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REMOVAL OF AZURE A DYE FROM AQUEOUS SOLUTIONS BY USING STRONTIUM CHROMATE – ZINC OXIDE NANOCOMPOSITE

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ABSTRACT

Water is one of the most important natural resource for human. Water pollution is one of the major problems faced by the humans. Several methods for waste water treatment have been suggested in the last few decades. These methods are based on chemical, physical and biological processes. In this paper, the Photocatalytic degradation of cationic dye Azure A observed in aqueous solutions containing strontium chromate – zinc oxide nanocomposites as Photocatalytic material. The effect of various parameters such as pH of solution, concentration of dye, amount of photocatalyst and intensity of light on rate of degradation of Azure A dye has been studied. Synthesized nanomaterials were investigated by using XRD and EDX techniques. The reaction takes place more effectively at pH 8.5 and it plays very important role in the characteristic of textile wastewater and generation of hydroxyl radicals. A tentative mechanism for the photocatalytic degradation of Azure A dye has been proposed.

KEY WORDS : Azure A, Photocatalytic Degradation, Strontium Chromate, Zinc Oxide.

INTRODUCTION

Human activities including industrialization and agricultural practices contributed immensely in no small measure to the degradation and pollution of the environment which adversely has an effect on the water bodies that is a necessity for life. Owa (2013) reported basically what water pollution is and equally to address the source, effect control and water pollution management as a whole. Water pollution is an environmental problem that is of major concern to us.

Amin (2008) synthesized activated carbons from bagasse pith by chemical activation with H_3PO_4(AC1) and $ZnCl_2$(AC2). Different activated carbons used for the removal of reactive orange (RO) dye from aqueous solutions. The photocatalytic degradation of evans blue studied under visible light in the presence of $SrCrO_4$ as a photocatalyst by Jangid *et al*. (2018) Strontium chromate was synthesized by precipitation method in a wet chemical process. The photocatalytic activity of strontium chromate was compared by investigating the photodegradation of Evans blue dye under visible light.

Lee *et al.* (2013) prepared One-dimensional nanostructures with very large aspect ratios, such as nanotubes, nanowires, nanorods, and nanobelts. $SrCrO_4$ was normally synthesized by conventional solid-state reaction with $SrCO_3$ and Cr_2O_3. Ramezani *et al.* (2022) reported preparation method for monazite type strontium chromate. Nitrogen and sulphur co-doped graphene decorated with $SrCrO_4$ nano crystals. Results shows the $SrCrO_4$-nitrogen and sulphur co-doped graphene ($SrCrO_4$/NSG) shows the highest discharge capacity as compare to $SrCrO_4$-reduced graphene oxide.

Maureen *et al.* (2018) investigated the potential of calcinated and uncalcinated zinc oxide as an effective photocatalyst for the degradation of malachite green dye (MG) from aqueous medium using UV light. the calcinated and uncalcinated zinc oxide, ZnO can be effectively used as an efficient photocatalyst for the degradation of Malachite

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green. Chowdhury *et al.* (2018) suggested photocatalytic degradation of methyl orange using ZnO as photocatalytic material. The results reveal that ZnO has high and significant photocatalytic activity and suitable alternative to TiO_2 as photocatalyst. Cai *et al.* (2014) prepared ZnO nanorod by a facial hydrothermal method. The catalytic activity of ZnO nano crystals with different exposed surfaces, including ZnO hexagonal nanorods with exposed reactive facets, hexagonal ZnO nanopyramids with nonpolar planes and pencil like morphology with exposed polar planes was tested towards the photocatalytic degradation of congo red (CR) and methyl orange (MO) azo dyes. Durmus *et al.* (2019) synthesized graphene oxide/zinc oxide (GO/ZnO) nanocomposite. It was found that the GO/ZnO nanocomposite formed a two-dimensional (2D) structure. Its utilization for photocatalytic degradation of basic fuchsin dye under UV light. Salavati-Niasari *et al.* (2019) synthesized zinc oxide nanotriangles by thermal decomposition from zinc oxalate, $[Zn(C_2O_4)\,2H_2O]$. The different combinations of triphenylphosphine, and oleylamine were added as surfactants to control the particle size. The synthesized ZnO nanoparticles have a hexagonal zincite structure.

