

Removal of Food Dye Tartrazine (E102) from Aqueous Solution using ZnO and CuO-TiO₂ as Photocatalysts

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Summary: Tartrazine dye has a major role in food as well as in other industrial products, like cosmetics, personal care products, pharmaceutical products and many more, therefore it is the cause of many environmental pollutions particularly water pollution. Its removal from water bodies is almost impossible with traditional techniques, because of heterogeneity in its composition. This investigation was carried out to examine the photo-catalytic degradation of food dye tartrazine (E102) from its aqueous solution, using ZnO (zinc oxide) and mixed CuO-TiO₂ (copper oxide-titanium dioxide) as photo-catalysts at room temperature. The influence of several parameters, such as pH of medium, time of irradiation, concentration of dye solution and amount of catalyst was investigated. Kinetic analysis was also carried out using Langmuir – Hinshelwood approach.

Maximum Photo-Catalytic Degradation (PCD) of E102 was observed to be at pH 1. Similarly significant rise in the degradation of E102 was observed with the time of irradiation, concentration of dye solution and amount of catalyst.

From the results obtained it was observed that ZnO and CuO-TiO₂ are effective photo-catalysts for the removal of E102 from its aqueous solution. However ZnO was observed to be more effective than CuO-TiO₂ in the degradation of E102 from aqueous solution.

Key Words: Tartrazine (E102), Dye, Zinc Oxide (ZnO), Copper Oxide-Titanium Dioxide (CuO-TiO₂), Photo-Catalytic Degradation, Langmuir – Hinshelwood Approach.

Introduction

Nowadays, water pollution becomes a serious issue. The most dangerous types of water pollutants are colorants and toxic ions of metal, which are found in industrial runoffs and repeatedly enter water bodies. [1] Dyes or colorants, are the materials that are used as coloring agents in paper, leather and textiles etc. industries. The applied color cannot be changed easily with washing, sun light, heating or other influences to which the material is possible to be exposed. [2] In terms of environmental protection, removal of these dyes and toxic materials is very important as their existence in water can be unsafe for humans, animals and marine lives.

In this study E102 has been considered as a model pollutant because of its wide industrial use. E102 is a pyrozone type (known as azoic acid) coloring additive having a lemon yellow shade with a chemical formula: C₁₆H₉N₄Na₃O₉S₂, authorized by European Union (EU) to be used as a coloring agent in the food industries. It is obtained synthetically from coal tar through azo coupling process (reacting diazonium compounds with aromatic compounds resulting into azo compounds) of diazotized sulfanilic acid (aminobenzene sulfonic acid). It gives food a yellow color and is very water soluble. [3, 4] Because of its easy solubility with water and fats, E102 also gives several shades of yellow color by dissolving it

in water and fats along with other dyes. E102 also has a property to give several green shades by treating it with Green S and Blue FCF. E102 does not tolerate direct light. When it come in contact with direct light radiations, the light rapidly start its decomposition to simpler compounds. This material is also tasteless and odorless. [5-7] E102 is a carbon-based sodium salt (trisodium salt of tartrazinic acid) and plays a major role both as a histological stain and a food coloring. [8] E102 can also be used in some makeups and personal care products. It also has a wide use as a coloring agent in several medicines. This color is normally added to antacids and syrups used for cough, lotions and vitamins. E102 is also used in many other materials like stamping inks, glues, colored chalk and inks. [9]

E102 for long time has been doubted to be the source of various side effects, although not all of them have been proved by research. Certain suspected effects are: Angioedema, Food intolerances, Asthma, Atopic dermatitis, Urticaria [10]. These side effects proved that E102 is harmful to terrestrial and aquatic species so its removal is very important from contaminated water.

The main problem in the treatment of effluents having azo colorants is linked to the

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maximum stability of these dyes, as they are not effected by moderate oxidizing agents, light and cannot be eliminated entirely by traditional procedures of anaerobic breakdown. The processes that are most common to treat the effluents having azo dye are: coagulation and flocculation, ozonation, adsorption and membrane separation. [11]

Most common and appropriate way to remove these dyes from an aqueous solution is the process of adsorption-photo-catalytic degradation. The current research is also carried out to investigate the effectiveness of PCD of organic dye E102. It is also the objective of this research, to investigate the impact of two different catalysts *i.e.* ZnO and mixed CuO-TiO₂ in order to degrade E102. Another objective is to improve the condition for Heterogeneous Photo-Catalytic Decomposition (HPCD) of E102. Also to assess the decomposition of E102 in the presence of UV radiations and also to determine its adequacy. The main objective of this work is to purify water from industrial wastes particularly dyes with low cost catalysts, adsorbents and procedure.

