

A new electrode reactor with in-built recirculation mode for the enhancement of methylene blue dye removal from the aqueous solution: Comparison of adsorption, electrolysis and combined effect

Ponnusamy Senthil Kumar[†], Maria Jacob Stani Raja, Mahathevan Kumaresan, Dinesh Kumar Loganathan, and Prabhakaran Chandrasekaran

Department of Chemical Engineering, SSN College of Engineering, Chennai 603 110, India
(Received 13 August 2013 • accepted 11 October 2013)

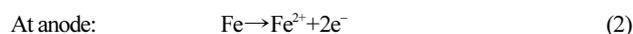
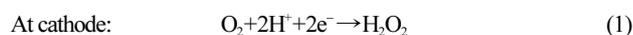
Abstract—The removal of basic dye such as methylene blue (MB) dye from the synthetic wastewater was experimentally investigated using an electrolytic cell (EC), adsorption and the combined effect of EC and adsorption technology called a three-phase three-dimensional electrode reactor (TPTDER). The performance of the each technology was checked on the basis of the efficiency of the systems. The experimental results are expressed in terms of the removal efficiency of the dye molecules. The results show that the TPTDER could efficiently remove the dye molecules from the aqueous solutions when compared with the EC and adsorption process. The removal efficiency reached as high as about 99% for an initial MB dye concentration in the range of 100-1,000 mg/L by TPTDER for 10 min at 12 V cell voltage and at specific airflow conditions. It was also observed that the removal of dye molecules depends upon the initial solution pH, applied cell voltage, contact time, and initial dye concentration. The recyclability of the particle electrodes in the TPTDER process was also checked. These findings suggest that TPTDER is a promising technology for the removal of dyes from the aqueous solution, and can be applied to the removal of dyes from the industrial effluents.

Keywords: Adsorption, Methylene Blue Dye, Three-phase Three-dimensional Electrode Reactor, Particle Electrodes

INTRODUCTION

The effluents from different industries such as textiles, leather, paper, plastics, cosmetics, and printing are the largest producers of the wastewater in Tamilnadu, India [1]. The effluents from these industries mainly consist of synthetic dyes that contain wastewater known to be carcinogenic and highly toxic to human beings [2-6]. These dyes can cause allergic dermatitis, skin irritation, cancer, and mutations [7]. Therefore, the toxic and unwanted dye pollutants need to be removed from the wastewater before it is discharged into the environment. For this reason, many wastewater treatment methodologies, like physical, chemical and biological methods, and their combinations have been employed to remove the pollutants from the wastewater [8-12]. However, the existing conventional wastewater treatment technologies have their inherent disadvantages in terms of their applicability, effectiveness and cost [13,14]. In recent years, the electrochemical oxidation process has attracted considerable interest due to its high efficiency, ease of operation and environmental compatibility [15]. Generally, the electrochemical process involves the transfer of heterogeneous electron between a solid electrode and the ionic species in an electrolytic solution [16]. It indicates that the rate of electrochemical reaction highly depends on the electron transfer rate, which is directly proportional to the specific surface of the electrode material. But, the surface area cannot be enlarged in a conventional two-dimensional electrochemical reactor. In particular, the electrochemical technologies based on the three-dimensional electrode reactor for wastewater treatments have attracted

much attention, because the electrodes have a large specific surface area and high performance in comparison to conventional two-dimensional electrodes [17-20]. Many small particles were utilized as particle electrodes in the three-dimensional electrode reactor when it was compared with the two-dimensional electrode. At a particular cell voltage under the influence of an electric field, these particles become polarized, which forms charged microelectrodes. For this reason, the electrolytic efficiency was increased because of the increase in the contact between the reactants and the particle, i.e., the specific surface area of the particle electrodes gets increased. However, most of the researches on three-dimensional electrodes mainly discussed organic electrosynthesis [21-23] and the removal of metal ions [24] or cyanide [25] from solution. Also, this technology was successfully applied for the removal of organic pollutants from wastewater [24,26-28]. Generally, stainless steel is used as electrodes for the treatment of organic wastewater [16,29]. The electro-Fenton reaction is preceded in normally such type of electrode, i.e., indirect oxidation of H₂O₂ and hydroxyl radicals. At first, H₂O₂ and Fe²⁺ are electro-generated at the cathode and anode and the equations are given as follows [30,31]:



After the above reactions, the H₂O₂ diffuses into the solution and reacts with the Fe²⁺ ions present in the solution. The Fenton reactions can be written as follows [32]:

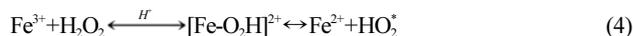


The catalytic reaction (3) is propagated by Fe²⁺ regeneration, mainly by the reduction of Fe³⁺ with H₂O₂ [33]:

[†]To whom correspondence should be addressed.

E-mail: senthilchem8582@gmail.com

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Our objective was to design a reactor, a new three-phase three-dimensional electrode reactor (TPTDER), in a laboratory scale model to treat the MB dye from the aqueous solution. The effect of operating parameters such as solution pH, cell voltage, initial MB dye concentration and contact time on the removal of MB dye was studied. The electrolytic cell and adsorption process on the removal of MB dye were carried out and their performance was compared with the TPTDER performance. The kinetics for the removal of MB dye from the aqueous solution was explained with the help of different models such as pseudo-first order, pseudo-second order and intra-particle diffusion model. In addition, the recyclability of the particle electrodes is also discussed in this report.

