



Nanocomposites - Electrochemical Oxidation of Organic Compounds

Sakshi Mokashi¹, Anil Sharma²

¹Research Scholar, Kalinga, University, Raipur, Chattisgarh, -492001, India, Assistant Professor, SVPM College of Engineering, Malegaon, Baramati Maharashtra, India.

²Professor, Kalinga, University, Raipur, Chattisgarh- 492001, India.

Emails: ssmokashi@engg.svpm.org.in¹, registrar@kalingauniversity.ac.in²

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Abstract

Electrochemical regeneration is very suitable approach for industrial effluents, but it suffers from low regeneration efficiency due to side reactions like oxygen evolution, as well as oxidation of the adsorbent. Utilizing PVA films through a solution casting method, incorporating varying concentrations of Cr₂O₃ nanoparticles to evaluate their effects on the material properties. The measurement of the viscosity of the PVA- nanoparticle solution shows that the viscosity increases with the addition of Cr₂O₃, indicating that the viscosity is related to the interaction between the nanoparticles and PVA chains.

1. Introduction

Adsorption is a promising approach for the removal of soluble and insoluble organics from wastewater effluents. Nevertheless, due to constraints that limit disposal, such as the toxicity of the adsorbate and the high cost of replacing adsorbent, managing the loaded adsorbent may be difficult. Recovering the adsorptive ability of the loaded adsorbents by electrochemical regeneration has shown promising results. Many reports in the literature [17, 18] show attempts for synthesis of metal nanoparticles based polymer nanocomposites, with the possibility of variation in their properties for their applications. in high performance capacitors, conductive inks, and other. , Hassan et al., has reported the synthesis of nano-sized Cr₂O₃ by sol-gel method and mixed with PVA to produce nanocomposites films. [1-5]

2. Nanoscience and Nanotechnology

Several of the most important technologies of the 21st century rely on developments in nanoscience and nanotechnology. It's the creation and application of substances at the lowest imaginable dimensions. All of the other scientific fields can make use of these materials [1]: chemistry, physics,

materials science, biology, and engineering. Nanotechnology operates on a scale below which human perception typically operates. One nanometer is equivalent to one one-hundred-and-ninety-ninth of a meter (nm). The following are examples of common occurrences:

- A human hair is around 80,000 nanometers in diameter, whereas a red blood cell is 7,000 nanometers.
- Because an inch is equal to 25,400,000 nanometers and a water molecule is only around 0.3 nanometers in diameter,
- The thickness of a sheet of paper is around 100,000 nanometers; on the off chance that a marble were a nanometer, the breadth of the Earth would be one meter.

Nanomaterials' altered characteristics may be attributed to the fact that their surface area is substantially higher than that of the same quantity of material generated in a bigger form. The strength and electrical characteristics of the materials will be altered, and their reactivity to chemicals will rise. Quantum effects, which have an influence on the

electrical, optical, and magnetic characteristics of materials, may become more prominent near the lower end of the nanoscale. The focus of nanoscience and nanotechnology is on the study of phenomena with sizes between 1 and 100 nm. Nanoscale materials in every one of the three aspects are practical to make, including slight movies, layers, and coatings from one viewpoint, nanotubes, strands, and nanowires on the other (for example, quantum dots, nanoparticles, nanorings, nanoshells, microcapsules). [6-10]

2.1 Metal Oxide Nanocomposites

Hazardous industrial effluents, which are not easily biodegradable and are disposed of improperly, have recently become the main contributors of environmental contaminants. Industries utilize a wide range of chemical goods in their many sub-sectors, resulting in waste water with a highly varied level of pollution. For textile dyeing, significant quantities of dyes from chemically diverse groups, including basic, diazo, azo, acidic, disperse, and anthraquinone-based dyes, have been utilized. A significant fraction of these colors are discharged into the environment as wastewater. When colored textile waste is discharged into bodies of water, the amount of dissolved oxygen decreases, creating hazardous circumstances for aquatic life. As well as hurting plants and creatures, contaminated water is exceptionally awful for the environment. In the material, food, plastic, paper, printing, drug, and corrective areas, colors are frequently used as shading specialists. Since the extra tones are released into the water, there is ecological concern [3]. Consistently, various organizations make north of 10,000 unique colors adding up to around 0.7 million tons for use in different techniques. Natural mixtures frequently highlight replacement bunches like azo, nitro, and sulpho, convoluted fragrant sub-atomic designs, and an engineered beginning [16, 18]. By far most of colors are impervious to oxidation and light. They stay in the water, keep daylight from entering the stream, decrease the photosynthetic reaction, slow the improvement of sea-going plants and natural life, and reduce the stream's worth as a sporting facility. These bright substances are harmful and malignant growth causing [4]. To meet customer demands for variety, style, dealing with, giving wanted characteristics, and so on a wide assortment of synthetics in colossal sums are used

in material wet handling. A portion of these substances, including colors and completing mixtures, remain joined to the materials, yet a huge part of these substances stay in the handled water, dirtying the water. Figure 1 shows an information/yield examination for a wet handling unit.