Photo-Catalytic Degradation (PCD)

Photo-catalysis is a technique that uses light radiations or energy to run couples of reactions. When the substance absorbs light radiations, the absorbed radiations creates an excited electron-hole couple. Because of their excited state, the hole and electron undergo redox reaction as these are very reactive in a reaction. [12]

Experimental

Materials and Techniques

Chemicals

The chemicals utilized in the current research are; Tartrazine or E102 (15-30%, Rangrez) purchased from local market and is used as such without any purification, Hydrochloric Acid (HCl) (37%, Merck), Potassium Hydrogen Phthalate (KHP) (99.9%, Merck), Potassium Dihydrogen Phosphate (KH₂PO₄) (99.95%, Merck), Sodium Tetraborate Decahydrate (Na₂B₄O₇·10H₂O) (99%, Merck), Sodium Hydrogen Carbonate (NaHCO₃) (95.5%, BDH), Potassium Chloride (KCl) (98%, Sigma Aldrich), Zinc Oxide (ZnO) (100%, Merck), Titanium Dioxide (TiO₂) (99.95%, Sigma Aldrich) and Copper Oxide (CuO) (99%, Merck).

Photo-Catalysts

Photo-Catalysts used were ZnO and a mixed catalyst of TiO₂ and CuO *i.e.* (CuO-TiO₂).

Preparation of Mixed Catalyst (CuO-TiO₂)

For the preparation of mixed catalyst equal amounts (20g) of CuO and TiO₂ were mixed together and a paste of the mixture was prepared using distilled water, then dried in drying oven at 110°C temperature and made into powder.

Apparatus

For the analysis of sample two types of spectrophotometers were used; Double Beam Model L7 UV-Visible Spectrophotometer made in China and Single Beam Spectrophotometer.

Radiation Source

Medium pressure mercury arc lamp was used as a source of radiation, as shown in Fig. 1.



Fig. 1: Mercury Arc Lamp (UV-Visible).

Preparation of Buffer Solutions

To determine the impact of pH on PCD of E102 buffer solutions of different pH were prepared, as shown in the Table-1.

Table-1: Table of Buffer Solutions.

pH 1-10	Reagent 1		Reagent 2	
	Conc. (M)	Vol. (mL)	Conc. (M)	Vol. (mL)
1	0.2M HCl	134mL	0.2M KCl	50mL
2	0.2 HCl	13	0.2 KCl	50
3	0.2 HCl	3	0.1 KHP	100
4	0.2 HCl	0.1	0.1 KHP	100
5	0.1 NaOH	45.2	0.1 KHP	100
6	0.1 NaOH	11.2	0.1 KH ₂ PO ₄	100
7	0.1 NaOH	58.2	0.1 KH ₂ PO ₄	100
8	0.2 HCl	21	0.025 Na ₂ B ₄ O ₇ .10H ₂ O	100
9	0.2 HCl	4.6	0.025 Na ₂ B ₄ O ₇ .10H ₂ O	100
10	0.1 NaOH	36.6	0.025 Na ₂ B ₄ O ₇ .10H ₂ O	100

