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Studies on Photocatalytic Degradation of Azo Dye Acid Red-18 (PONCEAU 4R) using Methylene Blue Immobilized Resin Dowex-11

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Abstract

Dowex-11 an anion exchanger resin immobilized in Methylene Blue is an efficient catalyst for the activation of O_2 at room temperature degrades dye in presence of visible light irradiation. The effect of various experimental parameters such as dye loading, catalyst loading, pH and light intensity were investigated during the process. This photo catalyst degrades 99% of the dye Acid red -18 into non toxic and biodegradable simpler molecules by degrading azo bonds in 160 minutes at pH 7.5, temperature 303K and the system follow first order kinetics, the value of rate constant k is $2.33\times10^{-2}min^{-1}$.

Keywords: Photocatalyst, Photocatalysis, Dowex-11, Acidred-18, Degradation.

Introduction

Textile processing is one of the most important industries in the world employing various organic chemicals (dyes) depending on the nature of raw material and products that makes the environment challenge for textile industry not only as liquid waste but also in its chemical composition[1]. These chemicals are different types of enzymes, detergents, dyes, sodas, salts and acid[2, 3]. The discharge of wastewater that contains high concentration of organic contaminants is a well-known problem associated with dyestuff activities[4-7]. The presence of these compounds in industrial wastewater and the discharge of textile wastewater, force us to look for alternative process to achieve it effective elimination of the contaminated water.

Early studies show that many of organic contaminant is degraded in the presence of oxygen and TiO_2[8-11] and also used for removing color from the dye effluents[12-21]. The heterogeneous photocatalytic oxidation process has been applied to decompose dirty, hazardous, bad smelling or toxic materials produced in daily life and the global environment[22,23].

Methylene blue immobilized resin (MBIR) Dowex-11 is a heterogeneous photo catalyst, which has capacity to exchange their one anion with dye solution anion, and activated oxygen of solution in presence of visible light [24]. This activated oxygen and photo catalytic action of this dye degrades azo bonds of dyes and complex organic molecules in simpler molecules[25].

MBIR Dowex-11 is a semiconductor catalyst[26]. There are some studies related to the use of semiconductor in the photo degradation of photo stable dyes[27, 28]. Photocatalytic reaction at the surface of semiconductor particles to organic synthesis is recognized as one of the most important and attractive target in field of chemistry.

Dowex -11 involved in oxidation-reduction process is excited by ultra violet light energy. UV light energy activates the catalyst surface by exciting an electron from the valence band (V.B.) to the conduction band (C.B.), leaving behind an electron hole[29]. An electron scavenger is needed to prevent recombination of excited electron back to the valence band in a mechanism called electron hole recombination.

The electron hole reacts with hydroxide ion (OH^-) or water molecules to create hydroxyl radicals ($OH^\cdot$). Hydroxyl radicals attack is assumed to be the primary mechanism for photo oxidation suggested by Turchi and Ollis[30]. Holes are likely to react with OH^- because it is readily absorbed to the catalyst surface.

$$\text{Semiconductor} + h\nu \rightarrow e^-_{cb} + h^+_{vb}$$
$$O_2 + e^- \rightarrow O_2^{\cdot -}$$
$$H_2O + h^+_{vb} \rightarrow OH^\cdot + H^+$$
$$\text{Dye} + OH^\cdot \rightarrow \text{Degradation products}$$

Material and Methods

Reagent and Chemicals: Dye - acid red -18(PONCEAU 4R) (figure-1), Molecular formula-$Na_1S_1O_3C_{10}H_6N{=}NC_{10}H_5S_2O_7Na_2$, Molecular weight-604.47 g/mol, Appearance - amorphous red colored powder, Solubility in water-soluble in water, λ_{max}- 506nm, Class -azo dye, Category-acid dye.

Photocatalyst: Methylene Blue immobilized resin Dowex-11 (MBIRD) is used as photocatalyst. Dowex -11: size of resin-20-50 mesh.