Gupta *et al.,* (2015) studied the photocatalytic degradation of azure A in the presence of semiconductor barium chromate. A tentative mechanism for photocatalytic degradation of azure A involving hydroxyl radical as an active oxidizing species also proposed. Rathore *et al.* (2015) proposed photocatalytic degradation of azure A using N-doped ZnO as photocatalyst. They found that the N-doped ZnO has shown six times enhanced photocatalytic activity than pure ZnO. Rao *et al.* (2016) compared the photocatalytic activity of pure ZnO and carbon doped ZnO by photodegradation of azure A under visible light. Final results shows that the C-doped ZnO has shown more than two times enhanced photocatalytic activity than pure ZnO. Jangid *et al.* (2018) suggested photocatalytic activity of strontium chromate ($SrCrO_4$) is for the photodegradation of azure-A dye. It was observed that strontium chromate has the highest catalytic activity in basic medium. Hussein *et al.* (2019) synthesized ZnO nanoparticles by sol-gel technique. Color removal of azure A dye in aqueous solution by ZnO nanoparticles. The photodegradation was strongly influenced by numerous parameters, mainly the initial H_2O_2 dosage.

MATERIALS AND METHODS

Preparation of Composite: Strontium chromate were synthesized by precipitation method using strontium chloride ($SrCl_2$) and sodium chromate (Na_2CrO_4). Zinc oxide used from Fisher scientific laboratory grade. Strontium chromate and zinc oxide were taken mole to mole (1:1) and mixed with mechanical method to fine powder. Composite characterized by SEM-EDS and XRD techniques.

Characterization

EDX Analysis

Energy-dispersive X-ray spectroscopy (EDX) detects X-rays emitted from the sample during bombardment by electron beam to characterise the elemental composition. The results are reported in Table 1 and presented in Figure 1.

Table 1. EDX data of strontium chromate – zinc oxide

Element	Series	Norm. C (wt. %)	Atom. C (at. %)
Strontium	L-Series	40.42	15.54
Oxygen	K-Series	31.81	66.96
Chromium	K-Series	24.13	15.63
Zinc	K-Series	3.64	1.88
Total	100.00	100.00	

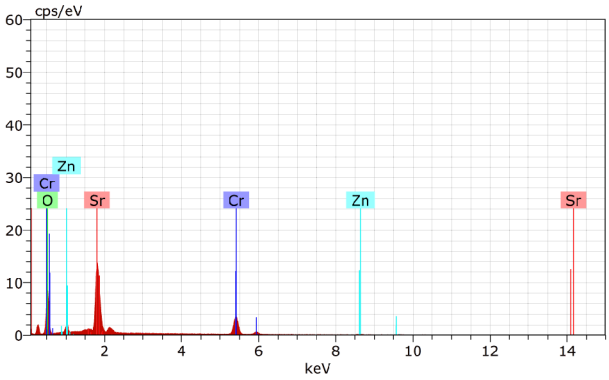

Fig. 1. EDX of strontium chromate – zinc oxide

XRD Analysis

X-ray diffraction is a method to determine crystallinity of a compound. The crystal size of the composite was determined by the X-ray diffractometer (XRD) using CuKα radiation (α = 0.154060 nm) in the 2θ scanning ranges from 20^0 to 80^0 with a scan rate at 10^0 min^{-1}. The powder XRD pattern of as prepared strontium chromate – zinc oxide nanomaterials is given in Figure 3.

The crystal size (D) was calculated using the Debye-Scherrer's formula:

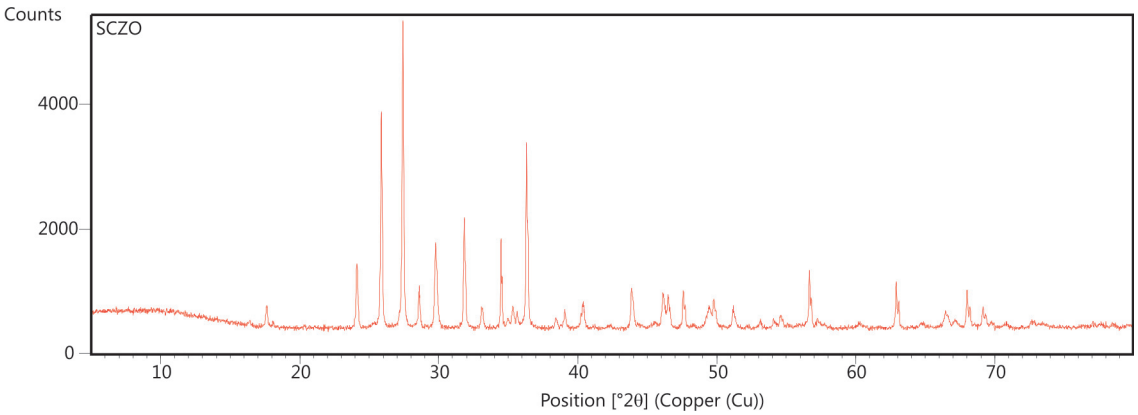

Fig. 2. XRD of strontium chromate – zinc oxide

$$D = 0.9\lambda/\beta \cos\theta \quad .. (1)$$

Where, θ = The wavelength of x-ray source (λ = 0.1540 nm for CuKα), β (in radians) = The full width at half maximum (FWHM) and θ = The Bragg's angle.

