



A Study on Treatment of Wastewater using Electrochemical Oxidation Techniques

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Abstract: Electrochemical oxidation process has gained increasing interest due to its exceptional technical features to eliminate a wide range of pollutants exist in various types of wastewaters, e.g., refractory organic matter, nitrogen species, microorganisms, etc. Serve as a clean, adaptable and powerful tool in removing pollutants, this review paper focuses on the fundamental mechanisms of electrochemical oxidation process and provides discussions on the possible applications in wastewater treatment. Electrochemical technique is suitable for the removal of various pollutants from industrial wastewater. The effect of electrolytic treatment on the properties of different effluents was evaluated. Three different electrodes namely iron, aluminium and steel were used. Three factors pH, voltage and time were varied in each experiment and the results were evaluated on the basis of COD and metal removal efficiency.

Keywords: Wastewater, Electrochemical, Oxidation, Treatment

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INTRODUCTION

The electrochemical oxidation process has also been described as a neat, flexible, and potent method for getting rid of organic wastewater contaminants. Additionally, the electrochemical approach has several major benefits due to its low energy consumption, wide applicability for the elimination of pollutants, and absence of the need for high pressures and temperatures to initiate the reaction. While electro-oxidation methods can be highly effective, their performance is highly reliant on the operating circumstances and the type of electrode materials used. Recently, electrochemical oxidation has been proposed as a means of satisfying the legal requirement to release wastewater within stringent limitations with health quality criteria. This method has been used effectively to cleanse wastewater from a variety of sources, such as municipal landfill and the food, textile, and tannery industries. Since electro-oxidation is both efficient and effective in disinfecting water, it is a viable option for use in recycling initiatives. However, treatment costs must be reduced before this technology can be implemented on a large basis. Therefore, using electrochemical oxidation with other technologies and running this process on renewable energy are two crucial measures needed to lower the overall operational cost.[1]

Electrochemical technologies have gained prominence again over the last two decades because to the improving quality of the world's drinking water supply and stricter environmental restrictions surrounding the disposal of wastewater. There are businesses that provide infrastructure for metal recoveries, water and wastewater treatment, oil and oil-in-water emulsion treatment, dairy and textile processing, and more. These days, electrochemical technologies are not only competitive with other methods in terms of price, but they also outperform them in terms of efficiency and size. Electrochemical methods may be the crucial

first step in treating wastewaters containing recalcitrant contaminants in certain cases. Electrochemical reactors for metal recovery, electrocoagulation, electro flotation, and electro oxidation are just few of the well-established methods I'll be discussing in this article. Electro photo oxidation and electro disinfection are examples of cutting-edge processes that will not be covered since they are still in their infancy. In addition, I won't be delving too deeply into the underlying sciences or mechanics, preferring instead to concentrate on the technology them selves.[2]

Wastewater Treatment Techniques

Historically, effluent from oil refineries has been treated using a four-step process: primary, intermediate, secondary, and tertiary. Two of the most important methods are the API separator and the Corrugated Plate Interceptor, which may either run in parallel or be curved. Dissolved air flotation/induced air flotation and equalization are two procedures that may be used between the two ends of the process. Biological treatment procedures, in their many iterations or combinations, fall under the category of secondary processes. These include conventional settling tanks, trickling filters, aerated lagoons, stabilization, and Rotating Biological Contactors. While Granular Activated Carbon adsorption, ozonation, and filtering all fall under the umbrella of "tertiary treatment,"[3]

The secondary oil removal system by dissolved air flotation unit is enhanced by the chemical precipitation of emulsified oil and sulfide. When sulfide concentrations are low, H₂O₂ may be used as a dosing alternative. All of the wasted caustic from the various units is mixed together in one equalization tank, and the regeneration effluent from the hydrocracker unit is collected in two equalization tanks and sent to the main treatment chain at a predetermined pace. The secondary treatment facilities include a traditional biological treatment system with two stages: the first is a random-fill plastic media bio-tower, and the second consists of an activated sludge extended aeration tank and a clarifier. After undergoing bio-treatment, the effluent is sent to a polishing treatment section that uses a pressure sand filter and granular activated carbon adsorption in a fixed bed to achieve a quality that is up to par for discharge. A designated area for treated process effluent receives the water that has passed through an activated carbon filter.