Property - anion exchanger. Immobilization of strong ion exchanger resin has been done by preparing M/1000 concentrated solution of methylene blue (photosensitized dye) in doubly distill water and Dowex -11 resin has been added to the solution and this mixture was placed in dark for 3 days for complete immobilization of methylene blue inside the pores of resin. After 3days in dark, Methylene blue immobilized resin was filter and washed twice with doubly distill water and used as photo catalyst.

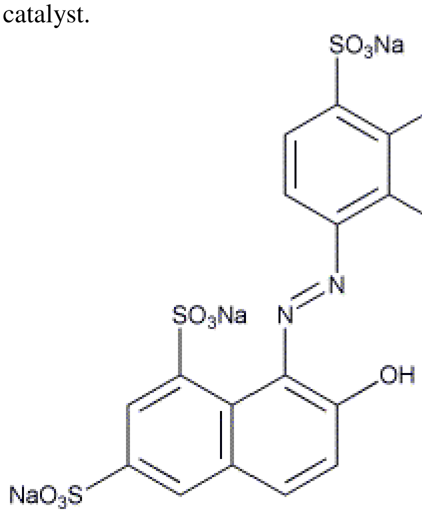

Figure-1
Structure of dye

Other: The water used in all the studies is double distilled. The other chemicals employed in this study such as oxalic acid, sodium hydroxide, phenolphthalein, sulphuric acid.

Procedure: All the solutions were prepared in double distilled water by direct weighing and kept in dark colored bottles. The photocatalytic degradation reactions were carried out in glass reactor containing a model solution and a defined amount of a photo catalyst. The solution in the reactor was continuously magnetically stirred during the experiment. After 15 minutes in dark, the reactor solution was illuminated with a 200W mercury lamp. The lamp was positioned above the reactor (figure-2).

Results and Discussion

The photocatalytic degradation of dye molecule was effected by catalyst, initial dye concentration, pH and light intensity.

Effect of variation in optical density with time: Photocatalytic degradation of dye molecule was reported by measuring the rate of decreasing optical density of solution with fixed time (table-1).