MATERIALS AND METHODS

1. Preparation of Particle Electrodes

The raw form of *Strychnos potatorum* seeds was received from Pudukkottai District, Tamilnadu, India. The seeds were thoroughly washed with double distilled water to remove impurities and then the seeds were dried in sun light till the moisture was completely removed. The dried seeds were ground into a fine powder by using a mixer grinder. The particle electrodes were prepared by treating one part of *Strychnos potatorum* seeds with two parts by weight of concentrated sulfuric acid for about 24 h. The excess acid in the mixture was removed by rinsing the dehydrated *Strychnos potatorum* seeds with double distilled water until the pH of the supernatants remained constant at pH 7.0. This material was dried at 80 °C for about 3 h and then the dried materials were ground into a powder by mixer grinder. The powdered materials were sieved to obtain the size of 0.354 mm. This prepared material was named as surface modified *Strychnos potatorum* seeds (SMSP) and this was utilized as particle electrodes in TPTDER.

2. Preparation of MB Dye Solution

Methylene blue dye powder (CI 52015, Molecular Formula: $\text{C}_{16}\text{H}_{18}\text{N}_3\text{SCl}\cdot 3\text{H}_2\text{O}$, Molecular weight: 373.9, $\lambda_{\text{max}}=664$ nm) was procured from Merck Chemicals, India and used without further purification. A stock solution of MB dye (1,000 mg/L) was prepared by dissolving the calculated quantity of MB dye in double distilled water. Several aqueous solutions with varying MB dye concentrations (100-1,000 mg/L) were prepared by the proper dilutions of a stock solution with double distilled water. The residual dye concentrations in the solution were analyzed by UV-Vis Spectrophotometer (JASCO, USA). The pH of the test solution was adjusted by using 0.1 M NaOH or 0.1 M HCl. The pH of the solution was measured with a pH meter (HI 98107, Hanna Equipments Private Limited, Mumbai, India). Fourier transform infrared spectroscopy (FT-IR) analysis was used to identify the different chemical functional groups present in the particle electrodes (PE IR SPECTRUM ASCII PEDS 1.60 spectrometer) [4]. The surface morphology of particle electrodes was carried out by the scanning electron microscope (SEM) analysis to check the surface nature of the particle electrodes (Quanta 200 FEG scanning electron microscope) [4]. All the chemicals used were of analytical reagent grade.

3. Experimental Studies

The experimental setup is a batch recirculation mode of rectan-

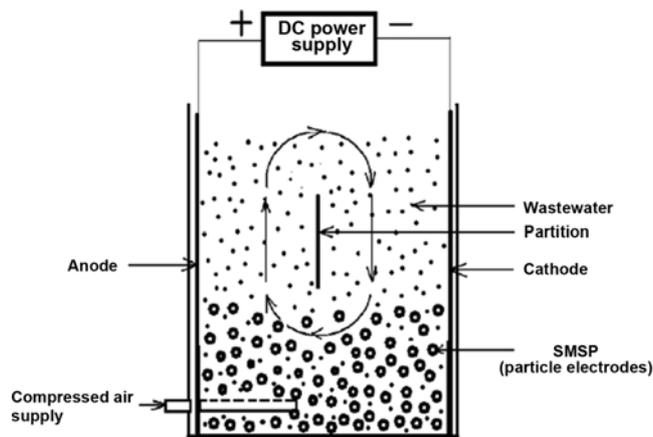


Fig. 1. Experimental setup (TPTDER).

gular shaped reactor, as shown in Fig. 1. The reactor is made from the plastic material with a size of 8 cm×8 cm×12 cm. This reactor mainly consists of anode, cathode, particle electrodes, and the provision for air supply. The anode and cathode materials were made from stainless steel plates and were placed in the two sides of reactor (Fig. 1). The 15 g of particle electrodes was packed between the anode and cathode electrodes which form three-dimensional particle electrodes in a reactor. The compressed air was supplied into the particle electrodes by a micropore plastic pipeline from the bottom of the reactor. The supply of the compressed air into the reactor will cause an increase in the height of the packed bed and the system will behave as like a fluidized bed. The combined effect of gas (air), liquid (wastewater) and solid (particle electrodes) was involved in the three-dimensional reactor called three-phase three-dimensional electrode reactor (TPTDER). A partition wall is provided within the TPTDER to separate the reactor into two compartments. The left side compartment consists of anode and the right side compartment consists of cathode. The compressed air was supplied at the bottom side of the anodic compartment to recirculate the wastewater within the compartments (Fig. 1). The electric power was supplied with regulated DC power supply. Three modes of experimental studies were conducted. The first was carried out without the presence of particle electrodes in the reactor, but with the presence of DC power supply to the anode and cathode material at a specified air flow rate; the system is called an electrolytic cell (EC). The second mode was without the presence of DC power supply to the reactor, but with the presence of particle electrodes at a specified air flow rate, called the adsorption process. The third mode was carried out in the TPTDER (consisting of both DC power supply to the electrodes and with the presence of particle electrodes at a specified air flow rate).

In the EC experimental studies, 500 mL of the known initial concentration of MB dye solution was taken in the reactor. The pH of the solution was adjusted to the required value by using the 0.1 M NaOH or 0.1 M HCl, in order to investigate the effect of pH on the removal of MB dye from the aqueous solution. The reactor was started operating when the DC power supply and the compressed air supply were switched on. The experimental studies were run until the system was operating under equilibrium condition. Due to the supply of compressed air, less amount of precipitate was formed

in the reactor. The supernatant was separated from the reaction mixtures by centrifuge and then the residual concentration in the supernatant was analyzed by UV-Vis Spectrophotometer. All the experimental studies were done in duplicate. In all other experimental studies, no electrolytes were added. The different operating parameters such as solution pH, cell voltage, initial MB dye concentration and contact time which influence in the removal of MB dye from the aqueous solution were studied.

