

Decolorization of anionic and cationic dyes by electro-adsorption process using activated carbon electrodes

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The performance of the Coconut shell (CS) and Bael shell (BS) activated carbon electrodes on removal of Methylene blue (MB) and Eosin-Y (EY) dyes have been carried out by electro-adsorption process. Modification of electrodes is done to enhance the decolourization performances. The colour removal capability of the electrodes are evaluated by varying the process parameters such as time (15-150 min), potential (5- 45 V) and initial dye concentration as (25-200 mg/L) in batch mode. The adsorption isotherm is determined by Langmuir, Freundlich and Jovanic-Isotherms models. The kinetic data are evaluated by using Pseudo-first and Pseudo-second order model and the rate of diffusion is determined by Intra-particle diffusion model. The electrochemical studies are carried out by cyclic voltammetry and Tafel plots. The experimental results depict that the adsorption isotherm follow the Langmuir isotherm model with the correlation co-efficient, $R^2 = 0.99$ for CS activated carbon electrode system, whereas the BS activated carbon electrode system strongly adhere to Freundlich Isotherm models. In addition, the rate kinetics follow Pseudo-first order kinetic model with $R^2 = 0.99$ for all the studies. The surface changes, elemental interaction, porosity, functional groups involved in electro-adsorption process and thermal stability are analysed for raw and modified form of electrodes using SEM, EDS, BET, FTIR and TGA respectively.

Keywords: Activated carbon, Methylene blue, Eosin-Y, Electrode, Electro-adsorption

A wide variety of organic pollutant (dyes) are released from different sources like textile industries, dye and dye intermediates, paper and pulp industries, pharmaceutical industries, tannery, and bleaching industries. Generally, these dyes are synthetic and toxic in nature with suspected carcinogenic and genotoxic compounds. The dye effluent which discharges from the industry to the water bodies like pond, river, lake and sea affects the aquatic species and also generates water scarcity in the environment^{1,2}. The whole dye consumption in the textile industry worldwide is more than 10,000 tonnes/year and approximately 100 tonnes/year of dyes are discharged into water streams. It is mainly used for dyeing the polyester and to some extent on nylon, cellulose, cellulose acetate, and acrylic type fibers⁷. It is generally recognized that newer methods could be very attractive for solving this problem. There are many desalination technologies which can remove ions from salty water. Conventional desalination technologies are thermal distillation, reverse osmosis, ion exchange, electric dialysis etc. But, the conventional methods having issues like secondary pollutants, complex pre-treatment,

maintenance, high temperature and high energy-consumption³⁻⁵. Recently electrochemical methods have been used to decolorize various types of dye solution.

The major mechanism involved in electro-adsorption process is, when an electrical potential is applied to the electrodes, charged ions present in the solution are forced to move towards the oppositely charged electrodes by the electrostatic interactions allowing the occurrence of charge separation on across the charge at interface⁶. Among the variety of dyes used, Eosin is one of the most widely used dye for acrylic, wool, nylon and silk because of its favorable characteristics of bright color, high solubility in water and low-energy consumption^{8,9}. This cationic dye decomposes into carcinogenic aromatic amines in the absence of oxygen. The discharge of effluents bearing the eosin-Y dye into water bodies can cause harmful effects for human beings such as allergic dermatitis, skin irritation, mutations and even cancer. Therefore, strict permissible standards are being followed to control the release of colored wastewater into the environment^{10,11}.

Hence, there is an urgent need for development of effective methods for the removal of dyes. Different physicochemical methods such as coagulation, ozonation, chemical oxidation, solvent extraction, ion exchange, photo-catalytic degradation, and adsorption have been tried by many researchers for the treatment of dye contaminated water^{7,12}. Besides the aforementioned methods, electro-adsorption is an effective and eco-friendly process due to its compact design, easy operation and its high efficacy to remove a wide range of organic and inorganic compounds¹³. Activated carbon is considered to be an effective adsorbent for removal of dyes present in aqueous medium. Several literatures confirmed that, the activated carbon is low cost, highly porous and more attractive bio-adsorbent.

In this present study, the efficiency of the Coconut shell (CS) and Bael shell (BS) activated carbon electrodes and modified form of these electrodes on removal of methylene blue and eosin-Y dyes by electro-adsorption process were discussed (Table 1). The removal capability of the electrodes were evaluated by varying the process parameters such as time, electrical potential and initial dye concentration in batch mode^{14,15}. The adsorption isotherm data was determined by Langmuir, Freundlich and Jovanic-Isotherms models. The kinetic data were evaluated by using Pseudo-first and Pseudo-second order model and the rate of diffusion was determined by Intra-particle diffusion model. The electrochemical studies were carried out by cyclic voltammetry and Tafel plots. The physico chemical properties of activated carbon before activation, after activation and after electro adsorption was analysed using SEM, EDAX, BET Analysis, FTIR and TGA respectively.

Experimental Section

Preparation of activated carbon and activated carbon electrode

A new activated carbon electrode and carbon composite electrodes was prepared from a non-usable Bael fruit shell (*Aegle marmelos*) and coconut shell. The

Table 1 — Comparison on dye removal efficiency of different adsorbent prepared with phosphoric acidactivation

Reacting Agent	Adsorbent used	Adsorption Efficiency (%)	References
H ₃ PO ₄	Bamboo stem	92.70	[34]
	Persea americana	92.00	[35]
	Pomegranate peel	85.67	[36]
	Peach stones	70.89	[37]
	Grape seeds	65.34	[18]
	Bael shell (BS)	96.57	Present study
	Coconut shell (CS)	99.96	Present study

preparation procedure was extracted from the previous studies¹⁶⁻²².

Preparation of stock solution

The model dyes chosen for the present investigation are Eosin-Y (anionic dye, chemical formula C₂₀H₆Br₄Na₂O₅, MW=691.85 g/mol) and Methylene blue (cationic dye, chemical formula C₁₆H₁₈ClN₃S, MW=319.87 g/mol) which are most widely used dyes in textile industries. The maximum absorbance wavelength of eosin-Y and methylene blue were found to be 516 nm and 664 nm respectively. 1000 mg/L stock solution was prepared by dissolving 1g of dye in distilled water and then made up to 1000 mL with distilled water. A 100 mg/L of working dye standards was prepared from the stock solution by dilution method and thereafter dye solutions in the concentration range of 1 mg/L-10 mg/L were used for constructing calibration curves^{23,24}.

Methodology

Electrochemical measurements

Electro-adsorption technology is a current-potential induced adsorption phenomenon. It takes place in the surface of the charged electrodes. The cathodic and anodic potential for AC electrodes was evaluated by cyclic voltammetry (CV) techniques using an electrochemical workstation (Model CHI760E-CH Instruments Inc., USA). The fabricated activated carbon electrode (ACE) was used as a working electrode; platinum electrode and calomel electrode were used as the counter electrode and reference electrode respectively. CV studies were carried out at in the scanning rate range between 0.01 and 0.1V/s at a potential range/window of -1.8 to 0.4 V in atmospheric temperature. The dye concentration was varied in the range of 2-10 mg/L and 10-50 mg/L.

