	4,000	400	55.7	75	0.496
4	2	2,000	600	63.82	70	0.98
5	4	4,000	200	48.97	74.24	0.405
6	4	4,000	400	51.86	77	0.458
7	4	4,000	400	45.112	76.85	0.4
8	4	4,000	400	53.721	73.89	0.45
9	4	4,000	400	49.075	78	0.544
10	6	2,000	200	62.09	75	0.816
11	6	6,000	600	65.84	93	0.675
12	4	2,000	400	64.28	76.6	0.686
13	6	4,000	400	63.59	78.92	0.635
14	6	6,000	200	80.28	92.68	0.233
15	2	6,000	600	105.18	75	0.728
16	4	4,000	600	47.95	74.32	0.654
17	6	2,000	600	68.37	76.94	0.885
18	2	4,000	400	60.6	78.33	0.786
19	4	6,000	400	75.91	80	0.556
20	2	2,000	200	79.2	70	1.212

Table 3
ANOVA results for the regression equations obtained for the studied responses

Response	Modified equations with significant terms	Probability	R^2	Adj. R^2	Adeq. precision	S.D.	CV	Probability for lack of fit
COD removal	$76.453 + 4.582A + 4.953B - 0.005C + 2.66875AB + 2.273A^2$	<0.0001	0.8306	0.7701	12.6728	2.80	3.61	0.1061
Effluent absorbance	$0.47285 - 0.131A - 0.1531B + 0.04C + 0.108875AC + 0.21075A^2 + 0.12125B^2$	<0.0001	0.8808	0.8257	13.26	0.1004	15.71	0.2107
SVI	$50.5329 - 8.023A + 10.105B - 3.098C - 7.2625AB + 10.6245A^2 + 18.6245B^2$	<0.0001	0.9156	0.8766	16.2144	6.34	9.73	0.0693