In the batch adsorption studies, 500 mL of the known initial concentration of MB dye solution was taken in the reactor along with 15 g of particle electrodes. The air was continuously sparged into the reactor to mix the wastewater and particle electrodes properly and also to recirculate the wastewater within the compartments. The different operating parameters such as solution pH, initial MB dye concentration and contact time which influence in the adsorption of MB dye onto the particle electrodes from the aqueous solution were studied. All the experimental studies were performed in duplicate.

A 500 mL of the known initial concentration of MB dye solution was taken in the TPTDER. The pH of the solution was adjusted to the required value by using the 0.1 M NaOH or 0.1 M HCl, in order to investigate the effect of pH on the removal of MB dye from the aqueous solution. The reactor was started operating when the DC power supply and the compressed air supply were switched on. The experimental studies were carried out by varying the different operating parameters such as solution pH, cell voltage, initial MB dye concentration and contact time on the removal of MB dye from the aqueous solution. Once the system attained the equilibrium condition, the supernatant was separated from the reaction mixture by centrifuge, and then the residual dye concentration in the supernatant was analyzed by UV-Vis Spectrophotometer. All the experimental studies were done in duplicate. The efficiency of the treatment was explained based on the estimation of the percentage removal of MB dye molecules from the aqueous solution and the equation is given as follows:

$$\% \text{ Dye Removal} = \frac{C_i - C_f}{C_i} \times 100 \quad (5)$$

Where C_i and C_f are the initial and final concentration of MB dye in the solution (mg/L), respectively. The amount of MB dye that gets deposited over the particle electrodes at any time t was estimated by the following equation:

$$q_t = \frac{(C_i - C_t)V}{m} \quad (6)$$

where C_t is the concentration of MB dye solution at time t (mg/g), V is the volume of MB dye solution (L) and m is the mass of the particle electrodes (g). The kinetic data were analyzed with the pseudo-first order, pseudo-second order and intraparticle diffusion models. The amount of MB dye that gets deposited over the particle electrodes at equilibrium was estimated by the following equation:

$$q_e = \frac{(C_i - C_e)V}{m} \quad (7)$$

where C_e is the concentration of MB dye solution at equilibrium (mg/L).

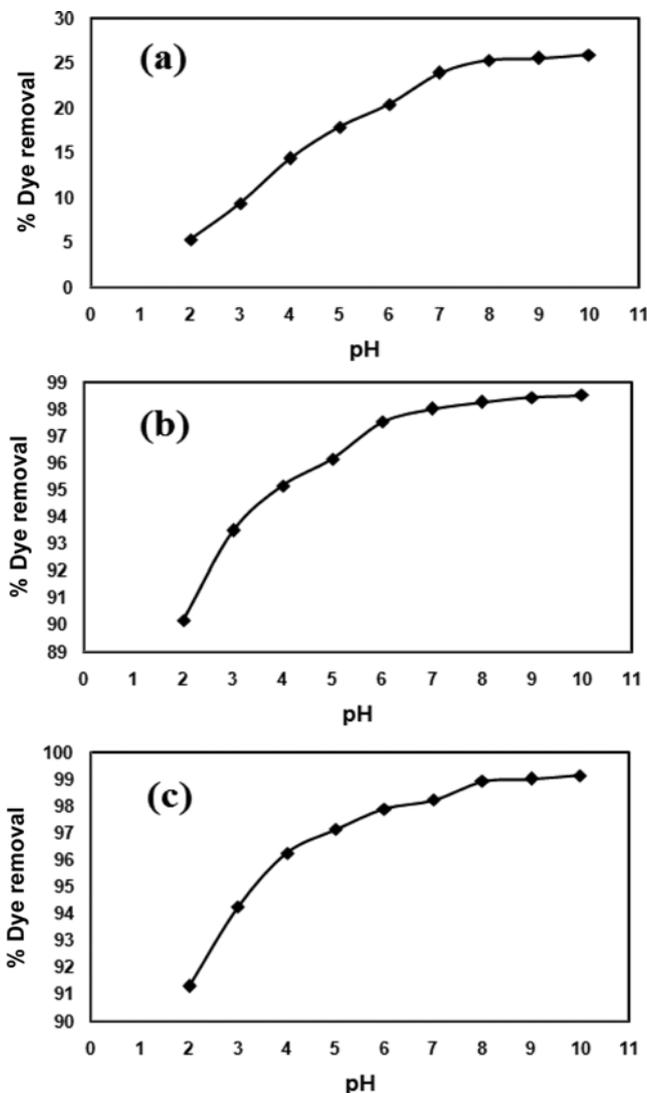


Fig. 2. Effect of solution pH on MB dye removal (a) Electrolytic cell, (b) Adsorption and (c) TPTDER.

RESULTS AND DISCUSSION

1. Effect of Solution pH

Fig. 2(a) shows the experimental results observed for the effect of solution pH on the removal of MB dye from the aqueous solution by EC process. The operating s for the EC process are: initial MB dye concentration of 100 mg/L, cell voltage of 12 V, contact time of 60 min and wastewater volume of 500 mL. From Fig. 2(a), the removal of MB dye from aqueous solution was increased with the increased in the solution pH, and it reached the maximum value at the pH of 8.0. A constant removal of MB dye of about 25.54% was attained when initial pH was over 8.0, which indicates that the dye could be effectively degraded in a slightly alkaline medium. The increase in the negative charge of dye molecules makes MB dye be adsorbed much more easily on the anode where MB dye is degraded by electrochemical oxidation. Fig. 2(b) shows the experimental results observed for the effect of solution pH on the removal of MB dye from the aqueous solution by adsorption process. The operating conditions for the adsorption process are: initial MB dye