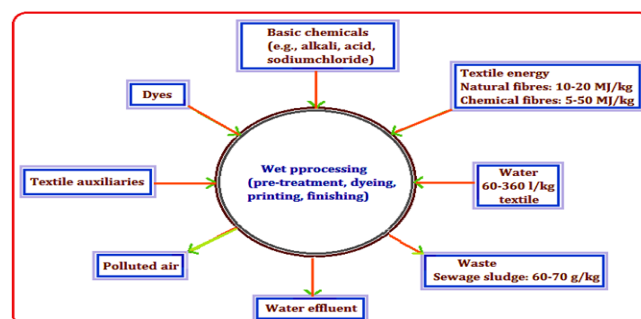


Figure 1 Analyzing the Inputs and Outputs of the Textile Finishing Process

The fundamental issue with conventional methods is that they need further treatment or disposal of industrial effluents as a result of their reliance on phase-transfer technologies. Although biological treatments (bioremediation) are less costly in the long run, they also take a long time until the effluent is once again considered safe. They would also generate a substantial quantity of sludge, the most majority of which is not recyclable. Using semiconductor photocatalysis, it may be possible to safely and effectively remove certain contaminants, most notably dyes, without negatively impacting the environment. For the oxidative obliteration of a great many natural mixtures, the semiconductors ZnO and TiO₂ have demonstrated to be the best photocatalysts to date [5]. As heterogeneous photocatalysis is a more productive oxidation process, it has gotten more noteworthy consideration. The utilization of nanosized semiconductors as photocatalysis to start interfacial redox processes has accumulated critical consideration on the grounds that to the exceptional physicochemical properties coming about because of their nanosized aspects and high surface to volume proportion. The metal oxide semiconductors TiO₂, ZnO, WO₃, SrTiO₃, and Fe₂O₃ have all been demonstrated to be powerful photocatalysts. High level oxidative cycles (AOPs) have gotten the interest of researchers because of their improved proficiency and life expectancy. These techniques

produce very responsive hydroxyl revolutionaries utilizing solid oxidizing specialists (O_3 , H_2O_2) or potentially impetuses (Fe, TiO_2) regardless of an illumination source (Goodness). Organic molecules in industrial effluents may be mineralized by the radicals. Heterogeneous photocatalysis is one of several AOPs that has recently attracted a lot of interest, particularly for its potential to be used in the textile industry's effluent degradation. One potential use for inorganic semiconductors is in the photocatalytic destruction of organic contaminants. Electron-hole pairs may be generated by exposing semiconductor particles to light at high enough energies. As these pairs reach the particle's surface, they may react with molecules that have been adsorbed to produce free radicals. Highly reactive free radicals like carbon dioxide (CO_2), water (H_2O), sulfur dioxide (SO_2), and simple mineral acids may degrade organic contaminants [6].

1.1 Chemical Oxygen Demand (COD)

Water's organic molecule concentration is often estimated using a surrogate, the chemical oxygen demand test. As COD may be used to quantify organic contaminants in both surface water (such as lakes) and wastewater, it provides valuable insight into water quality. All water quality management plans should include COD testing since it is a reliable indication of water quality. For 1 L solutions, the oxygen consumption rate is written as milligrams per liter (mg/L) or parts per million (ppm). The chemical oxygen demand (COD) test is based on the fact that under acidic circumstances, almost all organic molecules may be completely oxidized to carbon dioxide (CO_2), ammonia (NH_3), and water (H_2O). [11-13]

1.2 Potassiumdichromatemethod ($K_2Cr_2O_7$)

A water sample is treated with potassium dichromate as an oxidant and then digested at high heat in acidic conditions for two hours. Using silver sulfate as a catalyst, mercuric sulfate may undergo a chemical reaction that results in mercuric chloride. The amount of electrons required to convert Cr^{6+} to Cr^{3+} is a surrogate measure of oxidation that may be taken during digestion. This may be achieved by either titration or spectrophotometry. In an acidic environment, potassium dichromate becomes a potent oxidant (Sharpness is normally accomplished by the expansion of sulfuric corrosive). Generally speaking, a 0.25 N arrangement of $K_2Cr_2O_7$ is

utilized to decide COD, in spite of the fact that for tests with a COD of 50 mg/L, a 0.15 N arrangement works better. As with other redox reactions, the oxidation of organic compounds in the water sample results in the production of Cr^{3+} and the reduction of $K_2Cr_2O_7$. Indirect analysis of the organic content of a water sample may be used to determine the quantity of Cr^{3+} after oxidation has taken place.