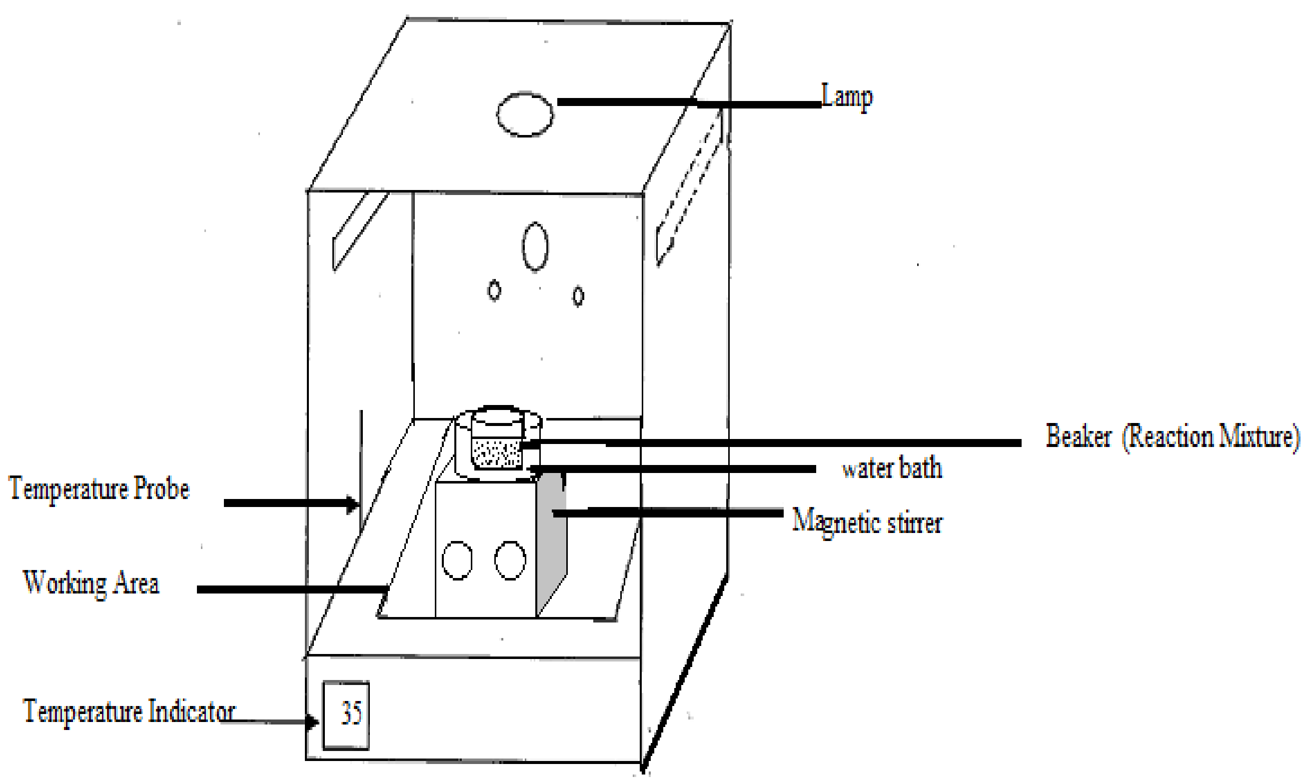

Figure-2
Experimental Set-up of Photochemical Reaction Chamber

Table-1
Variation of Optical Density with time

Time (min)	Optical Density	% of Photo degradation
0	1.369	0
10	0.981	23.39
20	0.823	36.55
30	0.658	49.47
40	0.522	59.30
50	0.403	67.26
60	0.312	74.16
70	0.244	81.07
80	0.199	86.19
90	0.173	89.27
100	0.155	90.98
110	0.128	91.79
120	0.101	92.85
130	0.091	94.39
140	0.070	95.93
150	0.063	97.40
160	0.058	98.86

Catalyst loading = 2.0 gm/L, Light intensity = 10.4 mW cm^{-2}, Solution volume = 50.0 ml, Temp. = 303K, Dye concentration = 40.0 mg/L, pH= 7.5

Effect of variation in light intensity: The degradation rate of dye molecules increases with increase in light intensity because more number of photon generated, required for electron transfer from valence band to conduction band of photo catalyst. The light intensity is simply altered by varying power of mercury lamp (5.2mW cm^{-2} to15.6mW cm^{-2}) (table-2 and figure-3).

Table-2
Effect of variation in Light intensity

Time (min.)	Optical density		
	Light intensity in $mWcm^{-2}$		
	5.2	10.4	15.6
0	1.366	1.369	1.368
10	1.048	0.981	0.978
20	0.878	0.823	0.721
30	0.733	0.658	0.545
40	0.600	0.522	0.432
50	0.503	0.403	0.346
60	0.438	0.312	0.289
70	0.401	0.244	0.221
80	0.363	0.199	0.175
90	0.320	0.173	0.140
100	0.290	0.155	0.129
110	0.255	0.128	0.115
120	0.229	0.101	0.093
130	0.191	0.091	0.078
140	0.185	0.070	0.065
150	0.173	0.063	0.041
160	0.160	0.048	0.029

Dye concentration = 40 mg/L, pH = 7.5, Solution volume = 50ml, Temp = 303K, Catalyst loading = 2.0 g/L

Effect of variation in dye concentration: When the amount of dye increase in the solution it became more intense colored and the path length of the photons entering in the solution decreased, thereby only fewer photons reached to catalyst surface and therefore the production of hydroxyl radicals and super oxide radicals was limited. So rate of degradation was also decreased (table-3 and figure-4).