concentration of 100 mg/L, SMSP dose of 15 g, contact time of 30 min and wastewater volume of 500 mL, From Fig. 2(b), it can be seen that the removal of MB dye from aqueous solution was increased with the increase in the solution pH, and it reaches the maximum value at the pH of 8.0. The maximum removal of MB dye from aqueous solution was measured at the optimum pH of 8.0. For further experimental studies, the initial solution pH was kept constant at 8.0. At low pH, the number of positively charged sites of the SMSP gets increased. This situation does not favor the adsorption of MB dye onto the SMSP sites due to the electrostatic repulsion, because MB dye is a cationic dye. At higher pH, the negatively charged sites of the SMSP get increased, which enhances the adsorption of positively charged MB dye due to the electrostatic forces of attraction [4]. Fig. 2(c) shows the experimental results observed for the effect of solution pH on the removal of MB dye from the aqueous solution by TPTDER. The operating conditions for the TPTDER are: initial MB dye concentration of 100 mg/L, cell voltage of 12 V, particle electrodes of 15 g, contact time of 10 min and wastewater volume of 500 mL. As can be seen from Fig. 2(c), the removal of MB dye was increased with the increase in solution pH, and maximum removal was observed at the pH of 8.0; after that the percentage removal remained constant. The major phenomenon in the removal of MB dye was mainly due to the adsorption process and slightly due to the electrochemical oxidation.

2. Effect of Applied Voltage

The effect of applied cell voltage on the removal of MB dye from the aqueous solution by EC process is shown in Fig. 3(a). The operating conditions for the EC process are: initial MB dye concentration of 100 mg/L, solution pH of 8.0, contact time of 60 min and waste-

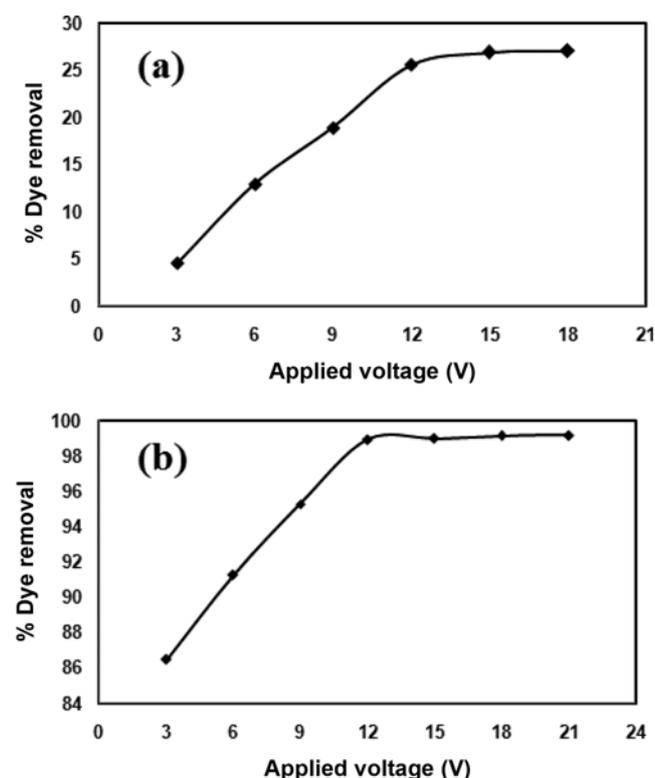


Fig. 3. Effect of cell voltage on MB dye removal (a) Electrolytic cell, and (b) TPTDER.

water volume of 500 mL. From Fig. 3(a), the percentage removal of MB dye was increased with the increase in applied cell voltage, and it reached the maximum value of 25.54% at the applied cell voltage of 12 V; after that only the less percentage removal of MB dye was observed. This shows the removal of MB dye exhibits a positive correlation with the applied cell voltage. The results may be due to the increase of hydroxyl radical by increasing applied voltage, because the hydroxyl radicals can be produced on the anode surface by oxidation of water molecules. The increase in applied voltage could also increase the amount of active intermediate such as hydroxyl radicals in the bulk solution, which would favor the indirect electro-oxidation of MB dye molecules. In view of energy efficiency and also optimum applied cell voltage, 12 V was selected for further experimental studies. The effect of applied cell voltage on the removal of MB dye from the aqueous solution by TPTDER is shown in Fig. 3(b). In aqueous solution, generally the particle electrodes, i.e., SMSP, have considerable electrochemical activity in addition to strong adsorption to MB dye molecules [4]. In the present research work, the SMSP was utilized as particle electrodes. Hence, it was expected that the TPTDER used in this present research could remove MB dye by both adsorption and electrochemical oxidation. The operating conditions for the TPTDER are: initial MB dye concentration of 100 mg/L, solution pH of 8.0, particle electrodes of 15 g, contact time of 10 min and wastewater volume of 500 mL. From Fig. 3(b), the removal of MB dye from the aqueous solution increased with the increase in applied voltage, and maximum removal of 98.92% was observed at a cell voltage of 12 V; after that the removal maintained constant. This may be due to the reduction in the concentration of MB dye molecules present in the wastewater. Less amount of precipitate is formed at the end of the reaction process. As based on the results, the removal of MB dye from the aqueous solution is mainly due to the adsorption process, and also there is a slight influence of electro-chemical oxidation.