The electro-adsorption experiments were carried out in batch mode using an Electrochemical cell (ECC) with two electrodes, as shown in Fig. 1. The working

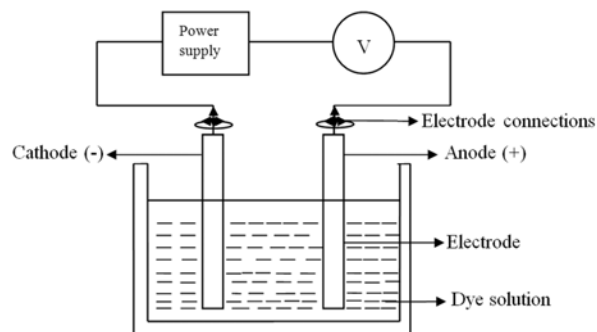


Fig. 1 — Experimental setup for Electro-adsorption

electrodes used in these experiments were Bael shell ACE, Coconut shell ACE and Modified (ACE & CCE) and copper was used as counter electrode. The two (working and counter) electrodes were connected to the power supply with a voltage varying meter/ a potentiostat [Model RPS 3002, Bee Technologies]. 200 mL of 100 mg/L synthetic dye solution was taken in ECC and the process parameters such as initial dye concentration, contact time and applied voltage were maintained in the required condition.

The percentage dye removals (% R) were calculated using the Eq.1.

$$\%R = \frac{c_i - c_o}{c_i} \times 100 \quad \dots (1)$$

where, C_i and C_o are dye concentrations before and after electro-adsorption.

Results and Discussions

Physicochemical characterization

The morphology of BS and CS activated carbon electrodes were characterized using scanning electron microscopy (SEM). Figure 2 depicted the SEM micrographs of BS and CS activated carbon electrode before activation, after activation and after electro adsorption. The electron micrograph confirmed that the surface of the activated carbon electrode was

smooth with long ridges, exhibited homogeneous surface texture and large surface area for MB and EY dye adsorption²⁵. Figure 3 shows the energy dispersive X-ray spectrogram of BS activated carbon and CS activated carbon before and after electro-adsorption of Eosin-Y dye. EDX spectra confirmed the presence of bromine after electro adsorption which is the dominating element in eosin Y dye.

Fourier transform infrared spectroscopy (FTIR) (Model-Agilent technologies- Cary 630) was used to identify the involvement of functional groups which was responsible for the interactions of MB and EY dyes. Figure 4(a) revealed the FTIR spectrogram for BS activated carbon. It shows that, the major peaks at corresponding wave numbers are found to be at 3910.12, 3454.06, 2933.61, 2863, 2362.56, 2300.23, 1623, 1364.56, 1056.28 and 940 cm^{-1} which specified the appearance of NH, C=C, OH, C-H, CO, and C-Cl or C-Br functional groups respectively. In the presence of EY, the shifts were noticed at 3912.42, 3468.24, 2943.644, 2841.64, 2366.15, 2301.11, 1632.41, 1371.89, 1091.62, and 959 cm^{-1} . The obtained result confirmed that, C=O from 1623 to 1632 cm^{-1} contributes the interaction of dye molecule²⁶. The shift observed in the other functional groups such as NH, C=C, OH, C-H, CO, and C-Cl or C-Br acknowledging the adsorption of EY dye ions adhesion on the surface of BS.

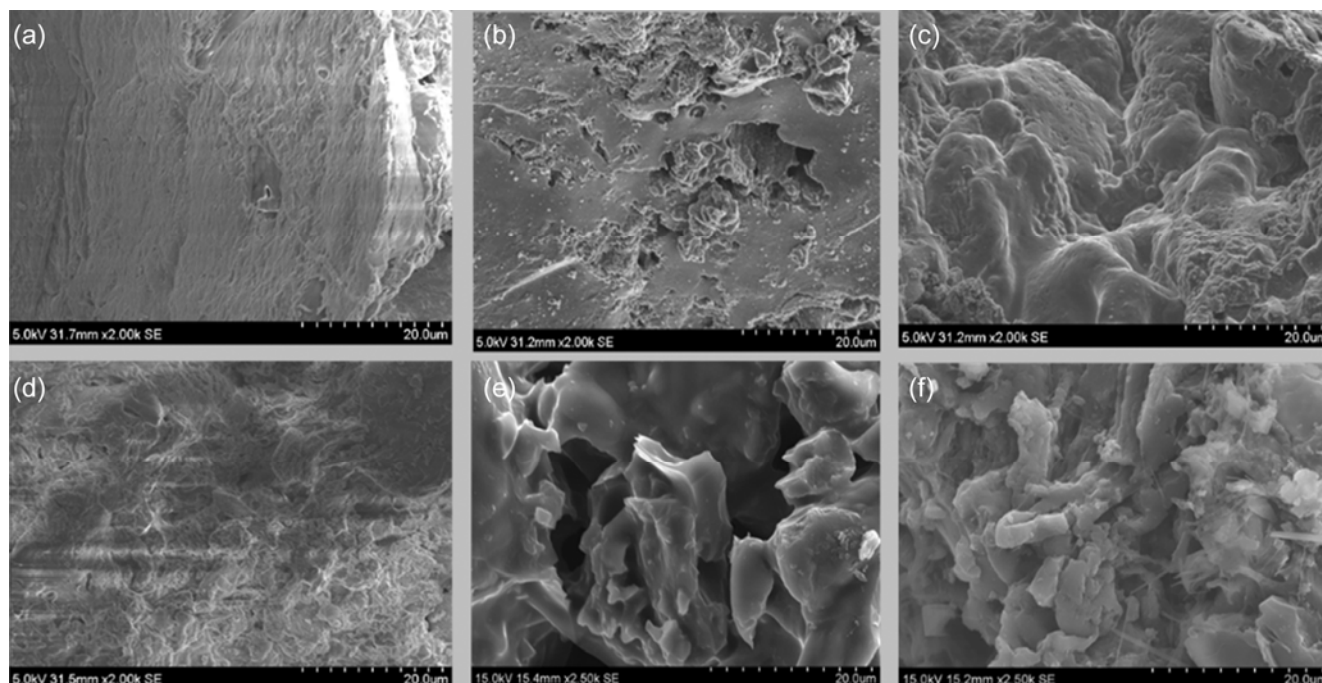


Fig. 2 — SEM morphology: (a) BS before activation (b) BS after activation (c) ACE-BS after electro-adsorption (d) CS before activation (e) CS after activation (f) ACE-CS after electro-adsorption

The FTIR spectra shown in Fig. 4(b) is for coconut shell activated carbon electrode before and after interacted with MB. In the absence of methylene blue the peaks were observed at corresponding wave

numbers of 3688.21, 3220, 2342.31, 2112.16, 2014.26, 1969.57, 1587.14, 1122.42, 1041.21, 945.19, 883.11 cm^{-1} which confirmed specified the appearance of N-H, O-H, C=C, -C≡C-, C-H, C-Cl and