Table-3
Effect of Variation in dye concentration

Time (min.)	Optical density				
	Dye concentration in mg/L				
	10	25	40	55	70
0	0.389	0.899	1.369	1.665	1.899
10	0.301	0.733	0.981	1.358	1.444
20	0.244	0.605	0.823	1.031	1.201
30	0.201	0.500	0.658	0.832	1.011
40	0.166	0.422	0.522	0.721	0.878
50	0.132	0.333	0.403	0.612	0.771
60	0.111	0.270	0.312	0.525	0.688
70	0.096	0.220	0.244	0.456	0.611
80	0.080	0.183	0.199	0.401	0.565
90	0.073	0.140	0.173	0.338	0.522
100	0.061	0.099	0.155	0.305	0.487
110	0.050	0.081	0.128	0.266	0.445
120	0.045	0.066	0.101	0.222	0.412
130	0.033	0.053	0.091	0.191	0.389
140	0.021	0.040	0.070	0.180	0.348
150	0.015	0.031	0.063	0.168	0.299
160	0.007	0.025	0.048	0.160	0.290

Catalyst loading = 2.0g/L, Light intensity = 10.4 m W cm^{-2}, Solution volume = 50ml, Temp = 303K, pH = 7.5

Effect of variation in catalyst loading: The degradation rate increased with increase in catalyst concentration because of availability of more catalyst surface area for absorption of photons and interaction of molecules of reaction with catalyst result is that no. of holes and hydroxyl radicals and super oxide radicals were increased (table-4 and figure-5).

Effect of variation in pH: The rate of degradation was very low in high acidic pH range when pH was lower than 3.5 rate of degradation was very less. But as pH increased rate of degradation also increased. When pH reached to basic range the rate of degradation increased fast, in pH range 7.5 to 9.0 rate of degradation was very good. On further increase in pH there was a decrease in photocatalytic degradation. So the rate of degradation in basic medium was higher than acidic medium because more availability of hydroxyl ion at pH 7.5 which generate more OH· radicals (table-5 andfigure-6).

Effect of different catalyst: The photo degradation of acid red 18 dye in different aqueous suspension containing methylene blue immobilized resin Dowex 11 and TiO_2 as photo catalyst under optimum condition i.e. dye concentration is 40mg/L, catalyst loading 2gm, pH 7.5, solution volume 50ml and light intensity 10.4mW cm^{-2} respectively.

Photocatalytic degradation increased linearly with both catalysts. Maximum degradation takes place when MBIR Dowex 11 is used as compared to TiO_2 because slow combination of electron hole pair and large surface area of MBIR Dowex 11.

Rate constant of MBIR Dowex 11 and TiO_2 used is 0.0233 min^{-1} and 0.008 min^{-1} respectively. The straight line shows that this reaction obeys first order kinetics.

Table-4
Effect of variation in Catalyst loading

Time (min.)	Optical density				
	Catalyst loading g/L				
	1g/L	1.5g/L	2g/L	2.5g/L	3g/L
0	1.365	1.370	1.369	1.368	1.366
10	0.967	0.998	0.981	0.966	0.953
20	0.760	0.825	0.823	0.780	0.743
30	0.648	0.688	0.658	0.650	0.611
40	0.541	0.551	0.522	0.532	0.487
50	0.455	0.430	0.403	0.434	0.400
60	0.400	0.352	0.312	0.340	0.303
70	0.356	0.280	0.244	0.266	0.223
80	0.307	0.222	0.199	0.211	0.178
90	0.289	0.193	0.173	0.180	0.153
100	0.263	0.180	0.155	0.165	0.111
110	0.225	0.175	0.128	0.143	0.082
120	0.198	0.167	0.101	0.126	0.065
130	0.180	0.152	0.091	0.098	0.048
140	0.165	0.143	0.070	0.081	0.033
150	0.151	0.130	0.063	0.062	0.028
160	0.148	0.125	0.048	0.040	0.016

Dye concentration = 40 mg/L, Light intensity = 10.4 $mWcm^{-2}$, Solution volume = 50ml, Temp = 303K, pH = 7.5