Photocatalytic process

The photocatalytic activity of the catalyst was evaluated by measuring the rate of degradation of azure A. 0.0291 gm of azure A dye was dissolved in 100 ml of doubly distilled water to prepare 1.0 x 10^{-3} M concentration of stock solution. pH of the dye solution was measured by a digital pH meter (Systronics model 335), and the desired pH of the solution was adjusted by the addition of standard 0.1 N sulphuric acid and 0.1 N sodium hydroxide solutions. The reaction mixture containing 0.10 gm photocatalyst was exposed to a 200 W tungsten lamp, and about 3 ml aliquot was taken out every 15 minutes. Absorbance (A) was measured at λ_{max} = 630 nm. A water filter was used to cut off thermal radiations. The intensity of light was varied by changing the distance between the light source and reaction mixture, and it was measured by nm. A water filter was used to cut off thermal radiations. The intensity of light was varied by changing the distance between the light source and reaction mixture, and it was measured by Suryamapi (CEL model SM 201). The absorbance of the solution at various time intervals was measured with the help of auto calorimeter (Systronics model LT-114). It was observed that the absorbance of the solution decreases with increasing the time of exposure, which indicates that the concentration of azure A decreases with increasing time. The calculation of degradation efficiency (Ψ) was made by the relation

$$\Psi = 100\frac{A - A_0}{A_0}$$

Table 2. Typical runs for photocatalytic degradation of Azure A:

pH = 8.5, Concentration [Azure A] =2.7 × 10^{-5} M,
Composite = 0.10 gm, Light intensity = 60.0 mWcm^{-2}
Rate constant = 1.003×10^{-4} Sec^{-1} (composite with 2-propanol) and 1.09×10^{-4} Sec^{-1} (composite without 2-propanol).

Time (min)	Composite with 2-propanol		Composite without 2-propanol	
	Abs	1+log A	Abs	1+log A
0	0.792	0.8987	0.779	0.8915
15	0.748	0.8739	0.731	0.8639
30	0.719	0.8567	0.706	0.8488
45	0.688	0.8375	0.659	0.8188
60	0.627	0.7972	0.603	0.7803
75	0.581	0.7641	0.578	0.7619
90	0.533	0.7267	0.492	0.6919
105	0.479	0.6803	0.446	0.6493
120	0.405	0.6074	0.388	0.5888
135	0.386	0.5865	0.334	0.5237
150	0.321	0.5065	0.292	0.4653
k Sec^{-1}	1.003×10^{-4}		1.09×10^{-4}	

Here, A_0 is initial absorbance, and A is absorbance after degradation of dye at time t. A plot of 1 + logA versus time was linear following pseudo-first order kinetics. Typical runs are given in Table 2 and graphically presented in Figure 3. The rate constant was calculated by using the expression:

$$k = 2.303 \times \text{slope} \quad .. (2)$$

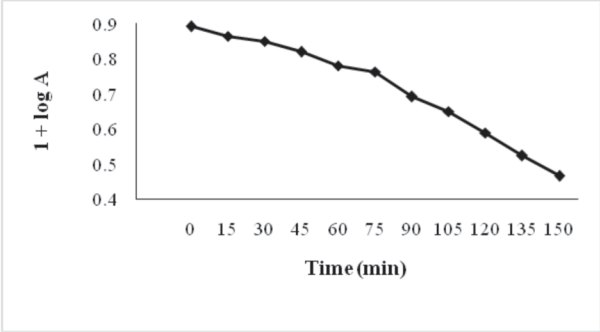

Fig. 3. Typical run for photocatalytic degradation of azure A

RESULTS AND DISCUSSION

Effect of parameters

(i) Effect of pH

The effect of variation of pH range 4.0 to 9.5 and all other parameters were kept to be identical. The results are given in Table 3 and Figure 4. It was observed that with an increase in pH, the rate of reaction increases. At pH 8.5 rate of reaction was highest. In this case, the presence of scavenger i.e., 2-propanol does not affect the rate of reaction adversely and hence, it may be concluded that •OH radical does not participate in the degradation. It was interesting to observe that strontium chromate – zinc oxide composite was active in basic range (6.5-9.5).

Table 3. Effect of pH on photocatalytic degradation of azure A.