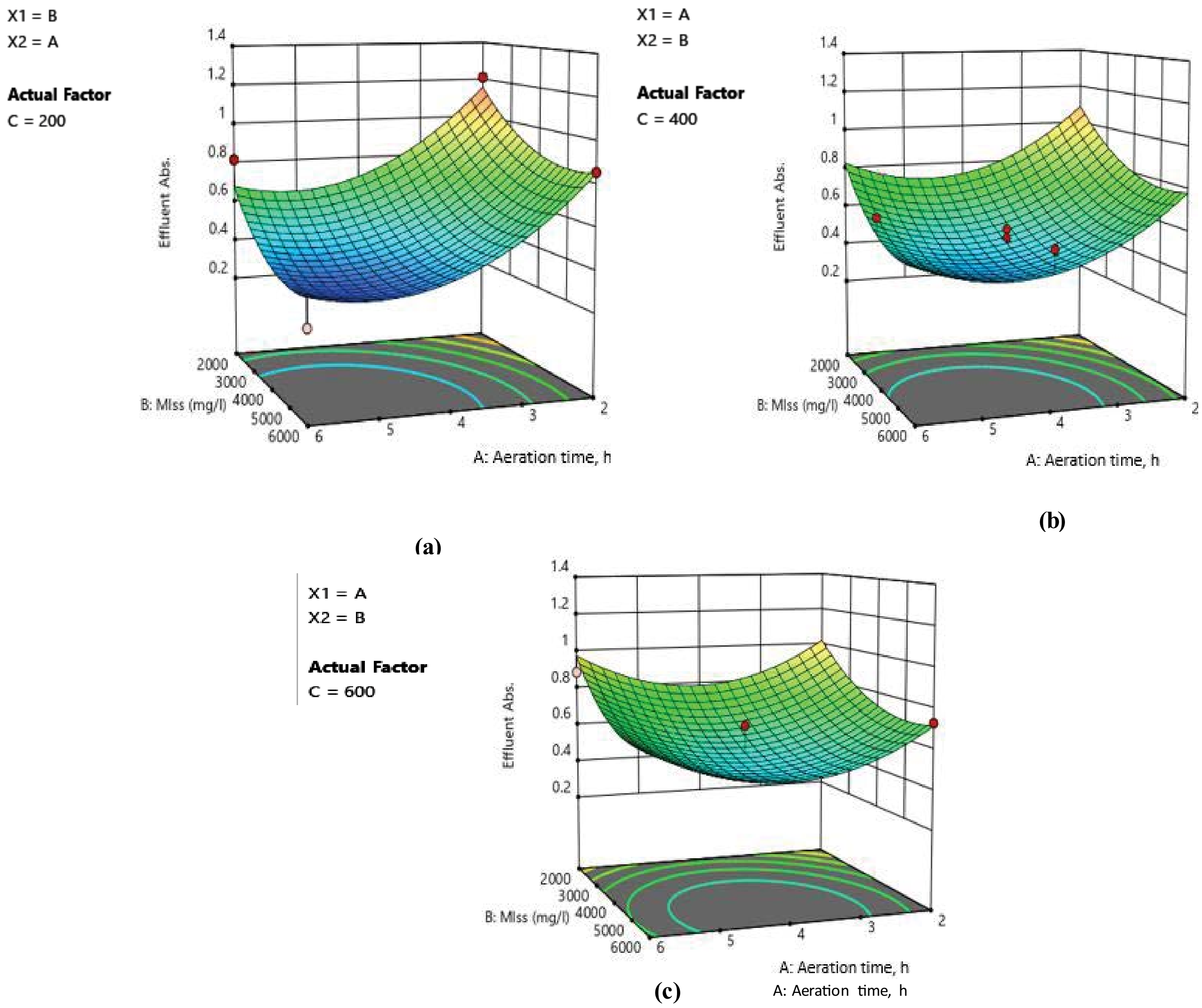
3.1.3. Sludge volume index

One of the operating factors for the activated sludge process is SVI as bulking sludge is the main problem for operating wastewater treatment plants. Fig. 4a–c illustrate the variation trend of SVI as a function of MLSS concentration and aeration time at activated carbon concentrations of 200, 400 and 600 mg/L. From the figures, activated carbon concentration showed no important effect on SVI. SVI data was in the range of 72–92 mL/g which is an acceptable range for the activated sludge process. SVI was influenced by MLSS concentration and aeration time, so that, the response was increased by increasing MLSS concentration and aeration time. The maximum SVI was predicted at 6,000 mg/L of MLSS concentration and 6 h of aeration time.

3.2. Process optimization and long-term study

In this section, the graphical optimization has been applied to optimize the process. The chosen criteria for optimization was COD removal ≥80%, effluent absorbance ≤0.25, and SVI ≤ 80 mL/g. The optimization graphs based on MLSS concentration and aeration time at activated carbon concentration of 200, 400, and 600 mg/L are presented in Fig. 5a–c. The regions which meet the chosen criteria are illustrated by yellow color in Fig. 5. Based on the figures a condition with 200 and 6,000 mg/L of activated carbon and MLSS concentration was selected to monitor long-term performance of the bioreactor.

To evaluate COD and color removal efficiency over long-term performance, the bioreactor was operated in an optimization condition according to Fig. 5a–c with activated carbon



(a)