3. Effect of Initial MB Dye Concentration

Fig. 4(a) shows the effect of initial MB dye concentration on the removal of MB dye from the aqueous solution by EC process. The operating conditions for the EC process are: initial MB dye concentration of 100-1,000 mg/L, cell voltage of 12 V, solution pH of 8.0, contact time of 60 min and wastewater volume of 500 mL. From Fig. 4(a), the percentage removal of MB dye increased from 25.54% to 48.88% with the increase in initial MB dye concentration from 100 mg/L to 1,000 mg/L, respectively. This may be because a large number of MB dye molecules may get easily precipitated at a higher MB dye concentration than the lower MB dye concentration at a fixed cell voltage. The effect of initial MB dye concentration on the removal of MB dye from the aqueous solution by adsorption process is shown in Fig. 4(b). The operating conditions for the adsorption process are: initial MB dye concentration of 100-1,000 mg/L, SMSP dose of 15 g, solution pH of 8.0, contact time of 30 min and wastewater volume of 500 mL. From Fig. 4(b), the percentage removal of MB dye slightly decreased with the increase in initial MB dye concentration. This may be because a fixed amount of materials was used in the present adsorption process [4]. The effect of initial MB dye concentration on the removal of MB dye from aqueous solution by TPTDER is shown in Fig. 4(c). The operating conditions for the TPTDER are: initial MB dye concentration of 100-1,000 mg/L, solution pH of 8.0, particle electrodes of 15 g, contact

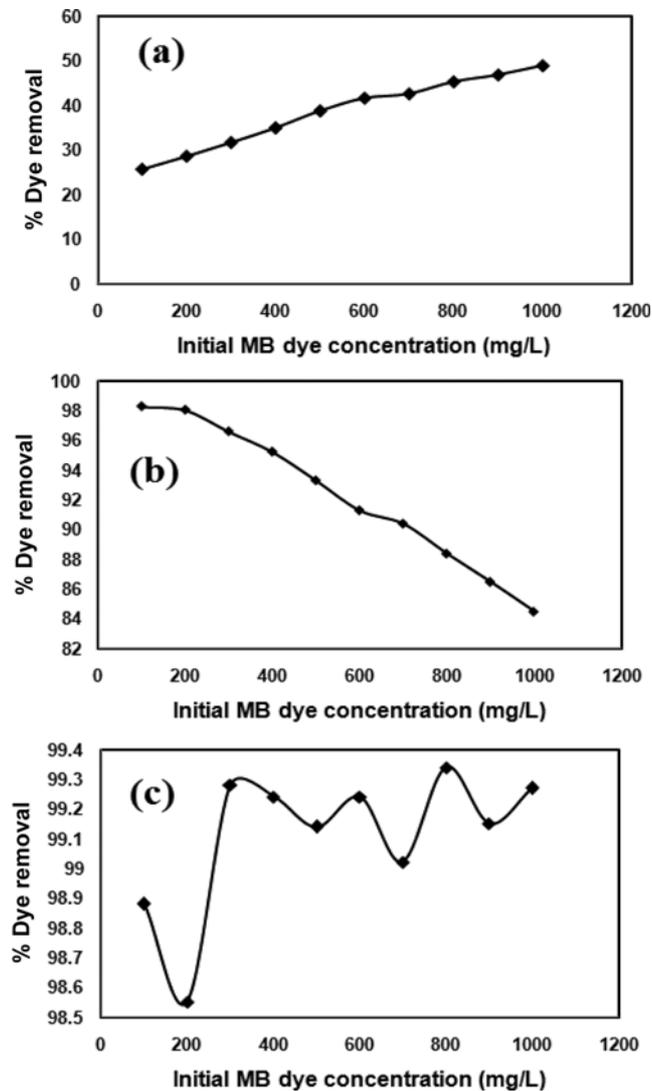


Fig. 4. Effect of initial MB dye concentration on MB dye removal (a) Electrolytic cell, (b) Adsorption and (c) TPTDER.

time of 10 min, applied cell voltage of 12 V and wastewater volume of 500 mL. From Fig. 4(c), the removal of MB dye was found to be the highest value of 99.0% (approx.) for all the MB dye concentrations studied. This indicates that the TPTDER is an excellent reactor to remove the MB dye molecules from the aqueous solution, and also the mechanism of the removal of MB dye from the aqueous solution was mainly due to adsorption process and slightly due to electro-chemical oxidation process.

4. Effect of Contact Time

The effect of contact time on the removal of MB dye from the aqueous solution by EC, adsorption, TPTDER process is shown in Fig. 5(a), 5(b), and 5(c), respectively. The operating condition for the EC process are: initial MB dye concentration of 100-1,000 mg/L, cell voltage of 12 V, solution pH of 8.0, and wastewater volume of 500 mL. For the adsorption process: initial MB dye concentration of 100-1,000 mg/L, SMSP dose of 15 g, solution pH of 8.0, contact time of 30 min and wastewater volume of 500 mL. For the TPTDER process: initial MB dye concentration of 100-1,000 mg/L, solution pH of 8.0, particle electrodes of 15 g, applied cell voltage

