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Comparative Study of the Effect of Hydrogen Peroxide, UV Light and Combination of both on Pharmaceutical Wastewater

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Abstract: *The wastewater formed in various processes in the pharmaceutical industry is considered environmentally delinquent because of its unsafe and potential for influences the aquatic ecology. Pharmaceutical wastewater comprises a high volume of organic matter, expired drugs, API, etc., that causes a lot of damage to the ecology. There are still trace quantities of suspended solids and dissolved organic material, even after secondary treatment. To advance the excellence of pharmaceutical wastewater sewage, advanced treatment is vital. Catalysts contribute extremely to the industrial revolution concerning reaction rates and a decrease in manufacturing costs. Widespread research has been recognized on numerous industrial catalyses in the previous few eras. The performance of catalysts is inclined by numerous parameters, counting synthesis approaches. In this study, a heterogenous copper-based catalyst is used which is prepared via the sol-gel method to understand its performance in the treatment of pharmaceutical wastewater. The characterization of the catalyst was done by analytical techniques. The treatment of synthetic pharmaceutical wastewater was carried out at the following operation conditions: different pH, oxidant dose (H_2O_2) of 1 ml – 5 ml, and the absorbance of the sample was measured using a UV spectrometer. The wavelength used was from 200nm to 1000 nm.*

Keywords: *Pharmaceutical wastewater, UV spectrometer, UV light, Catalyst, COD*

I. INTRODUCTION

When water is unfit for a specific use such as drinking, fishing or swimming then the water is termed wastewater. Wastewater is released from all sorts of industries, pharmaceuticals, households, etc. As clean water is used for every purpose so it is necessary to treat the wastewater from the sources that produce it in high quantities. Natural conditions also affect water but polluted water happens due to human activity. The lack of clean water sources has led to wastewater treatment and strict standards in their treatment. There is an increase in demand for clean for sanitation, drinking, irrigation, industrial use, etc. one of the high-tech and promising industries is the pharmaceutical industry. While being a high-tech and promising industry it leads to a lot of environmental problems. Pharmaceutical wastewater consists of organic matter in high amounts, suspended matter, dissolved matter, ammoniacal nitrogen, COD, BOD, color, toxicity, and other features.

There are 3 categories of effluent: home sewage, commercial sewage, and hurricane sewage. domestic sewage transmits used water from households and residences; it's also called sanitary sewage. Industrial sewage is used water from industrial or chemical developments. Storm sewage, or stormwater, is overflow from precipitation that is collected in a system of pipes or open channels. These are the elements that are mostly present in the pharmaceutical wastewater Cooper, Cobalt, Cadmium, Nickel, Lead, Zinc, Iron, silane, derivative of nicotinamide, Mercury, Oleic acid, etc.

In recent years, drug consumption has increased due to the increase in diseases. This helped the pharmaceutical industry to grow, in this growth, they created huge amounts of wastewater. This wastewater is harmful to the environment, people and animals. Therefore, it is necessary to clean wastewater before it is released into water bodies. Wastewater treatment can be done by a physical process, chemical, or biological process. Pharmaceutical wastewater has a high concentration of COD and a low concentration of BOD, so chemical and physical treatment will be much more effective than biological treatment. Electrochemical treatment to remove contaminants is also an effective treatment. There are many techniques for treating pharmaceutical wastewater, such as biological treatment, coagulation, sedimentation, flotation, an adsorption method, advanced oxidation process, per ozonation, direct photolysis, ozonation, chlorination, activated carbon, membrane process, etc. One of the leading and emerging methods is advanced oxidation treatment together with a catalyst that effectively cleans wastewater.

Accumulation of chemical agents to effluents, dispersing them all around by quick mixing, so that the steady pollutants are converted into unsteady pollutants and precipitable materials is coagulation. It's far a complicated mechanism. The key is in what way one can squeeze and eliminate water hydrophilic colloids in the advanced oxidation treatment. Sedimentation this method is done after the completion of coagulation. The pollutants that are denser than water is allowed to settle down with the help of gravity. Both are easy techniques but is difficult to eliminate the dissolved organic matter. Flotation also eliminates the suspended solids of the effluent. The technology distinguishing is creating a high amount of small bubbles by inserting air into wastewater, creating free floc with lesser density than wastewater. So, it floats and can be collected from the surface of the wastewater.