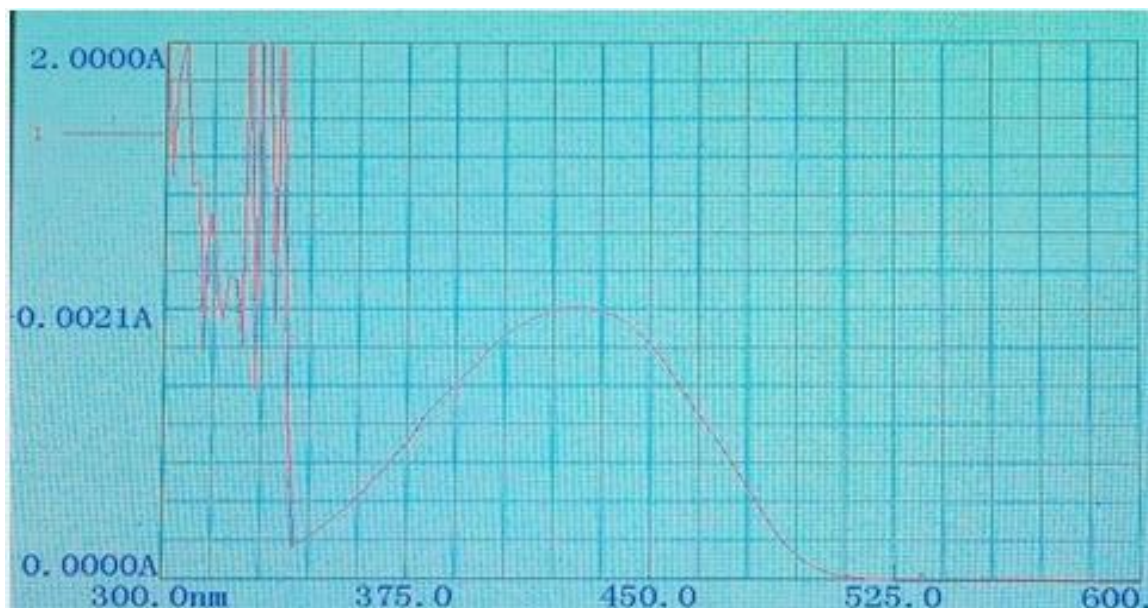


Fig. 2: UV-Visible Absorption Spectrum of Tartrazine.

Determination of Maximum Absorbance (λ_{max})

λ_{max} is the wavelength at which a substance shows maximum absorbance.

The following procedure was followed for the determination of λ_{max} .

100ppm solution of E102 was scanned using L7 Double Beam UV-VIS SP in the range of 300 – 600nm for absorbance. The observed λ_{max} of E102 was found to be at 426nm i.e. 1.0059A. Thus 426 nm was considered to be λ_{max} for E102, shown in Fig. 2.

Standard Calibration Curve (SCC)

For the development of Standard Calibration Curve (SCC), aqueous solutions of E102 of different concentrations were prepared from 100 ppm stock solution with the help of dilution formula ($C_1V_1 = C_2V_2$); i.e. 10ppm, 20ppm, 40ppm, 60ppm and 80ppm.

Using Double Beam UV-Visible spectrophotometer, the absorbance of these solutions were determined at λ_{max} (426nm), which were further used during data analysis. The SCC was plotted

between Absorbance and Concentration, as given in Table-2 and Fig. 3.

Table-2: Absorbance of Standard Solutions.

No	Concentration ppm	Absorbance
1	10	0.108
2	20	0.224
3	40	0.444
4	60	0.643
5	80	0.740
6	100	1.084

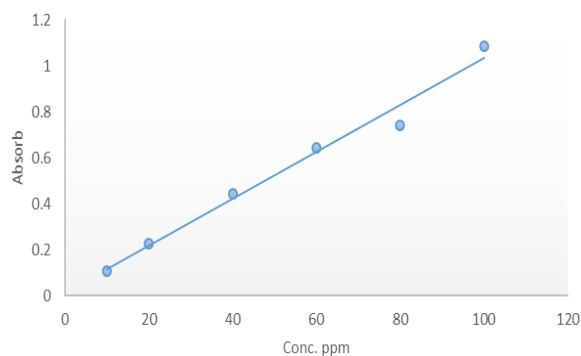


Fig. 3: Standard Calibration Plot of E102.

Table-3: Effect of pH (ZnO).

No	pH	Absorbance of irradiated solution	Concentration of irradiated solution ppm	Amount of solution decomposed ppm	Percentage decomposition
1	1	0.156	14.56	45.44	75.73%
2	2	0.160	14.93	45.07	75.12%
3	3	0.161	15.02	44.98	74.97%
4	4	0.162	15.12	44.88	74.80%
5	5	0.170	15.86	44.14	73.57%
6	6	0.173	16.14	43.86	73.10%
7	7	0.176	16.42	43.58	72.63%
8	8	0.250	23.33	36.67	61.12%
9	9	0.337	31.45	28.55	47.58%
10	10	0.307	28.64	31.36	52.27%

Table-4: Effect of pH (CuO-TiO₂).