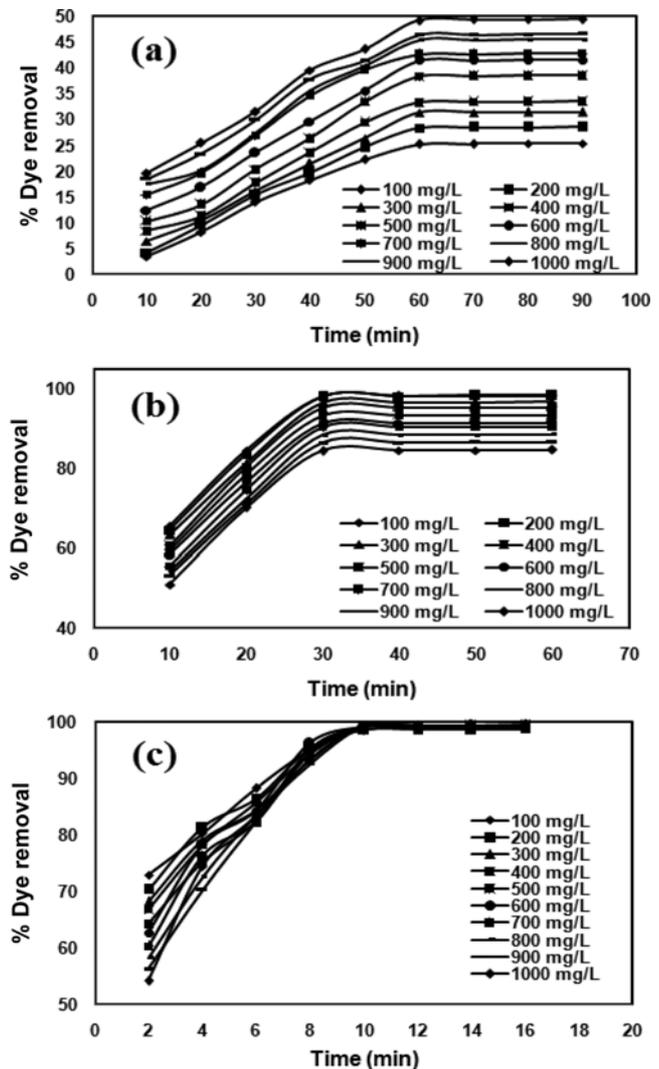


Fig. 5. Effect of contact time on MB dye removal (a) Electrolytic cell, (b) Adsorption and (c) TPTDER.

of 12 V and wastewater volume of 500 mL. From Fig. 5, the percentage removal of MB dye increased with the increase in contact time, and reached the maximum removal of MB dye at 60 min for EC process, 30 min for adsorption process, and 10 min for TPTDER process. The adequate residence time favors the removal of MB dye from the aqueous solution. This shows that the TPTDER is a superior technology when compared with the EC and adsorption process based on the performance of the each process.

5. Kinetics

The major phenomenon in the removal of MB dye by the TPTDER process is due to the adsorption process. The effect of contact time data obtained from the TPTDER process was fitted to the different models such as pseudo-first order, pseudo-second order and intraparticle diffusion models to check the kinetics for the removal of MB dye from the aqueous solution.

The pseudo-first order kinetic model is given as follows [34]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{8}$$

The pseudo-second order kinetic model is given follows [35]:

Table 1. Kinetic parameters for the removal of MB dye (TPTDER)

Kinetic models	Parameters	Concentration of MB dye solution (mg/L)									
		100	200	300	400	500	600	700	800	900	1000
Pseudo-first order equation	k_1 (min^{-1})	0.113	0.292	0.242	0.253	0.242	0.279	0.373	0.366	0.258	0.320
	q_e , cal (mg/g)	1.211	3.221	5.105	6.855	9.120	11.117	20.324	25.351	25.586	25.763
	R^2	0.874	0.885	0.883	0.885	0.879	0.880	0.897	0.901	0.889	0.889
Pseudo-second order equation	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	0.262	0.125	0.066	0.049	0.038	0.034	0.025	0.021	0.017	0.016
	q_e , cal (mg/g)	3.559	7.143	10.989	14.706	17.241	20.833	24.390	27.027	31.250	34.483
	h ($\text{mg g}^{-1} \text{min}^{-1}$)	3.322	6.369	7.937	10.526	11.364	14.706	15.152	15.385	16.129	18.868
	q_e , exp (mg/g)	3.56	6.632	10.115	13.452	16.876	20.112	23.245	26.657	30.382	33.418
	R^2	0.998	0.998	0.997	0.997	0.995	0.997	0.996	0.996	0.995	0.996
Intraparticle diffusion model	k_p ($\text{mg/g} \cdot \text{min}^{1/2}$)	0.358	0.752	1.272	1.746	2.409	2.854	3.581	4.409	5.221	5.742
	C	2.015	3.891	5.356	6.996	7.928	9.733	10.37	10.75	11.15	12.75
	R^2	0.900	0.886	0.912	0.898	0.891	0.868	0.883	0.898	0.892	0.867

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (9)$$

where q_e is the mg of MB dye adsorbed per g of SMSP at equilibrium (mg/g), q_t is the mg of MB dye adsorbed per g of SMSP at time t (mg/g), k_1 is the pseudo-first order rate constant (min^{-1}), t is the time (min), k_2 is the pseudo-second order rate constant ($\text{g/mg} \cdot \text{min}$) and $k_2 q_e^2 = h$, is the initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$). The kinetic parameters and other related values were calculated from the slope and intercept of the plot of the Fig. 5(a) and (b) and these values are listed in Table 1. A linear relationship with the high coefficient of determination (R^2) values between t/q_t and t was obtained, which indicates the applicability of the pseudo-second order kinetic model to better describe the adsorption process than the pseudo-first order kinetic model. Also, the calculated q_e values for the pseudo-second order kinetic model are very near to the experimental q_e values. This again confirms that the adsorption process followed a pseudo-second-order kinetic model.

The intraparticle diffusion model is given as follows [36]:

$$q_t = k_p t^{1/2} + C \quad (10)$$

where q_t is the mg of MB dye adsorbed per g of SMSP at time t (mg/g), k_p is the intraparticle diffusion rate constant ($\text{mg/g min}^{0.5}$), t is the time (min) and C is the intercept. It was observed that two straight lines with the different slopes can be found in the linear plot of q_t vs $t^{1/2}$, which indicates that the adsorption process was obviously divided into two steps. The first linear portion is a very fast stage due to the boundary layer effect, and the second linear portion is the slowest stage due to the intraparticle diffusion step. The results showed the intraparticle diffusion was not the rate-determining step because the linear line is not passing through the origin.