Table-5
Effect of Variation in pH

Time (min.)	Optical density		
	PH		
	3.5	7.5	11.5
0	1.365	1.369	1.367
10	1.180	0.981	1.061
20	0.933	0.823	0.853
30	0.755	0.658	0.651
40	0.605	0.522	0.532
50	0.500	0.403	0.420
60	0.445	0.312	0.325
70	0.412	0.244	0.260
80	0.368	0.199	0.211
90	0.326	0.173	0.190
100	0.293	0.155	0.171
110	0.261	0.128	0.162
120	0.245	0.101	0.153
130	0.228	0.091	0.135
140	0.199	0.070	0.128
150	0.188	0.063	0.111
160	0.175	0.048	0.109

Dye concentration =40 mg/L, Light intensity = 10.4 $mWcm^{-2}$, Solution volume = 50ml, Temp = 303K, Catalyst loading = 2.0 g/L.

Conclusion

MBIR Dowex 11 used as solar photo catalyst gives very good result and successfully improves the degradation rate of dyes. The photocatalytic degradation efficiency increases with increase in catalyst and decreases with increase in dye concentration. It has been concluding that this process can be used as an efficient and environment friendly technique for effluent treatment of industrial wastewater containing azo dyes. Development of this technology is of importance in Indian Context as sunlight is in abundance. This technology has very good potential of organic molecule degradation from complex molecule into simpler molecules. Azo dyes, which polluted water large part of textile effluent, can transform into colorless and toxic compounds so this catalyst may applicable for industrial purpose for improvement in quality of wastewater of textile industries and many others.

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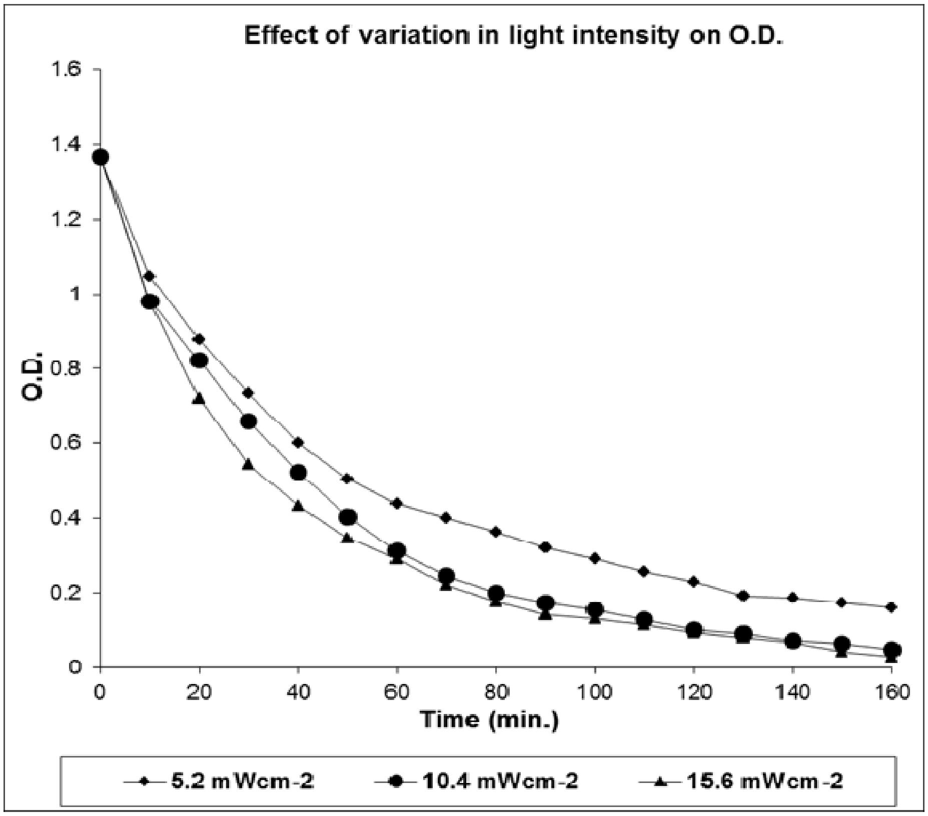