Concentration [Azure A]=2.7×10^{-5}, Light intensity=60.0mWcm^{-2} Composite=0.10gm,	
pH	Rate constant, (k) × 10^{-4} (sec^{-1})
4.0	0.21
5.0	0.27
5.5	0.39
6.0	0.43
6.5	0.51
7.0	0.63
7.5	0.72
8.0	0.83
8.5	1.09
9.0	0.98
9.5	0.85

Effect of Concentration of Dye Solution

The effect of concentration variation of azure A dye on its rate of degradation has been observed in the range from 1.5×10^{-5} M to 4.5×10^{-5} M and keeping all parameters to be the same. The results are given in Table 4 and Figure 5. It has been observed that the rate of degradation increases with increasing concentration of dye up to 2.7×10^{-5} M. Further increase in concentration beyond this limit results in a decrease in degradation rate. This may be explained on the basis that on increasing the concentration of dye, the reaction rate increases as more molecules of dyes were available but a further increase in concentration results appearing an internal filter effect which does not permit sufficient

Table 4. Effect of dye concentration on photocatalytic degradation of azure A:

pH=8.5, Composite=0.10 gm, Light intensity = 60.0 mWcm^{-2}	
[Azure A] × 10^{-5} M	Rate constant (k) × 10^{-4}(sec^{-1})
1.5	0.41
1.7	0.49
2.0	0.61
2.3	0.76
2.5	0.95
2.7	1.09
3.0	1.01
3.3	0.86
3.5	0.73
4.0	0.57
4.3	0.51
4.5	0.43

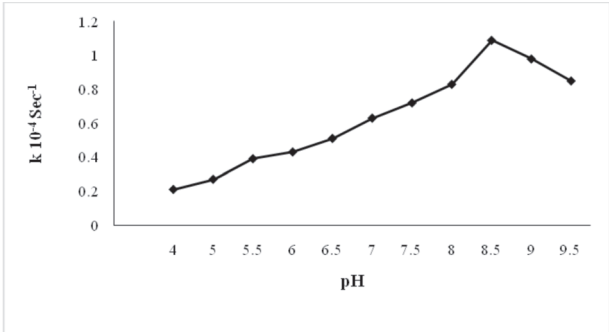

Fig. 4. Effect of pH on photocatalytic degradation of azure A

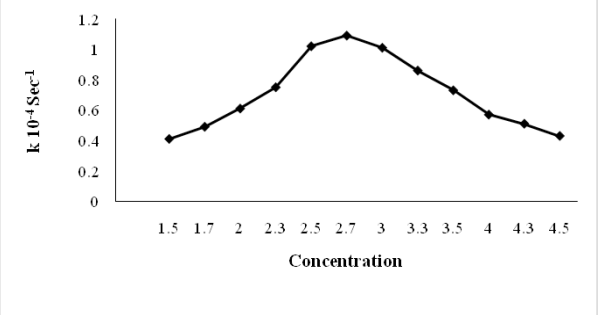

Fig. 5. Effect of dye concentration on photocatalytic degradation of azure A

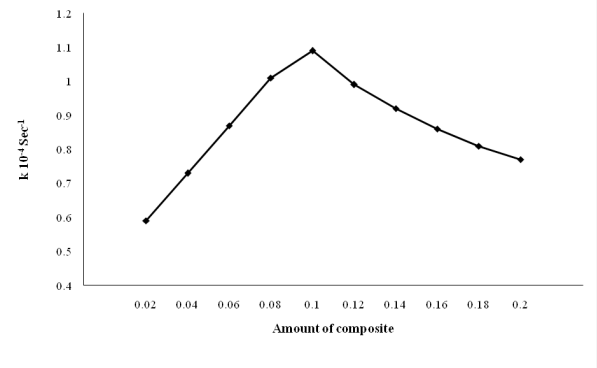

Fig. 6. Effect of amount of composite on photocatalytic degradation of azure A

amount of light to reach the surface of the photocatalyst thus, decreasing the rate of photocatalytic degradation of azure A dye occurs.

Effect of Amount of Photocatalyst

The amount of semiconductor may also affect the rate of degradation of dye and hence, different amounts of semiconductor were taken. The results are reported in Table 5 and Figure 6. It was observed that there was an increase in the rate of photocatalytic degradation with an increase in the amount of semiconductor up to 0.10 g, but after the amount 0.10 g of photocatalyst, it becomes almost constant. Beyond this point, the rate of reaction becomes virtually constant. This behaviour may be explained by the fact that with an increase the amount of catalyst, the exposed surface area of catalyst will increase. It may be considered like a saturation point; above which, any increase in the amount of semiconductor had negligible or no effect on the rate of photocatalytic degradation of dye, as an increase in the amount of semiconductor after this saturation point would only increase the thickness of the layer at the bottom of the reaction vessel. This was confirmed by taking reaction vessels of different dimensions. The saturation point shifted to the higher range for larger vessels, while the reverse was true for smaller vessels.