1.1 Measurement of Excess

$K_2Cr_2O_7$ (or another oxidizing chemical) must be used in large doses to completely oxidize all organic matter. After the oxidation process is complete, the amount of Cr^{3+} may be determined by gauging the concentration of $K_2Cr_2O_7$ left behind. Ferrous ammonium sulfate (FAS) is titrated against the excess $K_2Cr_2O_7$ after all of the oxidizing agent has been converted to Cr^{3+} . An Indicator of Oxidation and Reduction At this point in the titration process, ferroin is often added. The Ferroin indicator's color goes from blue-green to reddish-brown after the surplus dichromate has been removed. Adding FAS to a sample makes it seem as if additional $K_2Cr_2O_7$ has been added to the mixture. The indicator's color will progress from green to blue to reddish brown by the time the titration is complete.

1.2 Calculations

COD is determined using the following formula:

$$COD = \frac{8000(b - s)n}{\text{sample volume}}$$

Where: b = FAS volume used in the blank sample,
 s = FAS volume in the original sample, and
 n = FAS normality.

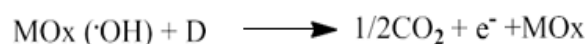
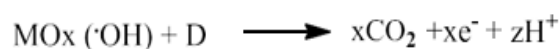
If volumes are always reported in milliliters, the COD calculation output will be in mg/L.

2. Electrochemical Oxidation and Degradation

All living things depend on water to stay alive. The agricultural, cattle-raising, tourism, medicinal, and industrial sectors may all benefit from its usage as well as the obvious human consumption. Water pollution is anticipated to worsen as industrialization and urbanization proceed at a faster rate, releasing more garbage into the environment through waterways. Water contaminated with chemicals including dyes, herbicides, insecticides, cosmetics, and medications has been the subject of several studies [7]. One of the most perceptible marks of water pollution is the presence of colors in shaded effluents. Color and the toxicity of some of the fundamental chemicals used to synthesize colors

may cause dye molecules to get unwarranted attention, despite the fact that they are not often the major source (such as some aromatic amines). While dyestuffs are frequently discovered in effluents at quantities lower than any other component reported in these wastewaters [55-57], they nonetheless pose a substantial aesthetic challenge in wastewater disposal. Although the textile industry makes use of many different technologies, enormous amounts of water are required throughout the dyeing, mending, and washing processes. Textile production wastewater often includes suspended particulates, a high concentration of dissolved solids, and unreacted dyestuffs and auxiliary chemicals. The opacity and gas solubility of water are drastically altered by dye concentrations as low as 10-20 mg/L. In the textile business, reactive dyes account for around half of the dye market (the azo group is used as chromophore 70% of the time, followed by the anthraquinone group). Before releasing toxic water into the environment, it is crucial to cleanse the water supply. That's why it's crucial to use the environmentally friendly method of electrochemical oxidation and disintegration of organic compounds. Degradation of organic compounds by electrochemistry has potential as a method for eliminating biodegradable contaminants to treat wastewater from color houses, electrochemical strategies for disposing of natural pollutants and bringing down the COD and BOD. If the statutory concentration limitations cannot be satisfied by more conventional means, or if there are substantial economic benefits to be had from doing so, then the alternatives must be used. This method is significantly easier to implement than conventional wastewater treatment [61]. The electrochemical process consists of two fundamental phases (i.e., direct and indirect). There are no intermediary intermediates in direct oxidation, which uses inert electrodes. In indirect oxidation, an electrochemically produced redox agent mediates the transport of electrons between the electrode and the substrate. After generating hydroxyl radicals ($\bullet\text{OH}$) in wastewater treatment, all that is left is water, carbon dioxide, and some inorganic salts. As it does not produce sludge and may potentially operate under moderate temperatures, the electrochemical technique to treating textile waste water is cost-effective and low-impact. This technique eliminates the dye and lowers the COD in

the effluent by oxidizing the dye at the anode. It's possible that organic colors may be oxidized using the electrochemical approach.



Where,

M = anode site and

D = dye molecule.