Activated carbon, as a type of adsorbent, has multiple advantages. It has a huge specific surface area, multilevel pore assembly, great adsorption capacity, and stable chemical properties. Therefore, it is extensively used as an adsorbent or catalyst transporter to eliminate pollutants. In industrial effluent handling, activated carbon is used for effluent, which is lethal and tough to accomplish discharge values. It is a significant technique for the advanced treatment of pharmaceutical effluent as well. Activated carbon adsorption can be categorized as physical adsorption and chemical adsorption. This method is broadly used for advanced treatment as it can be recycled, it's an improved treatment effect and extensive appropriateness.

The advanced oxidation process (AOPs), by forming free radicals can oxidize the pollutants. But, by common oxidization methods, these types of pollutants cannot be degraded. In Wet Air Oxidation (WAO) in this technique air or oxygen is used as the oxidant, at high temperatures and high pressure, it decomposes the organic matter into small molecules or inorganic molecules. Supercritical Water Oxidation (SCWO) is a reaction in supercritical water between organic pollutants and dissolved oxygen. At high pressure and temperature, supercritical water, organic matter, and air become a homogenous mixture as they mix completely. The Fenton system was primarily used in the organic blend, and with the development of one's understanding of it, the technique was progressively useful to industrial wastewater treatment.

Photocatalytic oxidation is another method that is used in the treatment of wastewater by the amalgamation of oxidant and UV radiation. This technique is also called ultraviolet photocatalytic oxidation. In this method, there is a production of free radicals that can oxidize the tough to decompose the organic matter.

Ultrasound oxidation is a chemical and physical degradation process, of organic matter, which is based on ultrasound cavitation outcome and its output of chemical and physical changes. Pyrolysis, free radical oxidation, and supercritical water oxidation are the three ways that are used in this technique.

Electrochemical oxidation is basically when the reactant will be oxidized at the anode as they lose its electrons. In the same way, the reactant will be reduced at the cathode as they lose its electrons. It is an environmentally friendly method of wastewater treatment with great advantages as compared to other techniques. The electrochemical method is the usage of electrochemical to eliminate toxic and destructive materials that are present in the water.

Ozonation is considered to be an effective method of wastewater treatment as a disinfectant and oxidant. Ozone is used as an oxidant in acidic conditions and depends on free radicals in alkaline or neutral conditions. In this technique, the organic matter can be degraded and oxidized effortlessly.

Another technique used for wastewater treatment is membrane separation, in this, a semipermeable membrane is used as a separating media to the selectivity of the water. Many techniques come under membrane separation. Microfiltration is the traditional filtration, that is done on a particular size sieve by passing the water at high pressure through it. Ultrafiltration is that it produces a pressure difference on both sides of the membrane so that the small molecules and inorganic salts get enclosed in the pores. Reverse osmosis in this membrane can be of two types, either aromatic polyamide or cellulose ester. Plate, tube and frame, roll, and hollow fiber type are its parts. Nanofiltration was possible with the help of this technique. RO can filter out a variety of dissolved impurities and organic matter and dissolved inorganic matter. Electrodialysis is a combined process of dialysis fusion and an electrolytic process. Dissolved salts in the wastewater have cations and anions both move to the cathode and anode, once a DC electric field is applied.

Under the advanced oxidation process, we have carried out the Fenton process in this treatment. The catalyst plays an important role along with H₂O₂ in this treatment. Catalyst preparation can be done using different methods like the sol-gel method, wet impregnation method, precipitation method, chemical deposition method, ion exchange method, hydrothermal and solvothermal method, etc. In the research work, the catalyst is prepared using the sol-gel method. The sol-gel technique is a greater chemical approach (moist chemical approach) for the synthesis of numerous nanostructures, particularly steel oxide nanoparticles. In this approach, the molecular precursor (usually metal alkoxide) is dissolved in water or alcohol and transformed into gel through heating and stirring through hydrolysis/alcoholization.