Electrochemical Technology

Water treatment efficiency and universal access to clean water have both been the subject of many studies in response to strict environmental pollution control and laws in many nations. Electrochemical technology is widely considered a clean and powerful technique for the elimination of organic contaminants in water, and it is one of the possible treatment approaches. There has now come a time when electrochemical technologies may be compared to one another not only in terms of price but also in terms of efficiency; indeed, in certain cases, they may be the only viable option for dealing with very stubborn contaminants.[4]

Need for Water and Wastewater Treatment

The ancient adage about water being more valuable than gold is gaining traction. It is generally known that increasing disparities between water availability and demand throughout the world are indicative of the unsustainable character of current consumption practices. The movement of people from rural areas to urban ones, climate change, and pollution are all key issues straining the world's ability to meet demand while also meeting supply. The demand is higher than the supply, which is the main problem. The

Population Reference Bureau reports that over the 20th century, worldwide water consumption increased by a factor of six—more than twice as fast as the global population rose during that time. This trend continues now as rapidly industrializing nations like China and India place increasing demands on their limited water supplies. Overall, it seems like the water shortage fears that have been around for a while may materialize.

Innovations in water and wastewater treatment are spurred on by the public's need for purified water. Less than one percent of the world's water is drinkable, while the rest is brackish, which is why wastewater treatment is so important. Therefore, there is a rising need for potable water. Due to the ever-increasing demand for potable water and the corresponding rise in wastewater production, the recycling of this once-neglected resource has become an absolute need. Therefore, there is a growing need for pollution-free water treatment methods that provide potable water with zero residual contaminants.

Applications of Electrochemical Oxidation in Wastewater Treatment

The efficacy of the electrochemical oxidation method in cleaning up a wide range of complex wastewaters that include a wide range of contaminants has been investigated. Recent years have also seen major developments in the electrochemical oxidation technique for the removal of micro-contaminants. Direct electrochemical processes or the development of killer chemicals like OH may inactivate bacteria in general. In water recovery and reuse, where effective removal of pathogens is vital to preserving public health, the combination of pollutant removal and disinfection of wastewater in a single treatment step is an appealing alternative.[5]

Research on the effectiveness of an electrochemical oxidation procedure for finishing up the treatment of effluent from slaughterhouses was conducted. Optimal conditions were found to be 220 mg/L influent COD, 30 mA/cm² current density, and 55 min reaction time. This resulted in a 96.8 percent reduction in color, an 81.3 percent reduction in BOD, and an 85.0 percent reduction in COD. Using electrochemical oxidation, we were able to remove 78% of the COD and 92% of the turbidity from the textile effluent under ideal operating circumstances. Leachate from landfills is electrochemically processed using graphite carbon electrodes. While operating at a 4 h reaction time and 79.9 mA/cm² current density, the initial COD of 1414 mg/L was removed by 68%. When compared with the results of another research. At a current density of 116.0 mA/cm² and 180 min of reaction, around 73% of COD was removed, 57% of TOC was removed, and 86% of color was removed.

Environmental effect

Colored effluents are a significant issue in textile wastewater treatment. Dye pollution is unsightly and may harm the environment even if it is not poisonous. Coloring the water prevents light from reaching marine life, which decreases its variety. [6]

One of India's rapidly expanding and most important export-oriented businesses, textile dyeing also happens to be one of the world's greatest consumers of water and a significant source of wastewater including a wide variety of refractory chemicals like dye, sizing agents, and dyeing aids. Therefore, it must be very cautious about discharging such effluent into the environment.

As a whole, the following is a summary of how pollution affects aquatic ecosystems:

i. Physical effects

There is often oil, grease, and dyestuff-derived color in industrial wastewaters. The turbidity and color of the water may be generated by both inorganic and organic particles in suspension. Loss of clarity due to increased turbidity and color lowers light penetration, which in turn slows photosynthesis and might negatively impact aquatic species' ability to hunt for food. Tiny particles may also become lodged in fish gills, preventing them from breathing and finally killing them. Sludge layers formed by settleable particles accumulating on plant leaves and the bed of the water body might suffocate benthic creatures. Sludge banks may form when sludge layers build up to a certain thickness, and if the sludge contains any organic material, the smelly byproducts of its decomposition will be released. Particles that are less dense than water will float to the top and create a scum layer, in contrast to the settleable material. [7]