Table 5. Effect of amount of catalyst on photocatalytic degradation of azure A:

pH=8.5, Concentration [azure A]=2.7×10^{-5} M, Light intensity=60.0 $mWcm^{-2}$

Photocatalyst (gm)	Rate constant (k) × 10^{-4}(sec^{-1})
0.02	0.59
0.04	0.73
0.06	0.87
0.08	1.01
0.10	1.09
0.12	0.99
0.14	0.92
0.16	0.86
0.18	0.81
0.20	0.77

Effect of Intensity of Light

The variation in light intensity may also affect the rate of photocatalytic degradation of dye. Hence, the distance between the light source and the exposed surface area was varied. The intensity of light at each distance was measured using Suryamapi (CEL Model SM201). The results are reported in Table 6 and Figure 7. The results showed that with increasing light intensity, the rate of reaction increases and maximum rates were found at 60.0mWcm^{-2} because any increase in the light intensity will increase the number of photons striking per unit area of semiconductor. However, by increasing the intensity above 60.0 $mWcm^{-2}$, there was a little decrease in the rate. This may be due to some thermal reactions.

Mechanism

On the basis of the experimental observations, a

Table 6. Effect of light intensity on photocatalytic degradation of azure A:

pH=8.5, Concentration [azure A]=2.7×10^{-5} M, Composite=0.10 gm

Light intensity ($mW\ cm^{-2}$)	Rate constant (k) × 10^{-4}(sec^{-1})
20	0.47
30	0.61
40	0.84
50	0.93
60	1.09
70	0.89

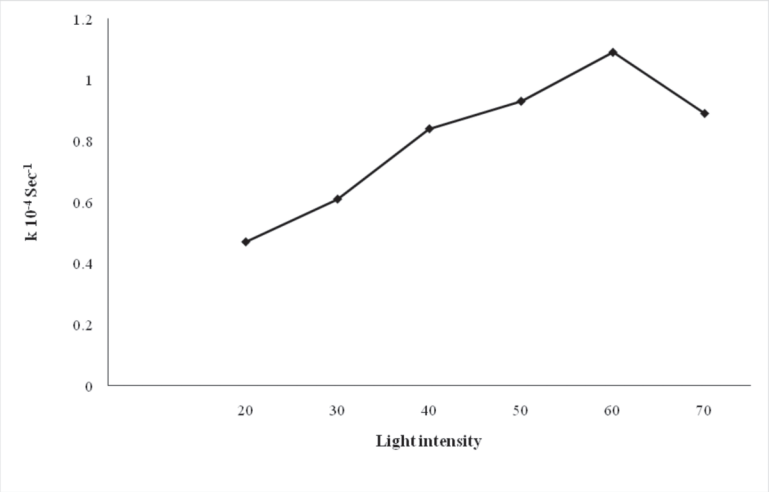

Fig. 7. Effect of light intensity on photocatalytic degradation of azure A

tentative mechanism for photocatalytic degradation of azure A dye has been proposed in the presence of strontium chromate – zinc oxide composite as follows:

Azure A absorbs radiation of suitable wavelength giving rise to its excited first singlet state after that intersystem crossing (ISC) to the triplet state. The semiconductor strontium chromate – zinc oxide also absorbs light energy to excite its electron from the valence band (VB) to conducting band (CB); thus, leaving behind a hole. This hole may abstract an electron from hydroxyl ions to generate hydroxyl radicals. These hydroxyl radicals will then oxidize the dye to its leuco form, which may ultimately degrade to products.

Carrying out the reaction in the presence of •OH radical scavenger, 2-propanol, the reaction rates were unaffected. This unambiguously shows that there was no involvement of •OH radicals in the reactions as an active oxidizing species.

CONCLUSION

Strontium chromate photocatalyst was synthesized via precipitation method. Strontium chromate – zinc oxide composite prepared by mechanical method further characterized to know its morphology. This composite was used for photocatalytic degradation of azure A dye. The experimental results showed that photocatalytic degradation efficiency of azure A was affected by pH, concentration of dye solution, amount of semiconductor and intensity of light. The use of the photocatalyst can be analyzed for the degradation of various pollutants.

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Conflict of Interest

The authors declare no conflict of interest.

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