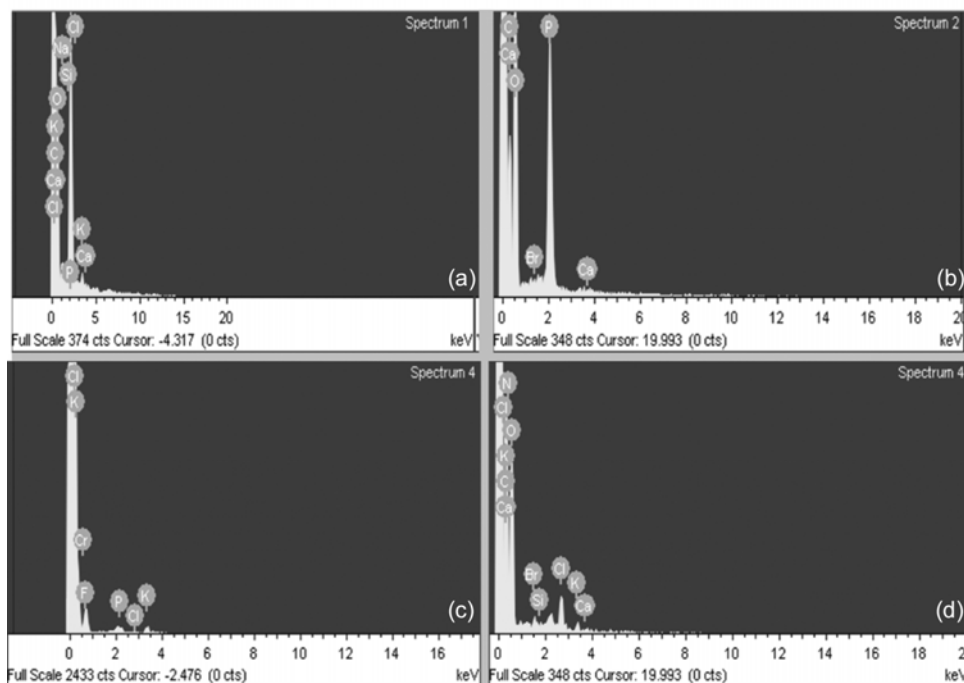


Fig. 3 — EDS Spectrogram (a) BS before dye electro-adsorption (b) BS after dye electro-adsorption (c) CS before dye electro-adsorption (d) CS after dye electro-adsorption

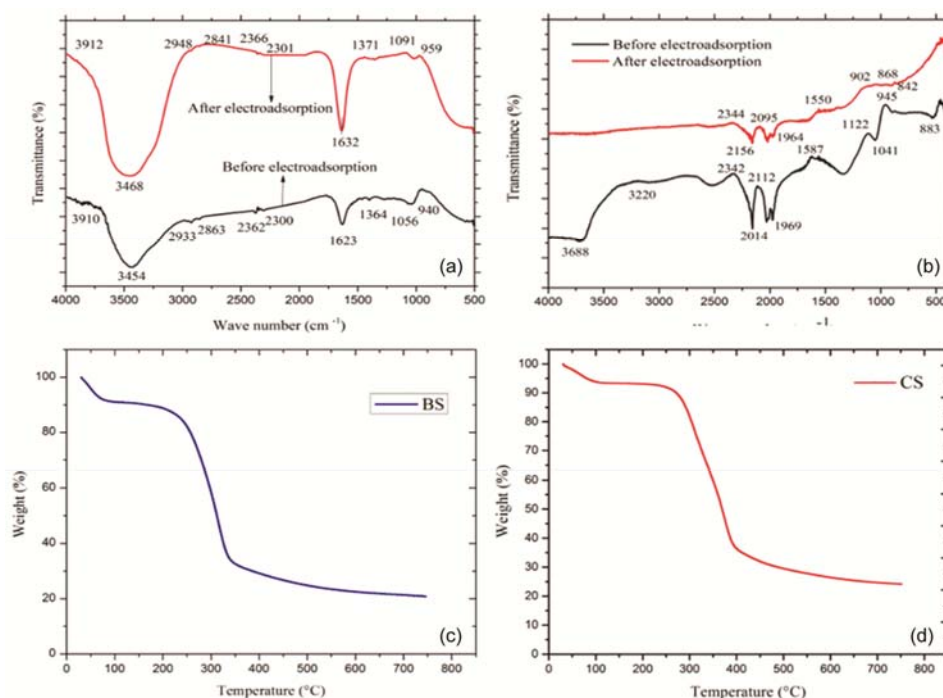


Fig. 4 — (a) FT-IR Spectra of before and after electro-adsorption of EY dye by BS (b) FT-IR Spectra of before and after electro-adsorption of MB dye by CS (c) Thermo Gravimetric Analysis curve of BS-ACE (d) Thermo Gravimetric Analysis curve of CS-ACE

CO groups respectively. After interacted with MB dye the peaks at 3688.21 and 3220 cm^{-1} were got disappeared and the major shift were observed at wave numbers of 2344.87, 2156.24, 2095.87, 1965.34, 1550, 902.64, 868.22, 842.78 cm^{-1} , which confirms that, the functional groups such as C=C, $\text{-C}\equiv\text{C-}$, C-H, C-Cl and CO are attributed for MB interaction on electrode surface²⁶.

Chemical and thermal activation of adsorbents play a main role in surface area and porosity development. The adsorption efficiency of BS and CS by H_3PO_4 activation was 96.57% and 99.96% respectively as shown in Table 1. The surface area and pore size was determined using Brunauer-Emmett-Teller surface analyzer (Micromeritics ASAP 2020 porosimeter). The surface area and pore volume of activated carbon prepared from CS and BS by H_3PO_4 activation were 788.52 m^2/gm , 0.562 cm^3/gm and 321.06 m^2/gm , 0.323 cm^3/gm , respectively, shown in Table 2, whereas the Bael fruit shell before activation was 87 m^2/g and 0.098 cm^3/g .

Thermo gravimetric analyses (TGA, Model-Hitachi STA 7200) were performed to evaluate the thermal stability of adsorbents (BS activated carbon and CS activated carbon). 10 mg of sample was taken in a silica crucible and subjected to pyrolysis at 750°C at a heating rate of 10°C/min in nitrogen atmosphere. Figure 4 (c-d) represents the two stages of thermal degradation of BS and CS. The obtained result shows that, the first stage of thermal degradation occurred at 95°C to 210°C for CS and in the case of BS it is around 50°C to 110°C. Comparatively, there is a weight loss of around 9% (CS) and 8% (BS) during the first thermal degradation of adsorbents. The second stage of the thermal degradation occurred at 380°C for CS and at 340°C for BS with a weight loss of 70% in CS and 63% in BS, which is six times higher than the weight loss obtained in the first stage. It is mainly due to weight loss was taken place due to

the vaporization of organic materials present in the CS and BS like cellulose, lignin, hemicelluloses²⁷. Finally, the TGA curve flattens with no change, when the sample was heated above 380°C and 340°C for CS and BS respectively. The TGA analysis confirms that the thermal stability of the CS is higher than BS.