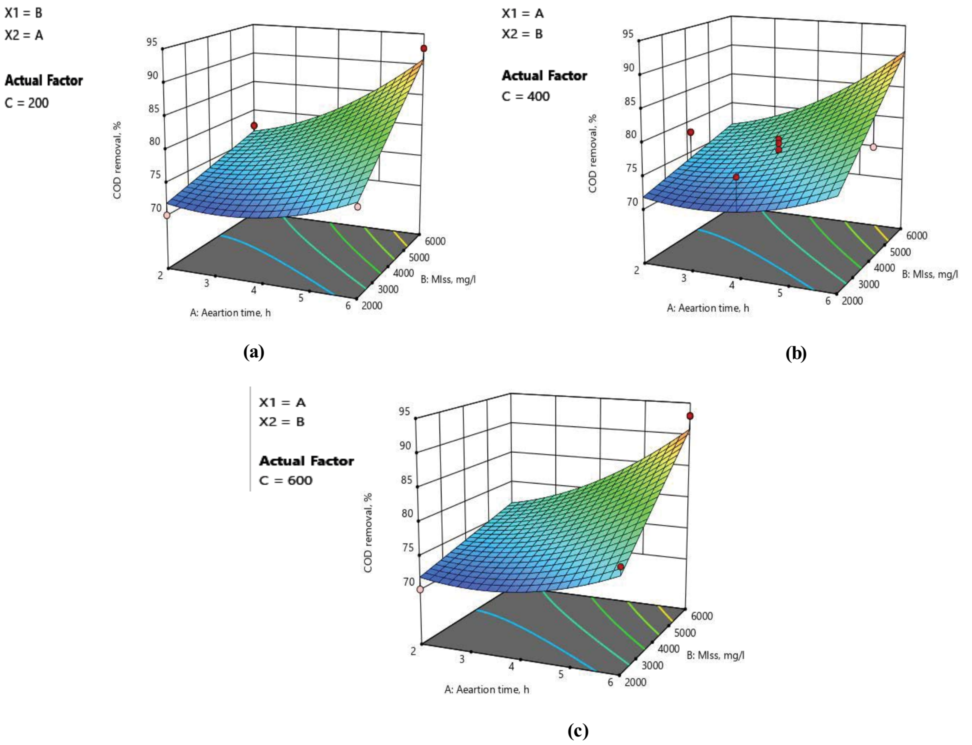
(b)

(c)

Fig. 2. Response surface plots for effluent absorbance as a function of MLSS concentration and aeration time at different activated carbon concentrations: (a) 200, (b) 400, and (c) 600 mg/L.

concentration and MLSS concentration of 200 and 6,000 mg/L, respectively. Moreover, in order to assess the effect of activated sludge on COD and color removal, another SBR with 200 mg/L of activated carbon without activated sludge was operated in parallel. The variation trends of absorbance and COD concentration for both systems were monitored over 48 h of operation which the obtained trends are presented in Fig. 6a and b. As observed in Fig. 6a, the absorbance of the system with activated sludge was significantly lower than the system without activated sludge. The absorbance of the system augmented by activated sludge was decreased after 2 h of aeration time to 0.2, however, the absorbance of the system with activated carbon alone was about 2. This result verified the key role of activated sludge for color adsorption. Besides, COD concentration (Fig. 6b) shows the high potential of activated sludge to remove COD from wastewater as COD concentration was decreased to 700 mg/L for the process augmented by activated sludge, while, COD concentration was not decreased with activated carbon meaningfully.

Overall, after 48 h of operation, COD concentration and absorbance of the activated carbon system augmented by activated sludge process were significantly low as compared with activated carbon process. It should be noted that, the reported absorbance of activated carbon system was decreased significantly over 25–30 h and the minimum value was attained after 30 h of operation, whereas, the absorbance was increased after 32 h of operation once more again. As an elucidation of this phenomenon, the maximum of adsorption sites was used after 30 h of operation, while, after getting the maximum capacity of adsorption, desorption has been occurred and adsorbed molecules of dye were released from the surface area [32]. The final effluent absorbance of 0.031 and the final effluent COD concentration of 81 mg/L were obtained after 48 h of operation for the activated carbon augmented by activated sludge, however, 1.067 and 498 mg/L for effluent absorbance and COD concentration were reported, respectively, for activated carbon process.