6. Recyclability

The recyclability of the particle electrodes was tested by taking the same amount of spent particle electrodes in a batch reactor, without any prior treatment. The operating conditions for checking the recyclability of the particle electrodes in a TPTDER process are: initial MB dye concentration of 100 mg/L, solution pH of 8.0, spent particle electrodes of 15 g, applied cell voltage of 12 V and wastewater volume of 500 mL. The same spent particle electrodes without any prior treatment were utilized nearly more than 10 cycles in the TPTDER process. The efficiency of the treatment maintains maxi-

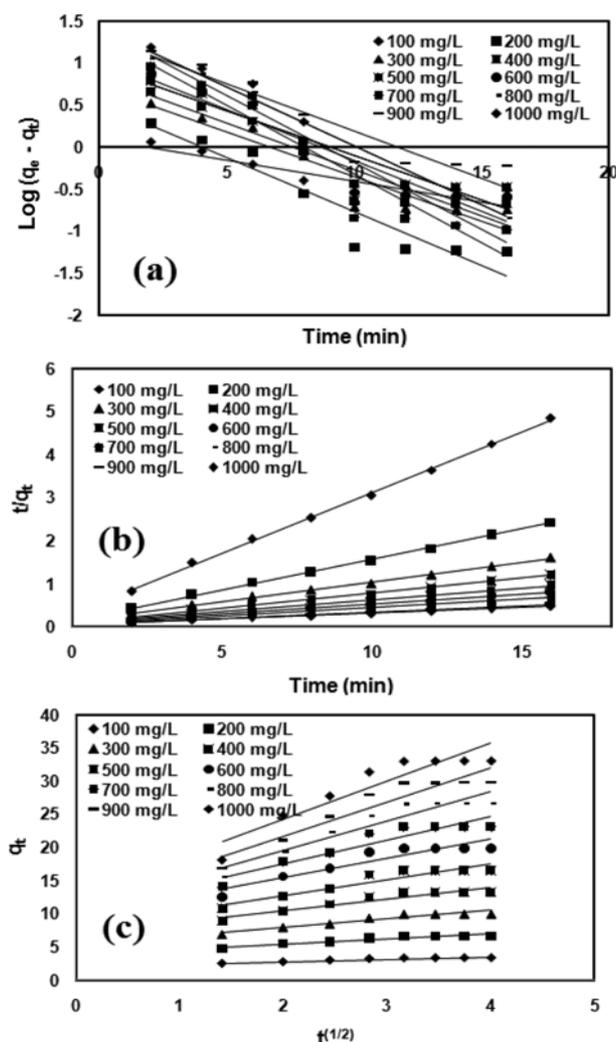


Fig. 6. Kinetics for the removal of MB dye in TPTDER (a) Pseudo-first order kinetic model, (b) Pseudo-second order kinetic model and (c) Intraparticle diffusion model.

imum removal of about 99% after the 10th cycle, but after that there is a slight decrease in the removal efficiency. This shows that the auto-regeneration of the spent particle electrodes may be possible

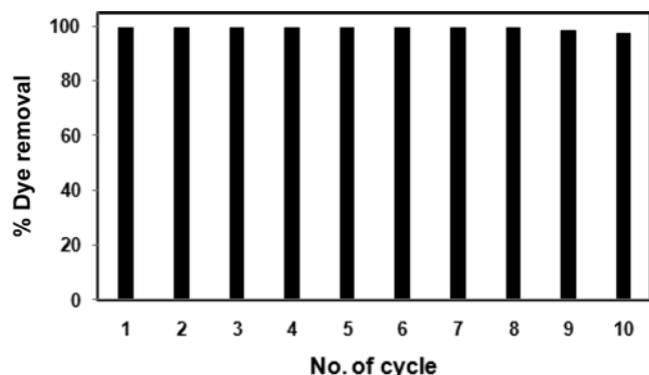


Fig. 7. Recyclability.

during the process. And also, much less amount of precipitate is formed during the process in the TPTDER. So, this reactor can be effectively utilized for the treatment of MB dye containing wastewater.

CONCLUSIONS

A novel approach to designing a new three-phase three-dimensional electrode reactor (TPTDER) for the removal of methylene blue (MB) dye from aqueous solution was proposed. It was confirmed that the MB dye can be effectively removed from the aqueous solution with the TPTDER using surface modified *Strychnos potatorum* seeds (SMSP) as particle electrode and compressed air as a gas source. The performance of the TPTDER is favorably affected by the initial solution pH, cell voltage, initial MB dye concentration and contact time. It was also explained that the removal of MB dye is much higher than that of electrolytic cell and adsorption process. The removal of MB dye from the aqueous solution may be due to the combination of many processes such as adsorption, electrochemical adsorption, direct electrochemical oxidation, indirect electrochemical oxidation, air-stripping and etc. But, the major phenomenon in the removal of MB dye from aqueous solution by TPTDER was due to the combined effect of electrochemical oxidation and adsorption. The recyclability of the particle electrodes was tested, and the results showed that the removal of MB dye from aqueous solution was consistent and there was not any loss in the particle electrodes, from the aspect of quality and quantity. Without any regeneration of the spent particle electrodes by the chemical agents, the same spent particle electrodes were utilized more than 10 times but their property was still the same. This may be due to the continuous supply of air in the TPTDER, which may act as an auto-regenerating agent. The kinetic studies showed that the removal of MB dye from aqueous solution in TPTDER could be better explained by the pseudo-second order kinetic model. The removal mechanism based on the adsorption process, i.e., the transport of MB dye molecules from the bulk solution to the particle electrode surface was checked with the intraparticle diffusion model. The results showed that the external and internal diffusion controls the removal of MB dye from the aqueous solution, the particle electrode surface. The above results confirmed that the removal of MB dye from aqueous solution by using TPTDER was effective and this reactor can be utilized for treatment of the industrial wastewater.