Electrochemical characterization

The AC electrode prepared by activated carbon and PVDF as a binding material, is referred as activated carbon electrode (ACE) which had good mechanical strength in electro-adsorption process. Cyclic voltammetry of ACE was studied at different MB dye concentration ranging from 2-10 mg/L and 10-50 mg/L to evaluate the sensitivity of CPE at lower and higher concentration range. Potential and scan rate was varied from of -1.8 to 0.4 V and 0.01 to 0.1V/s respectively. It is observed that amount of cationic ions present in dyes are electro adsorbed onto the surface of the working electrode. From Fig. 5 clearly indicates that redox process are less in lower concentration like 2 to 6 mg/L (a-c). Current density peaks, further increases when the concentration increases from 8 to 50 mg/L (d-i) which indicates that redox process are more in high MB concentration. The slope of the log(current) versus the potential denote the Tafel constant for the cathodic reaction, from the constant we can calculate number of reaction involved for the reduction process. The Tafel plot Fig. 6 shows in positive potential range, so the Gibbs free energy value becomes negative it indicates that electrochemical reaction is spontaneous reaction.

Influences of process parameters

The percentage of dye removal by ACE and CCE were determined at different operating conditions and the effect of time, effect of voltage and effect of initial dye concentration were studied in detail. The parameters were optimized to obtain maximum removal of anionic and cationic dyes from synthetic dye solution.

Effect of time

The effect of time on percentage of dye removal by ACE and CCE was studied by varying the contact time from 15 to 150 min and the other parameters such as initial dye concentration and bias potential were fixed at constant around 100 mg L^{-1} and 5V respectively. From Fig. 7 (a) the percentage MB removal by BS-ACE was found to be increase from 4.43% to 42.39% when the contact time increased 15

Table 2 — Surface area of the BS and CS adsorbent by different activation agents

Activation agent	BS		CS	
	Surface area (m^2/g)	Pore volume (cm^3/g)	Surface area (m^2/g)	Pore volume (cm^3/g)
NaCl	107	0.216	138	0.236
HCl	128	0.218	208	0.278
NaOH	176	0.289	296	0.294
H_2SO_4	256	0.304	363	0.351
KOH	289	0.311	561	0.377
H_3PO_4	321	0.323	788	0.562

to 150 min. For CCE similar trend was observed with maximum percentage of removal about 97.33%. Figure 7(b) depicted that EY dye electro-adsorption on BS-ACE was increased from 5.72% to 39.32% of color removal and the maximum percentage of EY removed by CCE was around 95.44%. The obtained result confirmed that, the CCE achieved maximum removal of dyes compared to ACE for both EY and MB dyes. The inclusion of copper metallic strip on to activated carbon has increases the conductivity. Also, CS electrodes give more decolourization efficiency than BS due to its higher surface area.

From the Fig. 7(c), it was observed that the percentage on removal of EY removal was increased from 5.96% to 62.19% respectively for ACE. In the

case of CCE, percentage of EY removal increased from 23.13% to 99.96% respectively. From the Fig. 7(d) it was noticed that the maximum percentage of EY removal achieved by CCE was found to 99.20 %.

Effect of potential

Potential is an important parameter to evaluate the amount of dyes removed by electro- adsorption process. In this study, the applied voltage was varied in the range of 5 - 45 V and the initial dye concentration and contact time were fixed as 100 mg/L and 30 min, respectively. The effect of potential was investigated for BS-ACE and CCE on removal of MB and EY. Fig. 8(a) shows that, the percentage of decolourisation of MB dye by ACE was found to be

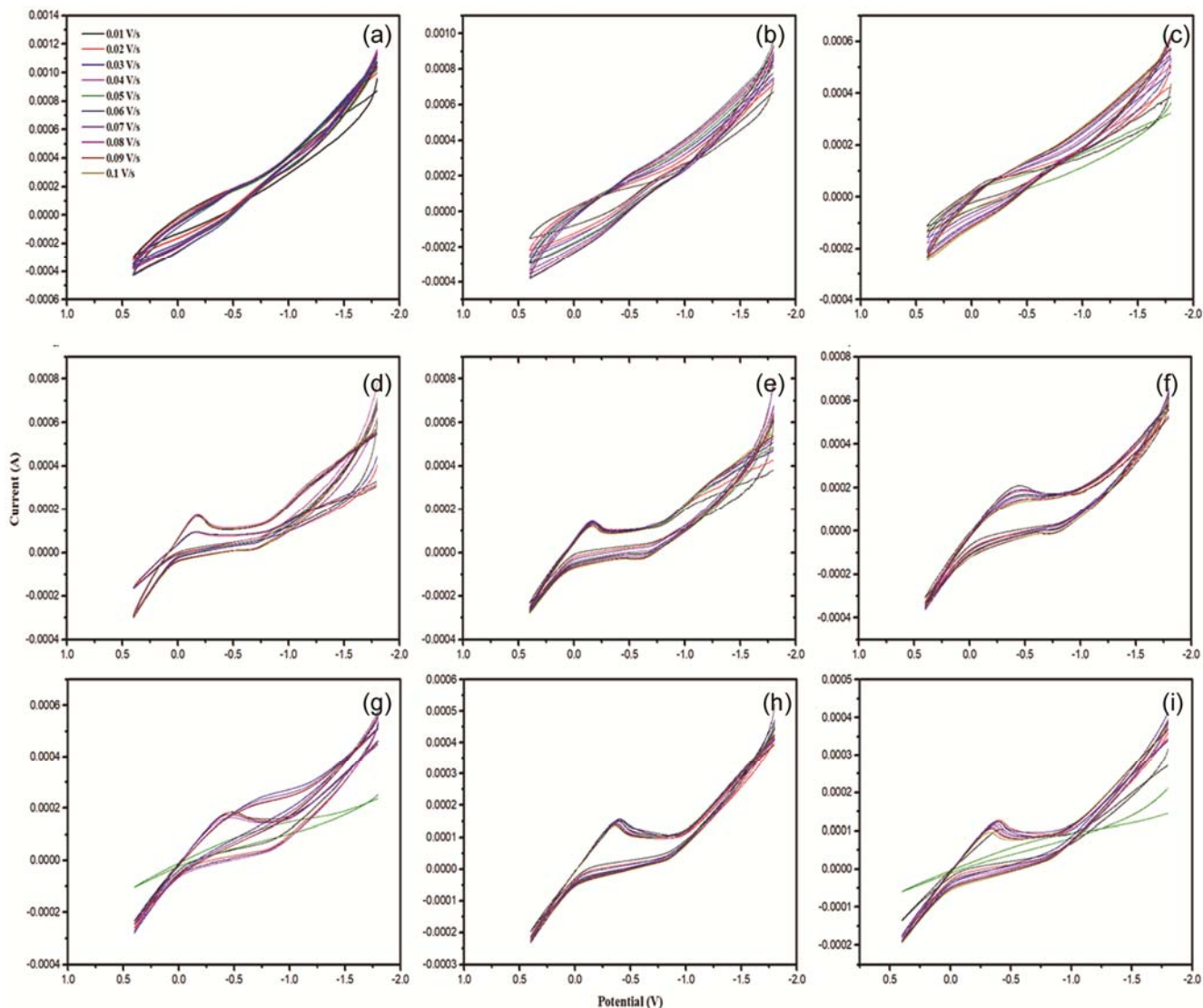


Fig. 5 — Cyclic voltammety at various scan rates (a) 2 mg/L (b) 4 mg/L (c) 6 mg/L (d) 8 mg/L (e) 10 mg/L (f) 20 mg/L (g) 30 mg/L (h) 40 mg/L (i) 50 mg/L