Catalyst preparation can be done by different heterogeneous methods such as sol-gel, wet impregnation, ion exchange, hydrothermal and solvothermal method, and deposition precipitation method. Catalyst helps the treatment to be effective and it can be recovered using different techniques. At times, it can be reused without losing its activity. The catalyst precipitation method affects physiochemical factors and the overall activity of the catalyst. The sol-gel process includes the solidified formation of precursor from a solution by continuous conversion. It is the most convenient method that controls the properties of the product such as its texture, composition, structure, and homogeneity. Sol-gel is an upfront way for the preparation of several constituents, and there are several samples of the practices of sol-gel for the preparation of catalysts. For example, hydrosols are shaped, by the precipitation of hydrous oxides, which are sol elements that aggregate prolonged further to either arrange as gel or flocculates. There are two divisions under sol-gel, first is the aqueous sol-gel method. In this using solvent, obtain the metal oxide and it required oxygen for formation which is provided by a water molecule. The second is the non-aqueous sol-gel method. Here precursors are used and they can be alcohol, aldehyde, and ketone as they behave as oxygen suppliers during the preparation of metal oxide.

The wet impregnation method is where on solid support (surface is high) a fixed volume of active phase metal precursor is made to contact. This can help us to prepare mixed and supported catalysts for specific metal loading. There are three essential steps: i. with the help of a metal precursor the support material is impregnation, ii. At high temperatures, the solvent is dried and evaporated, iii. To produce catalysts, specific temperature reduction should be done in the designated environment. The most conveniently used solvent is water for inorganic salt as it has high solubility. To avoid premature decomposition, organic solvents are also used in the bulk phase. Calcination and reduction are the final process technique to obtain the final product.

The ion-Exchange technique consists of a solution that has cationic or anionic metal precursors made to contact with a suspended solid material for a longer duration of time with a specific pH. Following this, the catalyst is separated by drying and calcination. This method provides high strength to the catalyst and can be used in various processes. This technique is communally used in hydrotalcite, zeolite preparation, and pillared clay and for the molding of progressive materials. It also helps in making a variety of layered structures. The ion exchange method can change the catalyst size and the catalytic activity to travel into internal pores. For a particular catalytic process, the catalyst can be modified so that it hits the target molecule.

The hydrothermal and solvothermal method has gained popularity in the past 10 years. A closed reaction vessel operation promotes the chemical reaction/decomposition of precursor and solvent while keeping the temperature higher than the solvent's boiling point. In this method, the pressure in the vessel is autogenous, which depends on either the pressure of filling the reaction vessel or the compression of the reaction medium during the synthesis. The main advantage of hydrothermal synthesis is that this process can be hybridized with other processes to improve the reaction kinetics and capacity to synthesize new materials. Therefore, hydrothermal synthesis can be hybridized with microwaves, electrochemistry, ultrasound, mechanochemistry, optical radiation, hot pressing, etc.

II. Materials and method

A. Materials

Pharmaceutical wastewater was prepared from an Ibuprofen tablet of 500 mg. The quality of the wastewater was maintained by storing it in a cold storage unit. The oxidizing agent used was H_2O_2 (30% w/v) and the pH of the wastewater was adjusted by H_2SO_4 and 0.1 N NaOH in the experiment as per requirement. A magnetic stirrer was used for homogenous mixing in the wastewater. UV reactor was used for the second set of experiment.