ii. Oxidation and residual dissolved oxygen

Oxygen can dissolve into the water from the air and be used by aquatic plants to produce oxygen, allowing bodies of water to oxygenate themselves. When it comes to the latter, algae is often involved. Dissolved oxygen levels may be restored to their original levels if the oxygen depletion caused by biological or chemical processes produced by the presence of organic or inorganic substances that exert an oxygen demand exceeds this reoxygenation's limited capacity. The latter may deteriorate to the point where septic conditions emerge. Malodours produced by facultative and anaerobic organisms would be an indicator of the existence of such circumstances. For instance, facultative bacteria may produce hydrogen sulfide by reducing compounds like sulfates, which contain incorporated oxygen. Loss of oxygen from the atmosphere would threaten the continued existence of aerobic species. However, negative effects are already seen at lower DO levels.

Chemical and Electrochemical methods

i. Chemical Method

Treatment of textile wastewater often involves chemical processes, such as ozonation, chlorine addition, and Fenton's reagent. Although chemical treatment techniques are often more effective in removing color than the biological and physical processes, they are also more labor intensive, need more frequent chemical additions, and are more costly. Although the dyes are eliminated, a disposal issue arises due to the buildup of concentrated sludge. Excessive chemical usage may also contribute to a secondary pollution concern. In addition to being expensive and economically undesirable, transporting and handling hazardous chemicals poses risks.[8]

- Sodium hypochlorite (NaOCl)/Calcium hypochlorite (Ca(OCl)₂)
- Fenton's reagent
- Ozone

ii. Electrochemical Method

Over the last 30 years, several electrochemical methods have been suggested and developed for the

elimination of hazardous and difficult-to-remove organic contaminants in wastewater treatment. Direct electrolysis of contaminants at the electrode is only indirectly addressed by most existing conventional approaches.

Both direct electron transfer reactions to and from the unwanted organic, as well as chemical reactions of the pollutant with previously electrogenerated species that remain adsorbed at the electrode surface, are capable of achieving this goal. Most electrochemical techniques rely on indirect electrolysis, in which active species created reversibly or irreversibly at the electrode remove the target pollutant from the solution. Figure 1.1 compares and contrasts the two methods.[9]

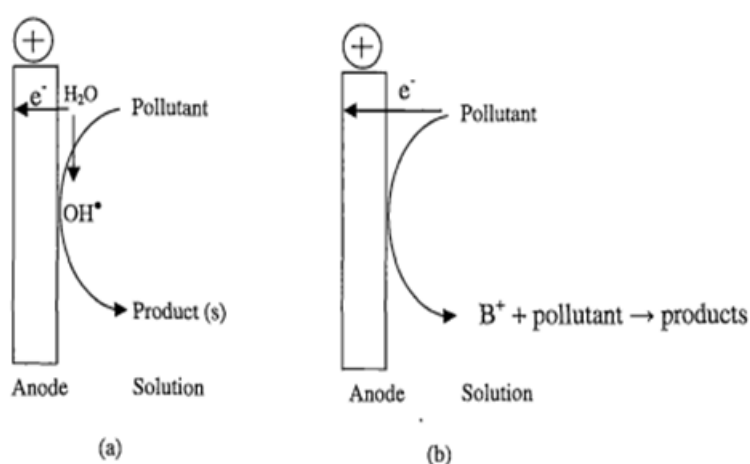


Figure 1: Schemes for different electrochemical treatments of organic pollutants.

LITERATURE REVIEW

Gleick, P. H., (2015) The water crisis facing the globe is becoming worse every year. The two greatest threats to global water security are the increasing human population and the diminishing availability of underground water supplies. The pace of rise in water consumption over the last century is twice as fast as the rate of population growth. The specter of a looming water catastrophe is raised by a confluence of geographical, agricultural, political, economic, and social factors. Due to excessive use, water sources like lakes and rivers are drying up, and aquifers are being drained at a rate that exceeds the rate at which they can be refilled by rainfall. More than a billion people worldwide do not have access to clean water, and the situation is only growing worse, as stated by Nature, which serves as a useful context for understanding the problem. The global water supply is expected to decrease by one-third over the next two decades, which might cause the deaths of millions of people.[10]