No	pH	Absorbance of irradiated solution	Concentration of irradiated solution ppm	Amount of solution decomposed ppm	Percentage decomposition
1	1	0.156	14.557	45.443	75.74%
2	2	0.516	48.149	11.851	19.75%
3	3	0.236	22.022	37.978	63.30%
4	4	0.322	30.047	29.953	49.921%
5	5	0.537	50.109	9.891	16.65%
6	6	0.554	51.695	8.305	13.842%
7	7	0.564	52.628	7.372	12.28%
8	8	0.633	59.067	0.933	1.56%
9	9	0.592	55.241	4.795	7.99%
10	10	0.572	53.375	6.625	11.041%

Experimental Setup

The process of PCD of E102 from aqueous solution was carried out in 100 mL Beaker (made from Pyrex), that was used as a reactor. The suspension of suitable amount of photo-catalyst *i.e.* ZnO or mixed CuO-TiO₂ in 40mL aqueous solution of E102 was taken in 100 mL Pyrex glass beaker and was irradiated for the desired duration of time. During the irradiation the suspension was continuously stirred using magnetic stirrer at room temperature. After completion of the irradiation time the suspension was filtered and analyzed spectrophotometrically using double beam UV-Visible spectrophotometer at $\lambda_{\max} = 426\text{nm}$. Each experiment performed was repeated at least three times to get accurate results. This setup is presented in Fig. 4.

Results and Discussion

The experimental studies describe the HPCD of E102 in aqueous solution using ZnO and mixed CuO – TiO₂ as photo-catalysts. These studies were carried out in liquid phase at room temperature.

Impacts of different parameters *i.e.* impact of pH, impact of time of irradiation, impact of dye concentration and impact of amount of catalyst were studied during this research work. Also a comparison of the effectiveness of two different catalysts *i.e.* ZnO and mixed CuO – TiO₂ was studied. The summary of results is given below;



Fig. 4: Experimental Setup.

Effect of pH

The impact of pH to decompose E102 was accomplished at pH values ranged from pH1 to pH10. For this investigation the mixture of 0.15g of photo-catalyst and 40mL of 60ppm aqueous solution of E102 was irradiated for 30 minutes at ambient temperature. During irradiation, the suspension was stirred continuously using magnetic stirrer. The results obtained are given in Table-3 and 4.

The results demonstrate that maximum decomposition of E102 is observed at pH1 in both cases, using ZnO as photo-catalyst and mixed CuO-TiO₂ as photo-catalyst. It has also been observed from these results that the decomposition of E102

decreases with increase in pH. These results may be due to the fact that, the adsorption of compound having sulfonate (SO_3^-) group with a negative charge, is inhibited by high pH. E102 dye is having negatively charged SO_3^- group that is why its degradation has been decreased with increase in pH. Lachheb, et al, have investigated the influence of pH on the adsorption of different dyes. Their results obtained on OG (Crocein Orange G) dye demonstrate that the adsorption of OG is suppressed by high pH because of the presence of SO_3^- group. [13]

These results are further verified by the comparison of the above results with the results obtained from the study performed by Tahzeeb ul Akhlaq, et al, on the photocatalytic degradation of E102 with CuO, as per their observations, E102 has been decomposed more at low pH (pH3) and its decomposition decreased with increase in pH. [14] In addition to this study, research performed by Nawazish Ahmad, et al, on Acid Brown 701 also proved that organic dyes having SO_3^- group are more degradable at lower pH (pH3) and degrade less at high pH. [15] This comparative study is plotted in Table-5.

Impact of Time of Irradiation

The study of the impact of irradiation time on the decomposition of E102 was carried out in time range of 15 – 90 minutes for ZnO catalyst and 10 – 80 minutes for CuO-TiO₂. This investigation was carried out by the irradiation of suspension of 40mL of 60ppm aqueous solution of E102 and 0.15g of photo-catalyst for the given duration of time at room temperature. During irradiation the suspension was

continuously stirred using magnetic stirrer. The obtained results are given in Table-6 and 7.