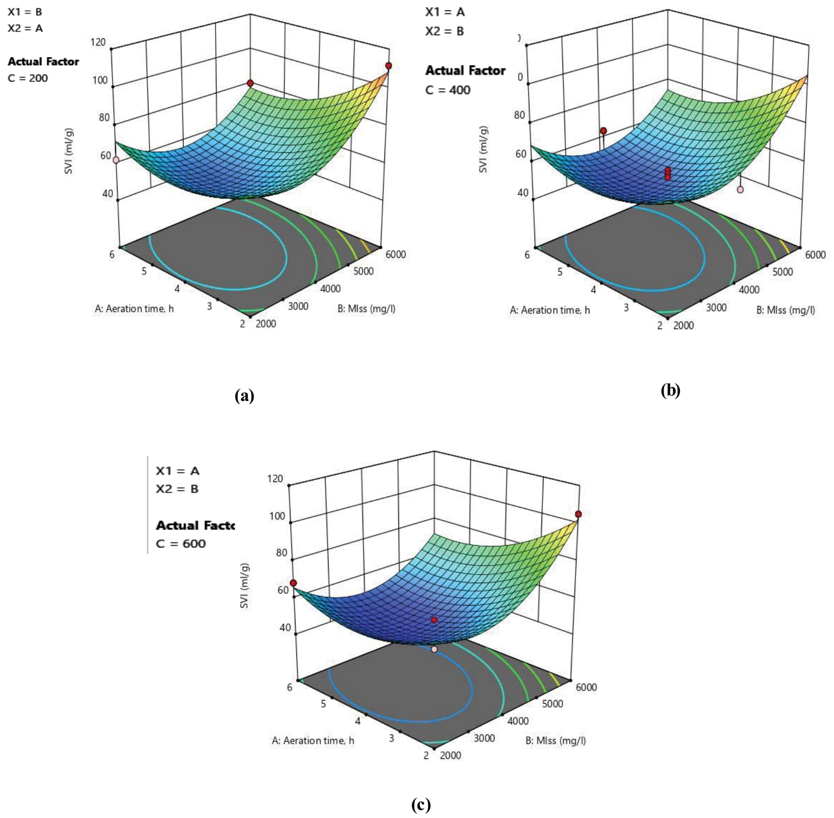


(a)

(b)

(c)

Fig. 3. Response surface plots for COD removal as a function of MLSS concentration and aeration time at different activated carbon concentrations: (a) 200, (b) 400, and (c) 600 mg/L.