47.06% at 45 V and the maximum percentage of MB removal achieved by CCE was around 98.31%. Fig. 8(b) shows the result on electro-adsorption of EY dye on BS- ACE and CCE. The results confirmed that

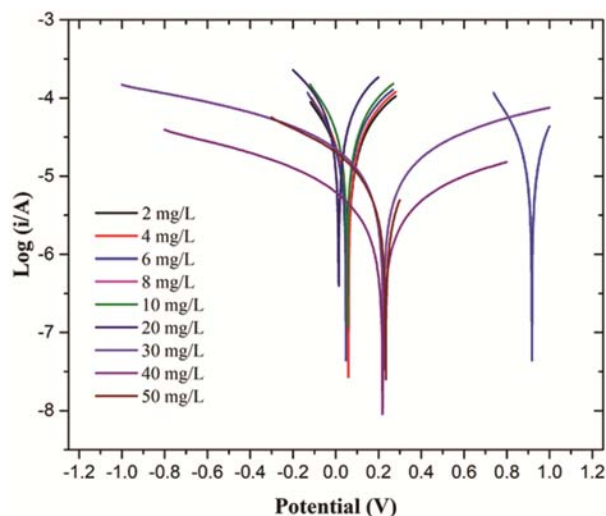


Fig. 6 — Tafel plot of various electrolyte concentration

the maximum removal of EY was achieved by CCE (96.43%) at 30V which was twofold higher than CS-ACE. The percentage of removal of EY remains same after 30V. As the potential increases from 5 to 45 V, the percentage colour removal increases from 6.82% to 64.12% respectively for MB dye electro-adsorption onto CS- ACE, like wise for CS - CCE the removal percentage increases from 21.83% to 99.83% . The maximum percentage of EY dye decolourization achieved by ACE and CCE were found to be 60.12% and 99.01% respectively as shown in Fig. 8(c-d).

Effect of initial dye concentration

The effect of initial dye concentration on (EY and MB) was investigated by varying the dye concentration between 25 to 200 mg/L at a fixed potential and contact time (5V and 30min respectively). From Fig. 9(a) it can be seen that in CS - ACE and CCE electro-adsorption performances decreases with the increase in initial dye concentration and obtained saturation after equilibrium time. The obtained result shows that the

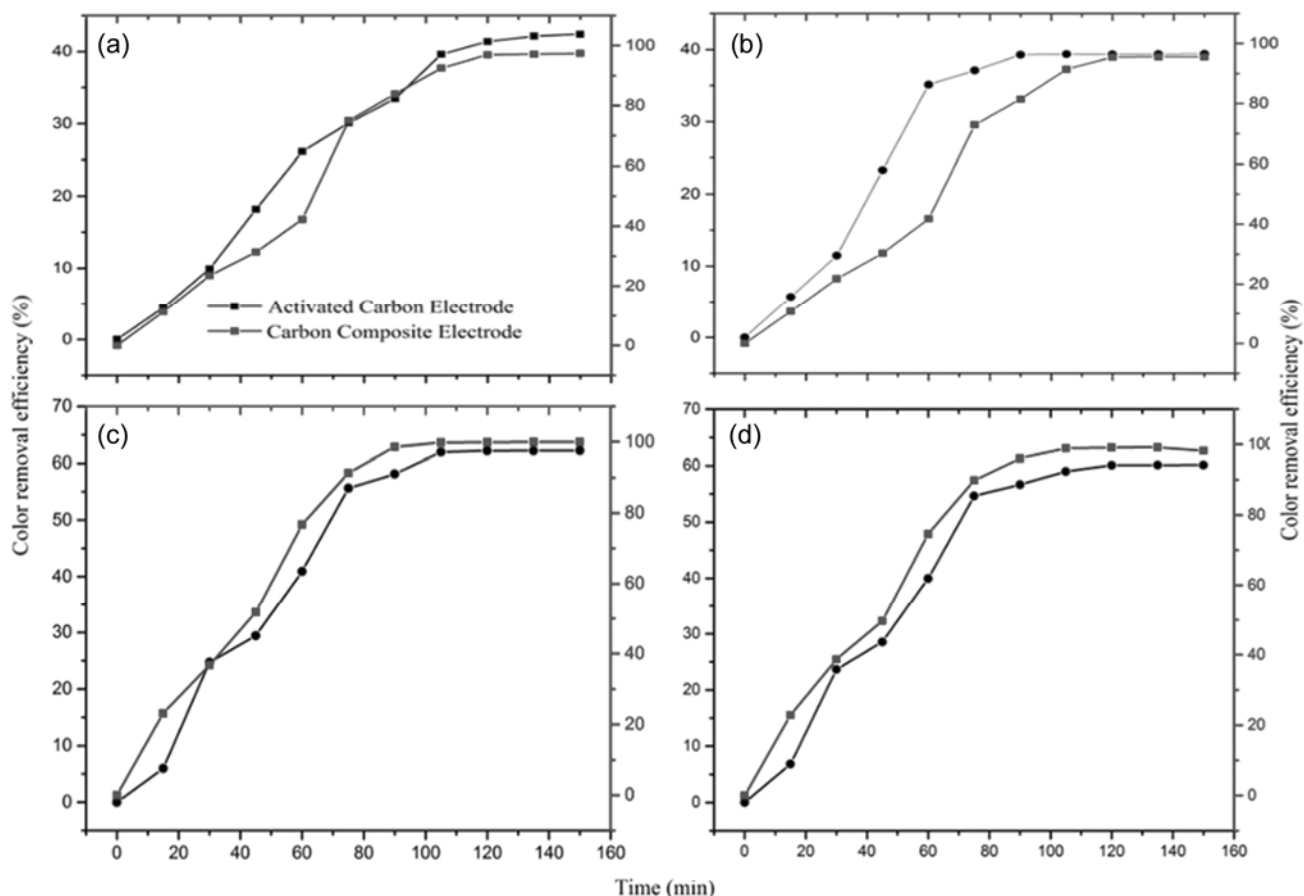


Fig. 7 — Theeffect of time on MB and EYremoval under optimum conditions (a) BS, (b) CS, (c - d) fabricated electrodes (dye concentration: 100 mg/L, bias potential: 5V)