From the obtained results, it is evident that the decomposition of E102 rises with rise in time of irradiation. In case of ZnO photo catalyst, at 15 minutes of irradiation 39.4355ppm of E102 solution has been decomposed i.e. 59.9408% decomposition occurred, and after 90 minutes of irradiation 55.8942ppm solution of E102 has been decomposed i.e. 93.157%, decomposition occurred. Thus these results demonstrate that ZnO as a photo-catalyst is observed to be effective towards the decomposition of E102 from its aqueous solution. While using CuO-TiO₂ as photo-catalyst at 10 minutes of irradiation 9.518 ppm of the dye has been decomposed (15.86%) and after 80 minutes, 18.009ppm of the dye has been decomposed (30.015%). From these results it is evident that CuO-TiO₂ is one of the effective photo-catalyst in the decomposition of E102. Aoudjit, L, et al, got the same result using TiO₂ as photo-catalyst i.e. the decomposition of E102 rises with rise in time of irradiation. [16] Amenaghawon, et al, studied the PCD of E102 by Periwinkle Shell Ash (PSA). They observed a progressive increase in the decoloring with increase in time of irradiation that reached a value of 81% at 50 minutes of irradiation and beyond 50 minutes equilibrium was established. [17] The current results also show that as compared to ZnO photo-catalyst, CuO-TiO₂ is less effective in the decomposition of E102 from its aqueous solution. Akyol, et al, have also observed a slightly better efficiency of ZnO as compared to TiO₂ in the degradation of dyes. [18]

Table-5: Comparison of Decompositions of two Different Dyes with Different Catalysts.

No	pH	Percentage Decomposition of Tartrazine with different Catalysts			Percentage Decomposition of Acid Brown 701 with different Catalysts			
		With ZnO	With CuO	With CuO-TiO ₂	With ZnO	With ZnO-CuO	With ZnO-TiO ₂	With CuO-TiO ₂
1	1	75.73%	71.55%	75.74%	42.22%	44.19%	57.57%	56.47%
2	2	75.12%	74.65%	19.75%	36.96%	27.20%	45.40%	44.85%
3	3	74.97%	96.42%	63.30%	47.59%	58.99%	59.89%	64.80%
4	4	74.80%	87.10%	49.921%	44.63%	49.67%	56.47%	63.60%
5	5	73.57%	81.82%	16.65%	41.45%	49.23%	54.39%	60.97%
6	6	73.10%	70.60%	13.842%	10.97%	19.63%	11.85%	12.07%
7	7	72.63%	68.58%	12.28%	10.42%	17.33%	15.58%	17.00%
8	8	61.12%	37.33%	1.56%	23.80%	32.79%	18.98%	16.67%
9	9	47.58%	26.77%	7.99%	24.13%	18.43%	17.99%	2.64%
10	10	52.27%	19.28%	11.041%	13.49%	16.87%	15.58%	2.31%

Table-6: Effect of Time of Irradiation (ZnO).

No	Time of Irradiation Minutes	Absorbance of irradiated solution	Concentration of solution after irradiation ppm	Amount of solution decomposed ppm	Percentage decomposition
1	15	0.219	20.4355	39.5645	59.9408%
2	30	0.174	16.2364	43.7636	72.939%
3	45	0.145	13.5304	46.4696	77.449%
4	60	0.052	4.8522	55.1478	91.913%
5	90	0.044	4.1058	55.8942	93.157%

Table-7: Effect of Time of Irradiation (CuO-TiO₂).

No	Time of Irradiation Minutes	Absorbance of Irradiated solution	Concentration of solution after irradiation ppm	Amount of solution decomposed ppm	Percentage decomposition
1	10	0.541	50.4823	9.518	15.86%
2	15	0.537	50.109	9.891	16.485%
3	30	0.519	48.429	11.571	19.285%
4	45	0.511	47.683	12.317	20.528%
5	60	0.488	45.537	14.463	24.105%
6	80	0.450	41.991	18.009	30.015%

Table-8: Effect of Dye Concentration (ZnO).