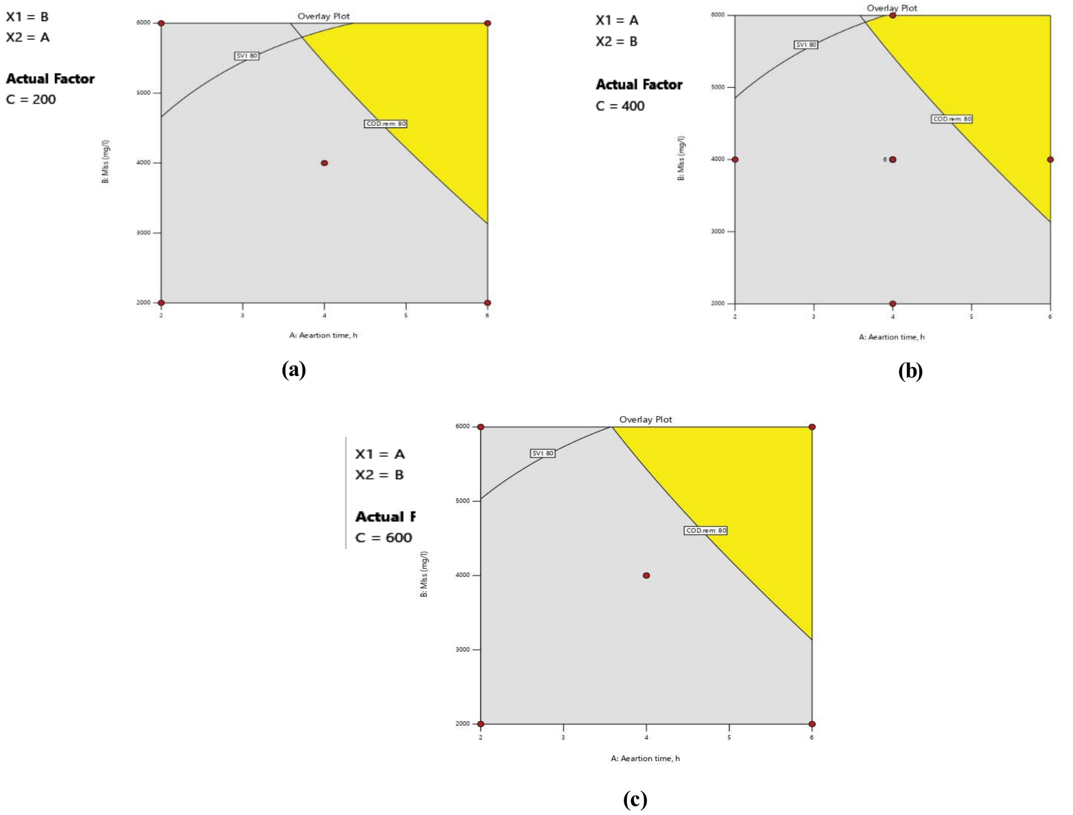


(a)

(b)

(c)

Fig. 4. Response surface plots for SVI as a function of MLSS concentration and aeration time at different activated carbon concentrations: (a) 200, (b) 400, and (c) 600 mg/L.



(a)

(b)

(c)

Fig. 5. Overlay plot for the optimal region at different activated carbon concentration: (a) 200, (b) 400, and (c) 600 mg/L.

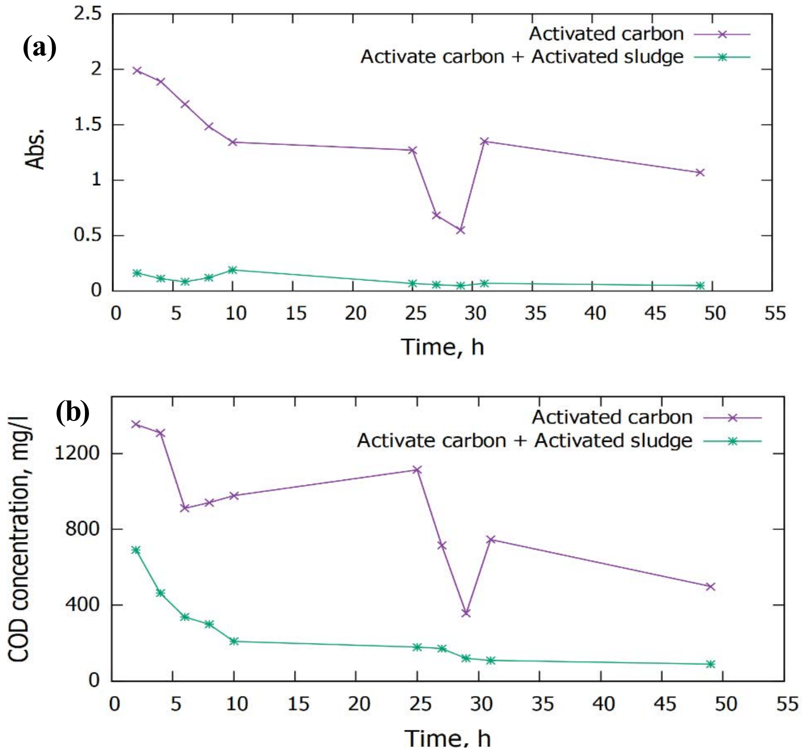


Fig. 6. Long-term performance of activated carbon process and activated carbon + activated sludge process: (a) absorbance and (b) COD concentration, mg/L.

4. Conclusion

In the present study, the performance of activated carbon augmented by activated sludge to remove Methylene blue from paste potato wastewater was evaluated. Aeration time, activated carbon concentration, and MLSS concentration were three independent variables which were chosen in three levels. COD removal, effluent absorbance of Methylene blue and SVI were the measured responses. As a conclusion, an experimental condition with 6 h, 200 mg/L and 6,000 mg/L of aeration time, activated carbon, MLSS concentration, respectively, resulted in the maximum color and COD removal.