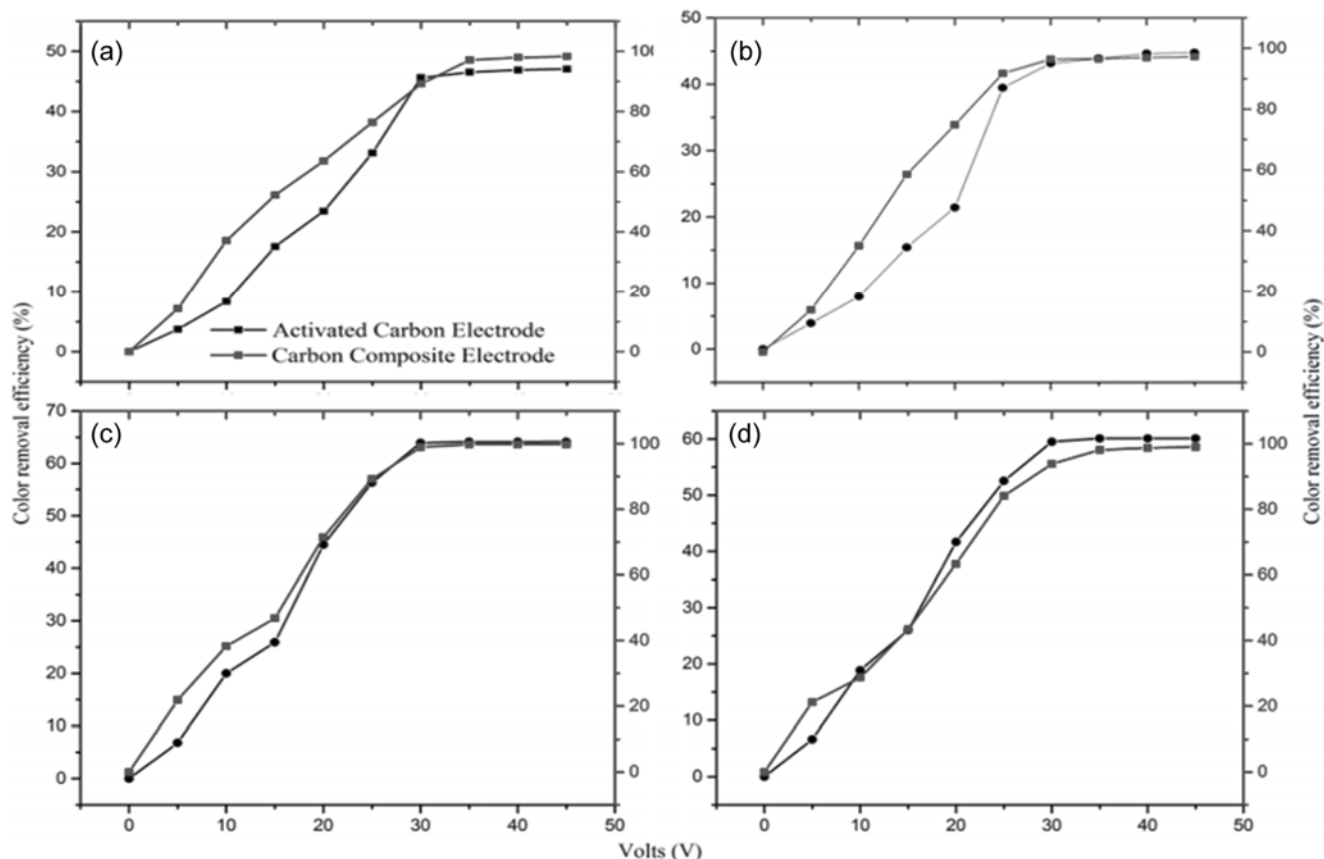


Fig. 8 — The effect of voltage on MB and EY removal under optimum conditions (a) BS , (b) CS, (c - d) fabricated electrodes (dye concentration: 100 mg/L, time: 30 min)

percentage EY removal decreases from 27.16% to 2.34% by ACE and 82.42% to 20.77% by CCE. Similarly, Fig. 9(b) shows EY dye electro-adsorption decreases from 29.92% to 1.56% for ACE and 82.42% to 20.77% for CCE. The removal of MB dye by electro-adsorption on BS -ACE and CCE was investigated and observed that the percentage of removal decreases from 49.43% to 10.16% (MB on to ACE) and 99.96% to 46.71% (MB on to CCE) with an increase in the initial dye concentration from 25 to 200 mg/L as shown in Fig. 9(c -d).

Adsorption isotherms

Electro-adsorption isotherms and kinetics are most essential study to estimate the electro-adsorption behavior and rate of adsorption of dyes on activated carbon electrodes surface. The electro-adsorption behavior had been evaluated by different isotherm such as Langmuir, Freundlich and Jovanovich adsorption isotherm and the kinetic models tested with kinetic models such as pseudo-first-order, pseudo-second-order and intra particle diffusion model²⁸.

Langmuir isotherm

Langmuir isotherm theory is mainly upon based on two assumptions (i) adsorbed molecules have no further interaction between the adsorbate (ii) the formation of saturated monolayer of solute molecules on the surface of the adsorbent. The linearized form of Langmuir adsorption isotherm equation is

$$\frac{c_e}{q_e} = \frac{1}{Q_o b_L} + \frac{c_e}{Q_o} \quad \dots (2)$$

The amount of dye adsorbed and Langmuir constants Q_o (mg/g) and b_L (L/mg) are calculated by plotting $\frac{c_e}{q_e}$ versus C_e . The results revealed that the

EY electro-adsorption on CS-ACE and CCE found to fit well Langmuir isotherm with correlation coefficients ($R^2=0.999$) which indicates that was homogeneous in nature²⁹. But, the EY electro-adsorption on BS-ACE and CCE are not well fitted for Langmuir model. The isotherm parameters and correlation coefficient are listed in Table 3.