B. Analysis

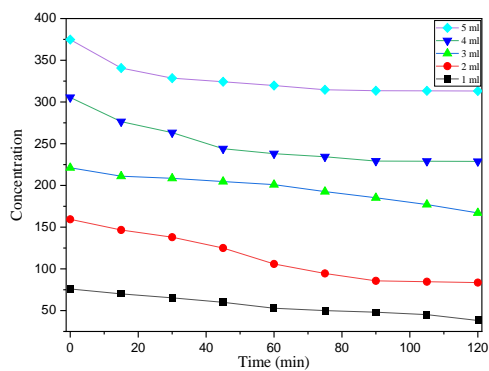
The Analysis was carried out on 100 ml of pharmaceutical wastewater. The pH of the solution was checked using pH meter and maintained its acidic condition using H_2SO_4 solution. First the experiment is done for 1 ml H_2O_2 and then the beaker was kept on a magnetic stirrer for 2 hours and sample was drawn from it at every 15 mins. Then the absorbance was measured of the collected sample using UV spectrometer. Similarly, was done for 2 ml, 3 ml, 4 ml and 5 ml of H_2O_2 . Later, the desired amount of Hydrogen Peroxide in the sample was exposed to UV reactor for the further experiments and sample was collected and absorbance was measured.

III. RESULT AND DISCUSSION

A. Effect of H_2O_2 on pharmaceutical wastewater

The effect of Hydrogen peroxide on pharmaceutical wastewater after 2 hours was analysed using UV spectrometer. The below graph shows the decrease in concentration with respect to time and the amount of H_2O_2 added.

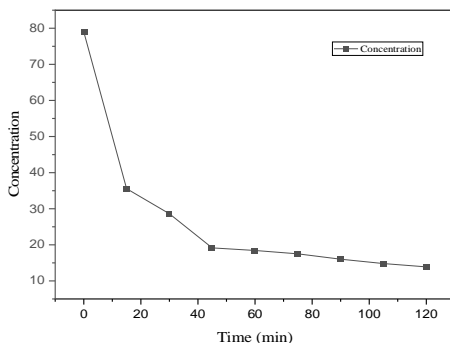
As we increase the volume of H_2O_2 from 1 ml to 5 ml the degradation rate increases. The H_2O_2 is a strong oxidizing agent, it oxidizes both organic and inorganic pollutants therefore it can be used for the purification of wastewater.



3.1.1. Effect of H_2O_2 on Pharmaceutical wastewater

B. Effect of UV Light on Pharmaceutical Wastewater

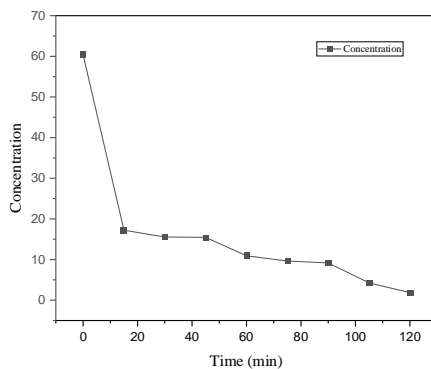
The effect of Ultraviolet light on the pharmaceutical wastewater after 2 hours stirring was analysed using UV spectrometer. Photodegradation is the process that happens in UV light. Here, the degradation rate is comparatively higher than H_2O_2 . UV light can break down polymer chains, can produce free radicals, reduce the weight of the compound present and also deteriorate its properties making them less harmful or useless after a certain point of time.



3.2.1 Graph of effect of UV light

C. Effect of H_2O_2 and UV light on pharmaceutical wastewater

The effect of UV and H_2O_2 process combined gives a better result than using them individually. Both processes combined can oxidize and break down harmful pollutants into useless products. Hydrogen peroxide can also control the odour of the wastewater. At 0 min the concentration was high, just after 15 min the concentration dropped and the process of degradation started. By the end of 120 min, the waste is treated and free from harmful substances.



3.3.1. Graph of effect of H_2O_2 and UV light

IV. CONCLUSION

The study is a combination of the conventional method and the green method. UV light is a conventional method and hydrogen peroxide is a greener method. The above experiment was conducted with H₂O₂ and UV light for the treatment of pharmaceutical wastewater, it was found that when combined, it gives better degradation results. When the wastewater was treated only with hydrogen peroxide it gave a maximum degradation of 84%, and a maximum degradation of 87% using only UV light and when the process was combined it gave a maximum degradation of 97%. This method is an easy process and it can degrade the higher-concentration compounds into harmless products efficiently. As compared to other processes, this can be easily carried out on the laboratory scale and then on a larger scale.

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