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References

[1] K. Kestioğlu, T. Yonar, N. Azbar, Feasibility of physico-chemical treatment and advanced oxidation processes (AOPs) as a means of pretreatment of olive mill effluent (OME), Process Biochem., 40 (2005) 2409–2416.

[2] M.T. Ghaneian, M. Dehvari, M. Taghavi, M. Amrollahi, B. Jamshidi, Application of Pomegranate Seed Powder in the removal of Reactive Red 198 dye from aqueous solutions, Jundishapur J. Health Sci., 4 (2012) 45–55.

[3] O. Gulnaz, A. Sahmurova, S. Kama, Removal of Reactive Red 198 from aqueous solution by *Potamogeton crispus*, Chem. Eng. J., 174 (2011) 579–585.

[4] Z. Aksu, S. Ertuğrul, G. Dönmez, Methylene blue biosorption by *Rhizopus arrhizus*: effect of SDS (sodium dodecylsulfate) surfactant on biosorption properties, Chem. Eng. J., 158 (2010) 474–481.

[5] Y. Fu, T. Viraraghavan, Fungal decolorization of dye wastewaters: a review, Bioresour. Technol., 79 (2001) 251–262.

[6] W. Somasiri, X.F. Li, W.Q. Ruan, C. Jian, Evaluation of the efficacy of upflow anaerobic sludge blanket reactor in removal of colour and reduction of COD in real textile wastewater, Bioresour. Technol., 99 (2008) 3692–3699.

[7] J. Yang, K. Qiu, Preparation of activated carbons from walnut shells via vacuum chemical activation and their application for Methylene blue removal, Chem. Eng. J., 165 (2010) 209–217.

[8] S. Chatterjee, A. Kumar, S. Basu, S. Dutta, Application of response surface methodology for Methylene blue dye removal from aqueous solution using low cost adsorbent, Chem. Eng. J., 181 (2012) 289–299.

[9] J.Z. Yi, L.M. Zhang, Removal of Methylene blue dye from aqueous solution by adsorption onto sodium humate/polyacrylamide/clay hybrid hydrogels, Bioresour. Technol., 99 (2008) 2182–2186.

[10] A.T. Paulino, M.R. Guilherme, A.V. Reis, G.M. Campese, E.C. Muniz, J. Nozaki, Removal of Methylene blue dye from an aqueous media using superabsorbent hydrogel supported on modified polysaccharide, J. Colloid Interface Sci., 301 (2006) 55–62.

[11] E. Bazrafshan, F. Kord Mostafapour, Evaluation of color removal of Methylene blue from aqueous solutions using plant stem ash of Persica, J. North Khorasan Univ. Med. Sci., 4 (2013) 523–532.

[12] J. Mittal, Permissible synthetic food dyes in India, Resonance, 25 (2020) 567–577.

[13] Y. Deng, R. Zhao, Advanced oxidation processes (AOPs) in wastewater treatment, Curr. Pollut. Rep., 1 (2015) 167–176.

[14] C.H. Liu, J.S. Wu, H.C. Chiu, S.Y. Suen, K.H. Chu, Removal of anionic reactive dyes from water using anion exchange membranes as adsorbers, Water Res., 41 (2007) 1491–1500.

[15] Z.M. Hasani, M.S. Alavi, M. Arami, Removal of CI Acid Blue 292 using polyaluminum chloride, J. Color Sci. Technol., 2 (2008) 87–94.

[16] M.R. Sohrabi, M. Ghavami, Photocatalytic degradation of Direct Red 23 dye using UV/TiO$_2$: effect of operational parameters, J. Hazard. Mater., 153 (2008) 1235–1239.