No	Concentration ppm	Absorbance of irradiated solution	Concentration of solution after irradiation ppm	Amount of solution decomposed ppm	Percentage decomposition
1	10	0.007	0.648	9.358	93.58%
2	20	0.024	2.143	17.857	89.375%
3	40	0.027	2.430	37.57	93.925%
4	60	0.063	2.430	57.57	95.95%
5	80	0.083	8.936	71.064	88.83%

Table-9: Effect of Dye Concentration (CuO-TiO₂).

No	Concentration ppm	Absorbance of irradiated solution	Concentration of solution after irradiation ppm	Amount of solution decomposed ppm	Percentage decomposition
1	10	0.063	4.907	5.093	50.93%
2	20	0.124	11.07	8.93	44.65%
3	40	0.348	31.35	8.65	21.63%
4	60	0.515	48.056	11.94	19.90%
5	80	0.643	69.51	10.49	13.11%

The obtained results also indicate that the decomposition of E102 from its aqueous solution increases almost linearly with increase in time of irradiation. It means that the reaction is chemically kinetically controlled.

Impact of E102 Concentration

The influence of E102 solution concentration on its PCD was carried out in the range of 10 – 80 ppm. This investigation was carried out by irradiating a reaction mixture of 0.15g of catalyst in 40mL of E102 solution of a given concentration at ambient temperature for 30 minutes. The mixture was continuously stirred by magnetic stirrer during irradiation. The results obtained are given in Table-8 and 9.

The obtained results demonstrate that the photo-catalytic degradation of E102 increases linearly with increase in concentration using ZnO as photo-catalyst. While the photo-catalytic decomposition of E102 using CuO-TiO₂ photo-catalyst increases with rise in concentration of the dye till 20 ppm, the decomposition remained almost constant from 20 – 40 ppm and there is again an increase in decomposition above 40 ppm. Thus there is increase in the decomposition of dye with increase in concentration. Generally the degradation rate decreases with rise in concentration of E102, because of the formation of OH⁻ radicals on the surface of catalyst, which reacts with dye molecules and

suppress its degradation. But the results observed in the current research are completely opposite. These observed results may be due the fact that the catalyst dose used in the current study is large (0.15g) which has the ability to degrade more dye molecules, so the increase in concentration of dye did not affect its decomposition but increased the degradation rate, due to the availability of more molecules of dye. *Khalid Saeed, et al*, observed that the photo-catalytic degradation of the dye (methyl violet) decreased with rise in the concentration. Their results might due to the fact that they had used a small amount of photo-catalyst (0.01g- 0.025g) than the amount we used in this research *i.e.* 0.15g and as a result there is decrease in degradation with rise in concentration.[19]. The results obtained in the current work may also be due to the fact, that very low concentration of dye is used in the study *i.e.* 0.1g/L for the preparation of stock solution. Since the concentration of dye is very low therefore the increase in concentration of dye has not effected its degradation, rather there is an increase in degradation rate of dye. *Khan Mamun Reza, et al*, observed opposite results, *i.e.* they observed a decrease in the decomposition of dye with rise in concentration of colorants. Their observation opposed to the current study might be due to higher concentrations of the dye solution they used *i.e.* 8×10^{-4} – 1.2×10^{-3} M has been taken as the concentration range for Reactive Yellow 17. [20] The concentration of dye solution used in the current study ranges form 10 – 80ppm.

Table-10: Results of Effect of Amount of Catalyst (ZnO).

No	Amount of catalyst g	Absorbance of irradiated solution	Concentration of solution after irradiation ppm	Amount of solution decomposed ppm	Solution decomposed per g of catalyst	Percentage decomposition
1	0.05 g	0.403	37.605	22.395	447.9	37.325%
2	0.1 g	0.378	35.272	24.728	247.28	41.213%
3	0.15 g	0.174	16.2364	43.764	291.76	72.939%
4	0.2 g	0.052	4.852	55.148	275.74	91.91%
5	0.25 g	0.045	4.199	55.801	223.20	93.001%

Table-11: Results of Effect of Amount of Catalyst (CuO-TiO₂).