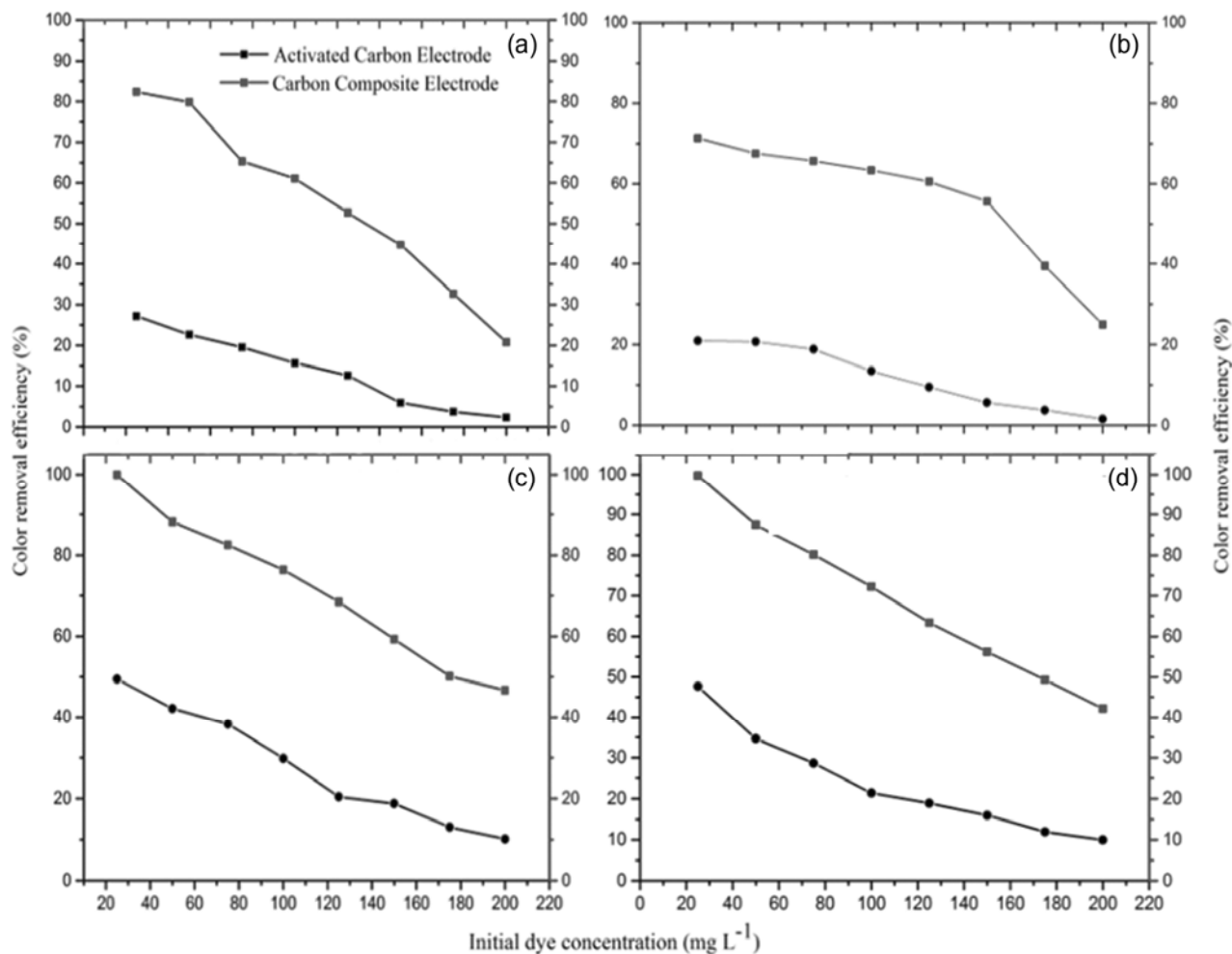


Fig. 9 — The effect of initial dye concentration on MB and EY removal under optimum conditions (a) BS, (b) CS, (c - d) fabricated electrodes (bias potential: 5 V, time: 30 min)

Freundlich isotherm

The Freundlich isotherm model equation describes intensity of adsorption and adsorption capacity with possible multilayer on a highly heterogeneous surface consisting of non-identical and energetically non-uniform sites. The linearized form of Freundlich adsorption isotherm equation is

$$\log q_e = \log k_F + \frac{1}{n_F} \log C_e \quad \dots (3)$$

The Freundlich constants $K_F(\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1})$ and n_F were calculated from the slope and intercept of the linear plot ($\log q_e$ versus $\log C_e$). From the obtained result, intensity of adsorption n_F value greater than one which confirms adsorption process is favorable. Also based on correlation coefficients ($R^2=0.923$) Freundlich isotherm found to fit well compared to

Table 3 — Isotherm model constant for EY adsorption on to BS and CS

Isotherm models	Parameters	BS	CS
Langmuir	$Q_o(\text{mg/g})$	47.61	52.63
	$b_L(\text{L/mg})$	0.023	0.442
	R^2	0.734	0.999
Freundlich	$K_F(\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1})$	1.976	16.59
	n_F	1.485	4.784
	R^2	0.923	0.944
Jovanovic	$q_{mj}(\text{mg/g})$	3.14×10^{-58}	2.22
	$K_j(\text{L/mg})$	-1.37×10^{59}	450
	R^2	0.891	0.929

other isotherms, which indicates that the EY electro-adsorption on (BS) ACE and CCE was heterogeneous and for (CS) ACE and CCE are not nearly fitted³⁰. The isotherm parameter values the linear form of Freundlich adsorption isotherm equation for EY electro-adsorption on BS- ACE and CCE are shown in Table 3.

Jovanovic isotherm

The jovanovic isotherm adsorption is similar to like Langmuir isotherm with the same approximation leads to the monolayer adsorption without any lateral interactions. The model considers the some few possibilities of mechanical connection between the adsorption and desorbing molecules. The linear form of jovanovic adsorption isotherm equation

$$\log q_e = q_{mj} - q_{mj} e^{k_j C_e} \quad \dots (4)$$

where q_{mj} (mg/g) and K_j (L/mg) are the adsorption capacity and Jovanovich isotherm constants respectively³¹. The model values were calculated from the plot of $\log q_e$ versus C_e and listed in the Table 3.

Kinetic studies

The electro-adsorption kinetics was simulated by Pseudo-first-order, Pseudo-second order and Intra-particle kinetics equation. From the observed result, it is found that Pseudo-first-order kinetics equation fit the experimental data better than Pseudo second-order kinetics equation.

Pseudo-first-order model

The pseudo-first-order rate equation of Lagergren as follows

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad \dots (5)$$

where q_e and q_t are the amounts of EY adsorbed (mg/g) at equilibrium time and at any time t , k_1 (min) is the Pseudo-first-order rate constant. The pseudo-first-order states that the rate of occupation of adsorption sites to be proportional to the number of

un-accommodated sites^{32,33}. The rate constant was determined by using Pseudo-first-order kinetic model by plotting the graph between $\log (q_e - q)$ versus t . The adsorption kinetics was fitted to the Lagergren law by nonlinear regression using the method of least squares. The rate constants were listed in Table 4. The obtained result states that the kinetic data well fitted with Pseudo-first-order model as shown in Fig. 10(a -b). The value of adsorption capacity indicates that the electro-adsorption of EY onto BS, CS was adhered Pseudo-first-order model.

Pseudo-second-order model

The Pseudo-second-order kinetic model can be shown as follows

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \dots (6)$$

where k_2 (g/mg/min) is the rate constant for Pseudo-second-order model

The value of rate constants for EY electro-adsorption on (CS, BS) ACE and CCE were calculated from the graph t/q_t vs t and the determined values are showed in Table 4.