This points to the production of oxidized intermediates, whose continuing breakdown eventually kills the dye molecule. Szpyrkowicz et al. examined the electrochemical debasement of color gushing utilizing a Ti/Pt-Iranode, and they observed that circuitous oxidation within the sight of chloride particles was liable for the decline in contaminations. Comparable oxidation techniques for material color effluents are given by Vijayaraghavan et al. [8], who use graphite as the anode and create hypochlorous corrosive on location. Electrochemical debasement of corrosive green color in wastewater dyestuff arrangements has been concentrated by N.M. Abu Ghalwa et al., who utilized a titanium cathode covered with lead oxide. Quick and productive expulsion of sulfur dark and corrosive green colors from watery arrangements at low ebb and flow densities and temperatures was noticed utilizing the combined PbO_2/Ti anode. Electrochemical debasement of phenol by $\text{Ti}/\text{RuO}_2\text{-Pt}$ and $\text{Ti}/\text{IrO}_2\text{-Pt}$ cathodes is portrayed by Miao Li et al. $\text{Ti}/\text{RuO}_2\text{-Pt}$ and $\text{Ti}/\text{IrO}_2\text{-Pt}$ anodes' reactant movement toward phenol was examined concerning current thickness, NaCl measurements, and starting phenol fixation [9]. Research on the electrochemical corruption of mash and paper profluent was attempted by Poopanna Antony Soloman et al. concentrating on the impacts of a RuO_2 -covered titanium cathode on the electrochemical corruption of rural waste from the mash and paper industry [10].

3. Material and Methods

In our lab, we use biological and electrochemical approaches to produce chromium oxide nanoparticles in three distinct ways. After this, films containing nanocomposites of Cr_2O_3 and PVA were produced.

3.1 Viscosity measurements

Using an Ostwald viscometer, we measured the solution viscosities of pure PVA and PVA-Cr2O3 nanocomposite at varying concentrations created using three distinct procedures. The Ostwald viscometer is the most common device. Care must

be taken that all readings should be taken for constant volume of solution. Table 1 shows Samples of PVA-Cr2O3 Nano composites were produced at Varying Cr2O3 Concentrations and Their Viscosities Were Measured.

Table 1 Samples of PVA-Cr2O3 Nano composites were produced at Varying Cr2O3 Concentrations and Their Viscosities Were Measured

Concentration of Cr ₂ O ₃ C(g/dl)	Concentration Of PVA (g/dl)	Flow time,t (sec)	Relative viscosity $t/t_0=\eta_r$	Specific viscosity η_{sp}/C	Reduced viscosity η_{sp}/C (dl/g)	$\ln \eta_r$	Inherent viscosity $\ln \eta_r/C$ (dl/g)	Intrinsic viscosity $[\eta](dl/g)$
0.0119	0.0008	146.17	1.0592	0.0592	74.00	0.0575	71.87	73.25
	0.0012	155.98	1.0892	0.0892	74.33	0.0854	71.16	
	0.0016	166.36	1.1195	0.1195	74.68	0.1128	70.50	
0.0238	0.0008	150.10	1.0876	0.0876	109.50	0.0839	104.87	106.20
	0.0012	162.29	1.1333	0.1333	111.08	0.1251	104.25	
	0.0016	175.41	1.1804	0.1804	112.75	0.1658	103.62	
0.0475	0.0008	155.00	1.1231	0.1231	153.87	0.1160	145.00	147.20
	0.0012	170.14	1.1881	0.1881	156.75	0.1723	143.58	
	0.0016	186.72	1.2565	0.2565	160.31	0.0228	142.68	

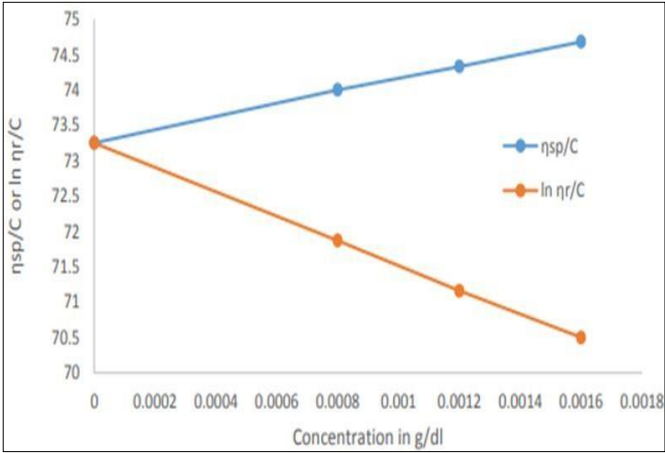


Figure 2 Plots of η_{sp}/C Versus C and $\ln \eta_r/C$

In figure 2, C for PVA- Cr2O3 nano composite samples of method1 with 0.0119g/dl of Cr2O3 nanoparticles.

Conclusion

Dye pollution in colorful effluents is a very visible sign of water contamination. Despite the fact that they are not often the primary source, dye molecules may garner a lot of attention because of their vivid hues and the toxicity of some of the basic compounds used to create colors (such as some

aromatic amines).At room temperature, it has been observed that an increase in the nanoparticles increases the intrinsic viscosity and electrical conductivity of PVA- Cr2O3 nanocomposites

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