[17] M. Sleiman, D. Vildozo, C. Ferronato, J.-M. Chovelon, Photocatalytic degradation of azo dye Metanil Yellow: optimization and kinetic modeling using a chemometric approach, Appl. Catal., B, 77 (2007) 1–11.

[18] E. Lorenc-Grabowska, G. Gryglewicz, Adsorption characteristics of Congo Red on coal-based mesoporous activated carbon, Dyes Pigm., 74 (2007) 34–40.

[19] E. Bazrafshan, F. Kord Mostafapour, S. Rahdar, A.H. Mahvi, Equilibrium and thermodynamics studies for decolorization of Reactive Black 5 (RB5) by adsorption onto MWCNTs, Desal. Water Treat., 54 (2015) 2241–2251.

[20] I. Ali, M. Asim, T.A. Khan, Low cost adsorbents for the removal of organic pollutants from wastewater, J. Environ. Manage., 113 (2012) 170–183.

[21] C. Arora, P. Kumar, S. Soni, J. Mittal, A. Mittal, B. Singh, Efficient removal of malachite green dye from aqueous solution using *Curcuma caesia* based activated carbon, Desal. Water Treat., 195 (2020) 341–352.

[22] A. Mittal, R. Ahmad, I. Hasan, Iron oxide-impregnated dextrin nanocomposite: synthesis and its application for the biosorption of Cr(VI) ions from aqueous solution, Desal. Water Treat., 57 (2016) 15133–15145.

[23] M. Karnib, A. Kabbani, H. Holail, Z. Olama, Heavy metals removal using activated carbon, silica and silica activated carbon composite, Energy Procedia, 50 (2014) 113–120.

[24] J. Mittala, R. Ahmadb, A. Mittalc, Kahwa tea (*Camellia sinensis*) carbon—a novel and green low-cost adsorbent for the sequestration of Titan yellow dye from its aqueous solutions, Desal. Water Treat., 227 (2021) 404–411.

[25] V.K. Gupta, S. Agarwal, R. Ahmad, A. Mirza, J. Mittal, Sequestration of toxic congo red dye from aqueous solution using ecofriendly guar gum/activated carbon nanocomposite, Int. J. Biol. Macromol., 158 (2020) 1310–1318.

[26] S. Soni, P.K. Bajpai, D. Bharti, J. Mittal, C. Arora, Removal of crystal violet from aqueous solution using iron based metal organic framework, Desal. Water Treat, 205 (2020) 386–399.

[27] Ü. Geçgel, G. Özcan, G.Ç. Gürpınar, Removal of Methylene blue from aqueous solution by activated carbon prepared from pea shells (*Pisum sativum*), J. Chem., 2013 (2013) 614083, doi: 10.1155/2013/614083.

[28] B.M. Mareai, M. Fayed, S.A. Aly, W.I. Elbarki, Performance comparison of phenol removal in pharmaceutical wastewater by activated sludge and extended aeration augmented with activated carbon, Alexandria Eng. J., 59 (2020) 5187–5196.

[29] G. Abdolmajid, G. Mitra, M. Mohammad, N. Ali, Performance evaluation of combined process of powdered activated carbon-activated sludge [PACT] in textile dye removal, J. Environ. Health Sustainable Dev., 1 (2016) 141–152.

[30] N. Aghamohammadi, H. Bin Abdul Aziz, M.H. Isa, A.A. Zinatizadeh, Powdered activated carbon augmented activated sludge process for treatment of semi-aerobic landfill leachate using response surface methodology, Bioresour. Technol., 98 (2007) 3570–3578.

[31] WEF, APHA, Standard Methods for the Examination of Water and Wastewater, American Public Health Association (APHA), Washington DC, USA, 2005.

[32] Y. Cai, L. Liu, H. Tian, Z. Yang, X. Luo, Adsorption and desorption performance and mechanism of tetracycline hydrochloride by activated carbon-based adsorbents derived from sugar cane bagasse activated with ZnCl$_2$, Molecules, 24 (2019) 4534, doi: 10.3390/molecules24244534.