Intra-particle diffusion

Intra-particle diffusion model insights the mechanisms and rate controlling steps that affect the electro-adsorption kinetics and represented using the following equation

$$q_t = k_{id} t^{1/2} + C \quad \dots (7)$$

where k_{id} is the intra-particle rate constant diffusion (mg/g/min^{1/2}) and C is the intercept. The graph was

Table 4 — Kinetic model rate constants for EY adsorption on to BS and CS

Kinetic model parameter	Initial eosin-Y dye concentration (mg/L) BS				Initial eosin-Y dye concentration (mg/L) CS			
	100	150	200	250	100	150	200	250
K_1 (min ⁻¹)	Pseudo-first- order				Pseudo-first- order			
	0.0299	0.0230	0.018	0.018	0.0184	0.0161	0.0161	0.018
R^2	0.969	0.909	0.850	0.846	0.879	0.904	0.963	0.914
K_2 (g/mg/min)	Pseudo -second-order				Pseudo -second-order			
	0.594	0.010	9.93 × 10 ⁻⁴	8.246 × 10 ⁻⁵	7.087 × 10 ⁻³	3.54 × 10 ⁻⁴	4.382 × 10 ⁻⁴	6.111 × 10 ⁻⁵
R^2	0.305	0.386	0.600	0.535	0.279	0.682	0.506	0.248
K_{id} (mg/g/min ^{1/2})	Intraparticle diffusion				Intraparticle diffusion			
	1.574	1.949	2.18	2.84	1.343	1.213	1.287	1.130
R^2	0.932	0.847	0.928	0.850	0.929	0.926	0.967	0.969

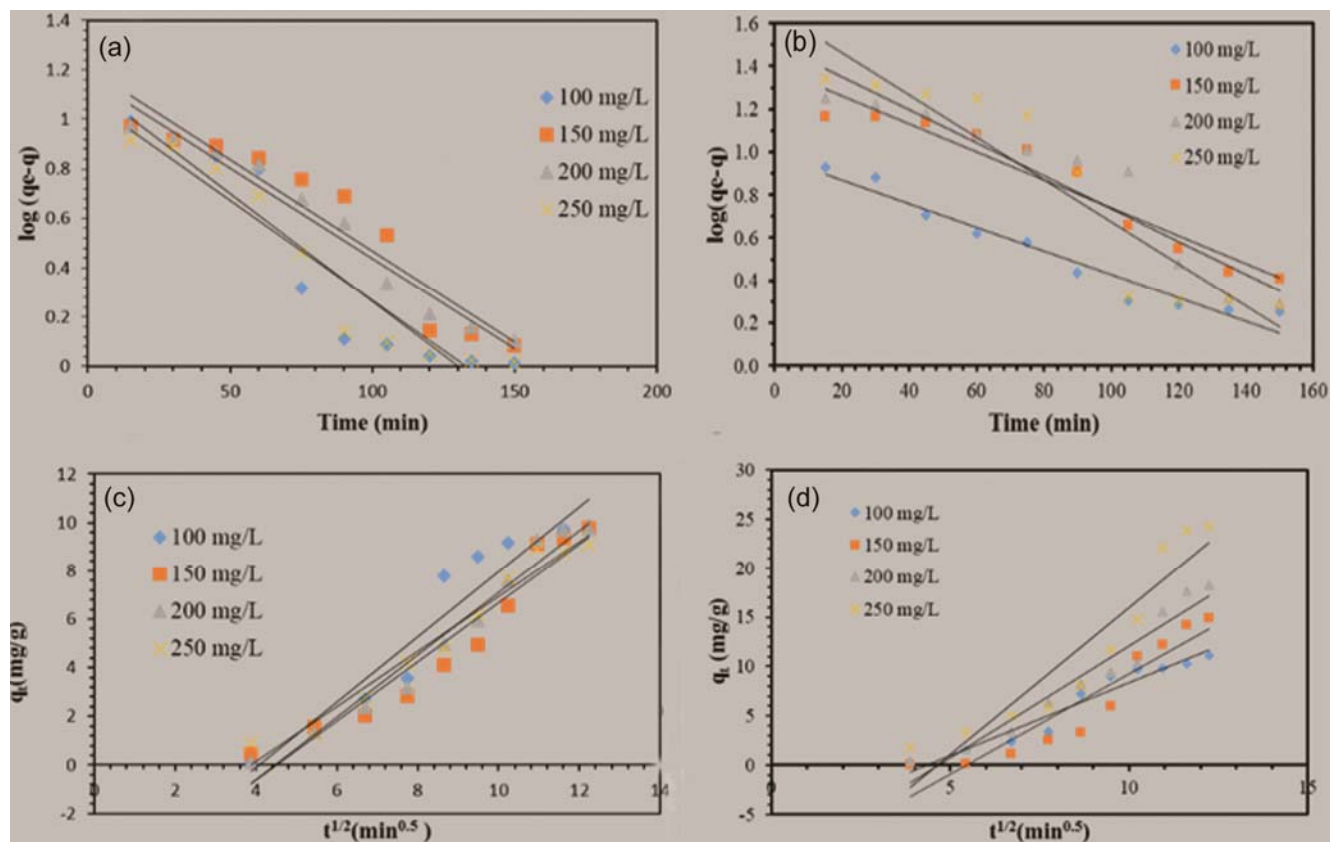


Fig. 10 — Pseudo-first-order kinetics for electro-adsorption of eosin-Y (a) onto CS (b) onto BS and (c - d) Intraparticle diffusion model eosin-Y onto CS and BS

plotted between q_t against $t^{0.5}$ illustrated in Fig. 10(c) & (d) and the kinetic model constant value were represented in Table 4. From the results it was observed that the plots were neither linear nor passing through origin, it states that the intra-particle diffusion was not only rate controlling step and also film diffusion might be involved in the electro-adsorption of EY dye by CS,BS^{30,32}.

Conclusion

The present study examined the preparation of activated carbon electrode from Bael fruit shell and Coconut shell. Also Carbon composite electrodes have been prepared for decolorization of MB and EY dye effluent. It confirms that, Carbon composite electrodes shows higher efficiency on colour removal compared to activated carbon electrodes prepared from Bael fruit Shell and Coconut Shell. The surface areas of both adsorbents with phosphoric acid activation are around 321.00 m²/g and 788.52 m²/g respectively. The maximum percentage of dye removal obtained by Coconut Shell activated carbon electrode efficiency is about

99.76% at optimum operating conditions are initial dye concentration (100 mg/L), contact time (30 min) and the applied potential of 30V. The characterization of activated carbon and activated carbon electrode using FTIR, SEM, EDAX, and TGA provided the physicochemical properties. Cyclic voltammetry of CPE on MB dye adsorption indicated that CPE is sensitive to lower MB dye concentration (2-10mg/L) compared to higher MB dye concentration (10-50 mg/L). Spontaneous nature of electro adsorption behaviour is confirmed by Tafel plot. The batch electro-adsorption equilibrium studies well fitted with Langmuir isotherm model and Pseudo-first-order kinetic model for EY adsorption onto CS activated carbon electrodes whereas the electro-adsorption equilibrium studies well fitted with Freundlich isotherm model and Pseudo-first-order kinetic model for EY adsorption onto BS activated carbon electrodes. The activated carbon electrode from coconut shell resulted in higher decolourization efficiency compared to BS activated carbon due to its high surface area and pore volume properties.

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