Figure-3
Effect of variation in light intensity

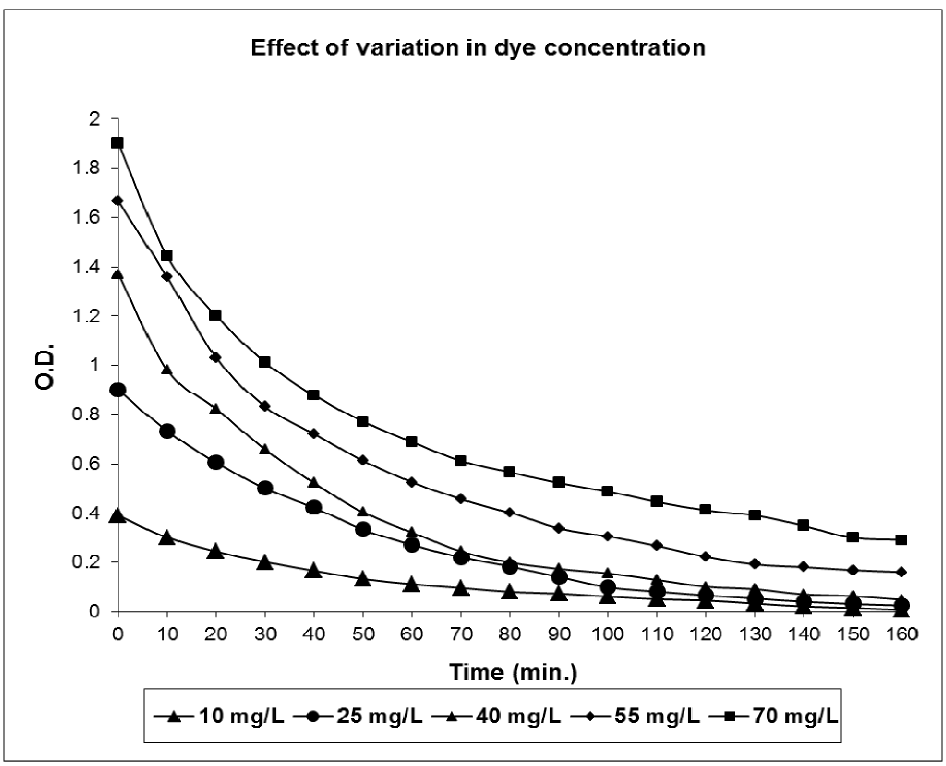

Figure-4
Effect of variation in dye concentration

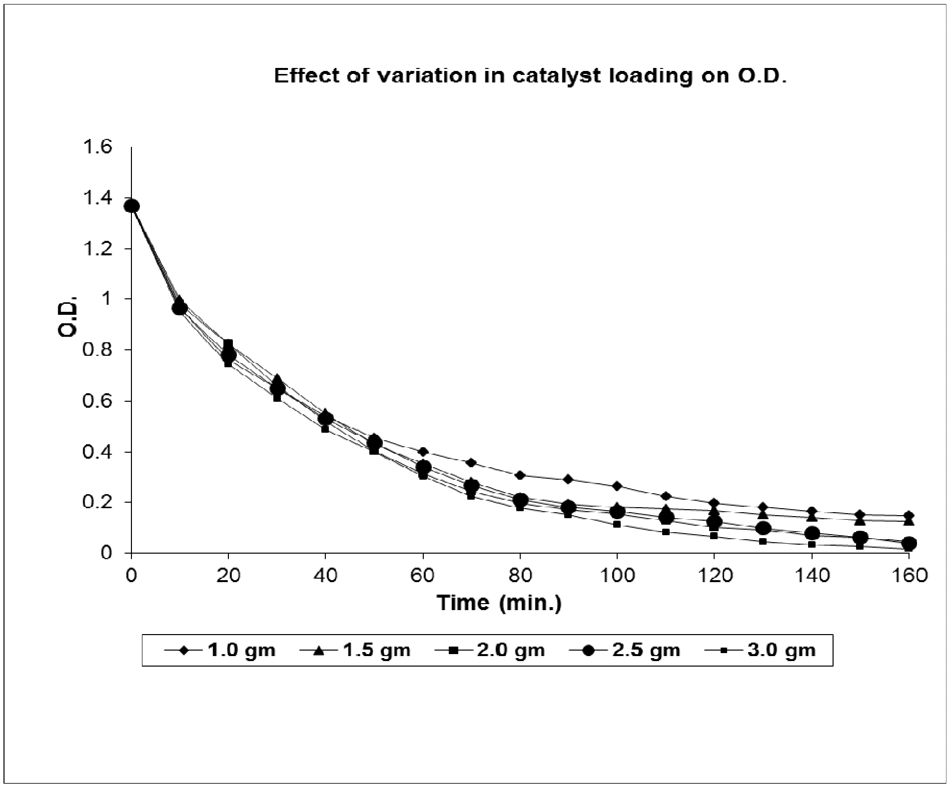