ACKNOWLEDGEMENTS

The authors are grateful for the financial support from the SSN Trust, Chennai.

REFERENCES

1. P. SenthilKumar, N. Umairambika and R. Gayathri, *Environ. Eng. Manage. J.*, **9**, 1031 (2010).
2. P. S. Kumar, R. V. Abhinaya, K. G. Lashmi, V. Arthi, R. Pavithra, V. Sathyaselvabala, S. D. Kirupha and S. Sivanesan, *Colloid J.*, **73**, 651 (2011).
3. P. S. Kumar, S. Ramalingam and K. Sathishkumar, *Korean J. Chem. Eng.*, **28**, 149 (2011).
4. C. Senthamarai, P. S. Kumar, M. Priyadarshini, P. Vijayalakshmi, V. V. Kumar, P. Baskaralingam, K. V. Thiruvankadaravi and S. Sivanesan, *Environ. Prog. Sustain. Energy*, DOI:10.1002/ep (2012).
5. P. S. Kumar, M. Palaniyappan, M. Priyadarshini, A. M. Vignesh, A. Thanjiappan, P. S. A. Fernando, R. T. Ahmed and R. Srinath, *Environ. Prog. Sustain. Energy*, DOI:10.1002/ep (2013).
6. P. S. Kumar, R. Sivarajanee, U. Vinothini, M. Raghavi, K. Rajasekar and K. Ramakrishnan, *Desalin. Water Treat.*, DOI: 10.1080/19443994.2013.792016 (2013).
7. M. Ertas, B. Acemioglu, M. H. Alma and M. Usta, *J. Hazard. Mater.*, **183**, 421 (2010).
8. L. Xu, H. Zhao, S. Shi, G. Zhang and J. Ni, *Dyes Pigment.*, **77**, 158 (2008).
9. M. F. Coughlin, B. K. Kinkle and P. L. Bishop, *Chemosphere*, **46**, 11 (2002).
10. T. X. Wu, T. Lin, J. C. Zhao, H. Hidaka and N. Serpone, *Environ. Sci. Technol.*, **33**, 1379 (1999).
11. S. M. Ghoreishi and R. Haghighi, *Chem. Eng. J.*, **95**, 163 (2003).
12. H. Y. Shu, C. R. Huang and M. C. Chang, *Chemosphere*, **29**, 2597 (1994).
13. Y. Xiong, C. He, T. An, X. H. Zhu and H. T. Karlsson, *Water Air Soil Pollut.*, **144**, 67 (2003).
14. W. Chu and C. W. Ma, *Water Res.*, **34**, 3153 (2000).
15. L. C. Chiang, J. E. Change and S. C. Tseng, *Water Sci. Technol.*, **36**, 123 (1997).
16. E. Fockedy and A. V. Lierde, *Water Res.*, **36**, 4169 (2002).
17. C. Brown, D. Pletcher, F. C. Walsh, J. K. Hammond and D. Robinson, *J. Appl. Electrochem.*, **24**, 95 (1994).
18. K. Rajeshwar, J. G. Ibanez and G. M. Swain, *J. Appl. Electrochem.*, **24**, 1077 (1994).
19. P. Tissot and M. Fragniere, *J. Appl. Electrochem.*, **24**, 509 (1994).
20. J. O. Bockris and J. Kim, *J. Appl. Electrochem.*, **27**, 890 (1997).
21. F. Pasquini and P. Tissot, *J. Appl. Electrochem.*, **26**, 211 (1996).
22. L. L. Scott, J. Winnick, P. A. Kohl and L. A. Bottomley, *J. Electrochem. Res.*, **145**, 4062 (1998).
23. G. R. Dieckmann and S. H. Langer, *J. Appl. Electrochem.*, **27**, 1 (1997).
24. Y. Xiong and H. T. Karlsson, *Adv. Environ. Res.*, **7**, 139 (2002).
25. E. A. El-Ghaoui, R. E. W. Jansson and C. Moreland, *J. Appl. Electrochem.*, **12**, 69 (1982).
26. Y. Xiong, C. He, T. An, H. T. Karlsson and X. H. Zhu, *Chemosphere*, **50**, 131 (2003).
27. A. M. Polcaro, S. Palmas, F. Renoldi and M. Mascia, *Electrochim.*

- Acta*, **46**, 389 (2000).
28. C. L. K. Tennakoon, R. C. Bharadwaj and J. O. Bockris, *J. Appl. Electrochem.*, **26**, 18 (1996).
29. T. C. An, X. H. Zhu and Y. Xiong, *Chemosphere*, **46**, 897 (2002).
30. B. Boye, M. M. Dieng and E. Brillas, *Environ. Sci. Technol.*, **36**, 3030 (2002).
31. M. A. Oturan, J. Peirotten, P. Chartrin and A. J. Acher, *Environ. Sci. Technol.*, **34**, 3474 (2000).
32. E. Neyens and J. Baeyens, *J. Hazard. Mater.*, **98**, 33 (2003).
33. E. Brillas, B. Boye, I. Sires, J. A. Garrido, R. M. Rodriguez, C. Arias, P. L. Cabot and Ch. Comninellis, *Electrochim. Acta*, **49**, 4487 (2004).
34. S. Lagergren, *Kungliga Svenska Vetensk Handl.*, **24**, 1 (1898).
35. Y. S. Ho and G. McKay, *Proc. Biochem.*, **34**, 451 (1999).
36. W. J. Weber and J. C. Morris, *J. Sanit. Eng. Div. Am. Soc. Civ. Eng.*, **89**, 31 (1963).