No	Amount of Catalyst	Absorbance of irradiated solution	Concentration of solution after irradiation ppm	Amount of solution decomposed ppm	Amount of solution decomposed per g of catalyst	Percentage decomposition
1	0.05 g	0.620	57.85	2.15	43	3.58%
2	0.1 g	0.608	56.73	3.27	32.7	5.45%
3	0.15 g	0.519	48.43	11.57	77.13	19.28%
4	0.20 g	0.450	41.99	18.01	90.05	30.02%
5	0.25 g	0.390	36.39	23.61	107.31	39.35%

Effect of Amount of Catalyst

The impact of amount of photo-catalyst on the PCD of E102 was carried out in the range of 0.05g – 0.25g. This study was carried out by irradiating the suspension of 40mL of 60ppm aqueous solution of E102 with a given amount of photo-catalyst *i.e.* 0.05gram, 0.1gram, 0.15gram, 0.2gram and 0.25gram for 30 minutes time of irradiation. The solution was stirred continuously during irradiation using magnetic stirrer. This investigation was carried out at room temperature. The observed results are given in Table-10 and 11.

The obtained results demonstrate that the PCD of E102 rises with increase in amount of catalyst. This may due to the rise in the availability of active sites. Similar results are obtained by *Khalid Saeed, et al.* They studied the effect of TiO₂/Pt catalyst concentration on the degradation of Methyl Violet. [19]

However, the degradation of the dye per gram (ppm per g) of ZnO catalyst decreases with increase in amount of catalyst as shown in Table-10. The observed result may due to the fact that the number of catalyst particles increases with increase in amount of catalyst. This results an increase in the decomposition of the dye. However with increase in amount of catalyst, the catalyst to photon ratio decreases and the amount decomposed per gram of catalyst decreases. However using CuO – TiO₂ photo-catalyst opposite trend to the above is observed *i.e.* the degradation of E102 per gram (ppm per g) of catalyst rises with rise in amount of catalyst as shown in Table-11. This result may due to the fact that there is the possibility of multilayer formation as a result of physisorption over the surface of photo-catalyst because TiO₂ has the ability of physisorption along with chemisorption. As observed by *Mounir Kassir et al.*, while studying the surface properties of TiO₂ by

investigating the adsorption mechanism of n-(6-aminoethyl) aminopropyltrimethoxysilane on TiO₂. They observed that both chemisorption and physisorption occurred on the surface of TiO₂ and thus displayed unlike performance. The physisorbed amount was far greater than chemisorbed amount. This indicates that the majority of the adsorbed layer is occupied by physically adsorbed molecules. They demonstrate that the chemically adsorbed molecules are on the spots showing maximum energy and physically adsorbed molecules are on the spots showing minor energy. [21]

Kinetics of Degradation of E102

Langmuir – Hinshelwood approach was used for the study of kinetic degradation of E102. According to this approach:

$$r = \frac{dC}{dt} = k\theta - \frac{kKC}{1 + KC}$$

In this equation, r is degradation rate, k is degradation rate constant, θ is fraction of occupied site, C is concentration and K is adsorption equilibrium constant.

$$K = \frac{k_{ads}}{k_{des}}$$

At low concentration, KC << 1, therefore

$$\frac{dC}{dt} = -k_{app}$$

k_{app} contains both k and K (rate constt and adsorption equilb. constt).

Integrated form of this equation is:

$$\ln \left(\frac{C_0}{C_t} \right) = k_{app} t$$

This is the first order integrated rate equation, where C₀ = initial dye conc. and C_t = conc. of dye solution after time t.

Table-12: Pseudo 1st Order Kinetic Model of Photocatalytic Degradation of E102 (ZnO)

No	Time (min)	Initial Conc. (ppm) C_0	Conc. at Time t (ppm)	$\ln(C_0/C_t)$	$k_{app} \text{ min}^{-1}$
1	15	60	20.4355	1.077	0.0718
2	30	60	16.2364	1.308	0.0436
3	45	60	13.5304	1.489	0.0330
4	60	60	4.8522	2.515	0.0419
5	90	60	4.1058	2.682	0.0298

Table-13: Pseudo 1st Order Kinetic Model of Photocatalytic Degradation of E102 (CuO-TiO2).