Figure-5
Effect of variation in catalyst loading

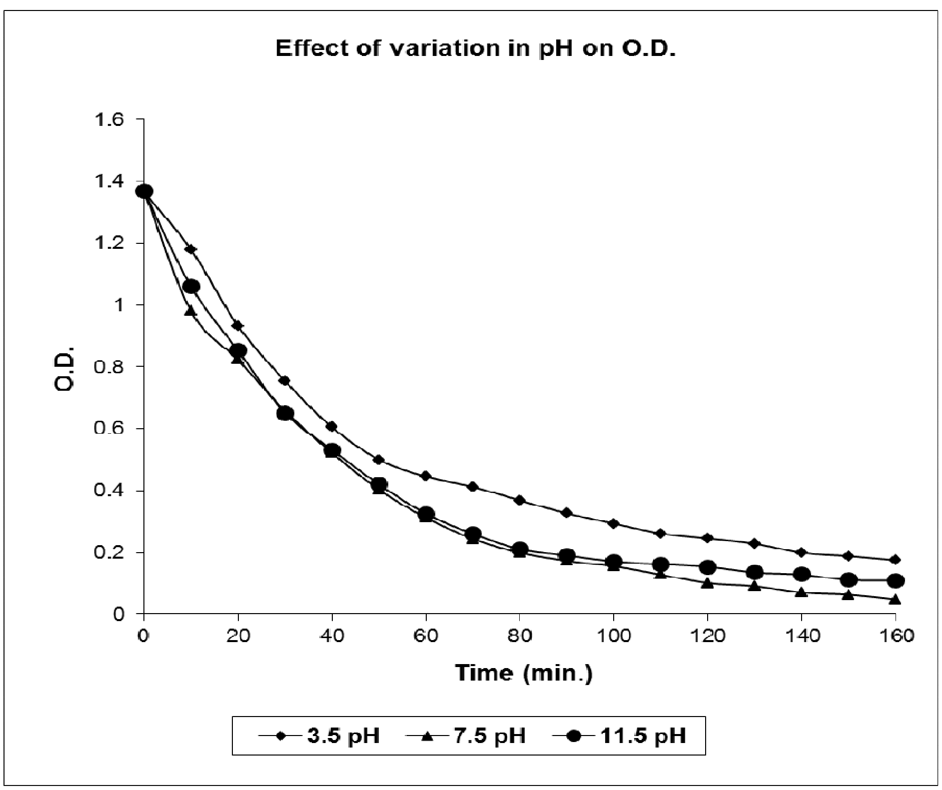

Figure-6
Effect of variation in pH

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