No	Time (min)	Initial Conc. (ppm) C_0	Conc. at Time t (ppm) C_t	$\ln(C_0/C_t)$	$k_{app} \text{ min}^{-1}$
1	10	60	50.4823	0.1727	0.01727
2	15	60	50.109	0.1801	0.01200
3	30	60	48.429	0.2142	0.00714
4	45	60	47.683	0.2298	0.00510
5	60	60	45.537	0.2758	0.00459
6	80	60	41.991	0.3569	0.00446

Using this equation values of k_{app} are calculated at different times, given in Tables-12 and 13 and plotted in Fig. 5 and 6.

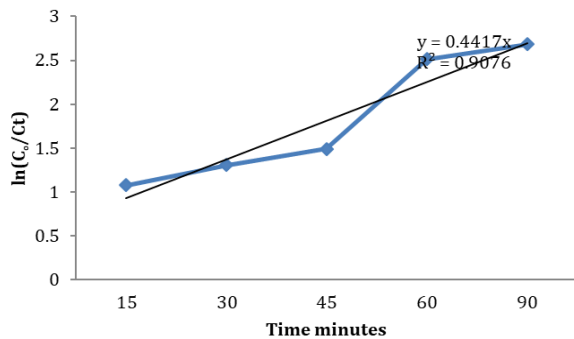


Fig. 5: 1st order kinetic plot for photo catalytic degradation of E102 (Heterogeneous) (ZnO).

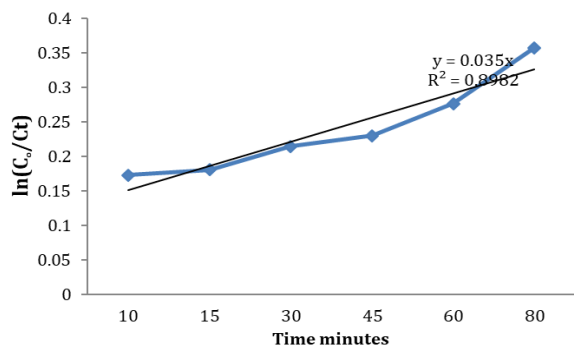


Fig. 6: 1st order kinetic plot for photo catalytic degradation of E102 (Heterogeneous) (CuO-TiO2).

These tables indicates pseudo 1st order kinetics for the degradation of E102. From the value of k_{app} it is evident that there is continuous decrease in rate constant in the range of 15 – 45 minutes but a sudden increase occurred at 60 minutes and again decrease at 90 minutes of irradiation using ZnO as

photo-catalyst. While using CuO-TiO₂, a continuous decrease in the value of k_{app} has been observed.

From the Fig. 5 it is evident that the value of k_{app} for the degradation of E102 is 0.4417 with R^2 value 0.9076, using ZnO photo-catalyst and it is 0.035 with R^2 value 0.8982, shown in Fig 6 for CuO-TiO₂ photo-catalyst.

Conclusions

From the obtained results it is concluded that:

- i. There is significant increase in the decomposition of E102 with increase in time of irradiation using ZnO as a photo-catalyst and the same trend is observed using CuO-TiO₂ as a photo-catalyst. These results demonstrate that both ZnO and CuO-TiO₂ are effective photo catalysts to remove E102 from its aqueous solution. However ZnO is more effective than CuO-TiO₂ in the degradation of E102 from aqueous solution.
- ii. From the results obtained it is also evident that decomposition of E102 from its aqueous solution increases with increase in concentration. There is continuous increase in the PCD of E102 using ZnO as a photo-catalyst. However in case of CuO-TiO₂ the degradation of E102 increases up to 20 ppm. The degradation of E102 then remains constant in the range 20 – 40 ppm and again increases above 40 ppm concentration.
- iii. With increase in amount of catalyst the PCD of E102 increases. However, the degradation of E102 per gram (ppm per g) of catalyst decreases with increase in amount of catalyst using ZnO as a photo-catalyst, however using CuO-TiO₂ photo-catalyst the degradation of E102 per g of catalyst also increases due to the formation of multilayer on catalyst surface. This may due to the dominant physisorption ability over chemisorption ability of TiO₂.

- iv. Maximum PCD of E102 was observed to be at pH 1 in both cases, using ZnO and CuO-TiO₂ as photo-catalysts. This may be because, E102 have negatively charged sulfonate group. While the compound with negatively charged sulfonate group degraded more at acidic pH, because high pH suppress its degradation or adsorption property.

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