Adepoju-Bello (2015) Water shortage is a problem that has been the subject of several reports both internationally and domestically. United Nations Environment Program, World Bank, and World Resources Institute's joint publication, World Resources, presents a grim warning that water scarcity will be one of the most critical resource challenges of the 21st century. Even though the world's population is expected to quadruple by the year 2020, more than eighty nations, home to forty percent of the world's population, are already experiencing water shortages. If present water use patterns persist, the agricultural sector will face severe water shortages by the year 2025, says the International Food Policy Research Institute. Worse, the

World Health Organization estimates that 1 billion people worldwide do not have access to clean water for even the most basic of human requirements.[11]

Cabeza A, Primo O, (2017) While water shortage is a serious issue in certain places, poor water quality seems to be the biggest concern in most emerging nations. Water contamination is a major concern in our century. Water pollution refers to any decline in water quality, whether caused by chemical, physical, or biological means, that harms the health of organisms that consume, utilize, or dwell in that water. The United Nations Environment Programme estimates that 1.2 billion people are afflicted by filthy water and that this issue is responsible for 15 million annual fatalities among children. The yearly volume of wastewater "generated" is estimated by the UN to be over 1,500 km³. Water resources in underdeveloped nations are often contaminated since 70% of industrial pollutants are disposed of in the water.[12]

Dong, J., Xu, Z., Wang, F., (2018) The level of contamination in our water supply is unprecedented. We are well into the new century, yet the health risks connected with microbial contamination of water sources continue to be a worldwide problem, as shown by recently published data from epidemiological studies. Waterborne diseases claim the lives of around 1.8 million people annually throughout the world. An estimated 3,900 young people under the age of 15 die every day due to water-related diseases or improper hygiene practices. Groundwater contaminated with naturally occurring arsenic today impacts roughly 140 million people in 70 nations across all continents. Nitrate pollution has more than quadrupled in the Eastern Mediterranean and Africa since 1990, contributing to an overall 36% increase in mean nitrate levels in world waterways.[13]

Ghosh, A., (2017) These pollutants have polluted around 70% of the country's surface water resources and an increasing proportion of its groundwater reserves. India has recently begun to emphasize the need of maintaining high water quality for its citizens. The Canadian Provinces and Territories Bacterial and Organic Pollution Board (CPCB) conducted water quality monitoring from 1995 to 2009 and discovered severe bacterial and organic contamination. Groundwater quality is a big issue that has to be addressed all around the nation. Because they discharge their untreated sewage and industrial waste straight into water sources, urban areas are a significant contributor to this issue. Urban regions are responsible for the majority of its severity. Poor access to clean water, sanitation, and hygiene are responsible for the deaths of as many as 0.4 million people per year, while air pollution is responsible for the deaths of another 0.52 million.[14]

METHODOLOGY

Repeated subcultures with infected water samples will develop pure culture *Escherichia coli*. In a 500 ml conical flask and pure culture of *E*, two 250 ml sterile nutrient bouillons will be prepared. Any flask had *coli* will be inoculated. The conical bottles will be incubated for 24 hours at 37°C. A sterile distilled water solution of 0.01M and 0.001M will be formulated for silver nitrate. The community will be centrifugated at 10,000 rpm for 20 minutes following 24 hours of incubation. The surfactant will be moved to a conical sterile bottle without combining the pellet and the resultant pellet will be disposed of. Silver nitrate solution will have been applied to the supernatant 0.01M and 0.001M. These will be stored for 12 hours under reduced light at room temperature. Periodically, reaction fluid aliquots will be extracted and U-V visible spectrophotometer absorptions will be measurement.

RESULT

Bio-synthesized Ag nanoparticles in Water Treatment

Biosynthesis of Silver Nanoparticle Using Microorganisms

Without the addition of the silver nitrate solution, the culture supernatant would have had a yellowish tint. Within 12 hours of adding either 0.01M or 0.001M silver nitrate to the broth, the hue shifted from yellow to light brown. When the solution turns brown, the Ag^+ has been converted to Ago. What this meant was that silver nanoparticles were being formed. (Fig :2).



Figure 2: Microbially synthesized silver nanoparticles

Characterization

UV-Visible Spectra

The UV visible spectrophotometer was used to characterise the generated silver nanoparticles. In a 0.001M (Fig.3) and 0.01M Silver nitrate solution, a strong yet wide, surface plasmon peak was detected at 420nm and 418 nm, respectively. Small amounts of particle aggregation may cause a lengthy tailing on the long wavelength side.

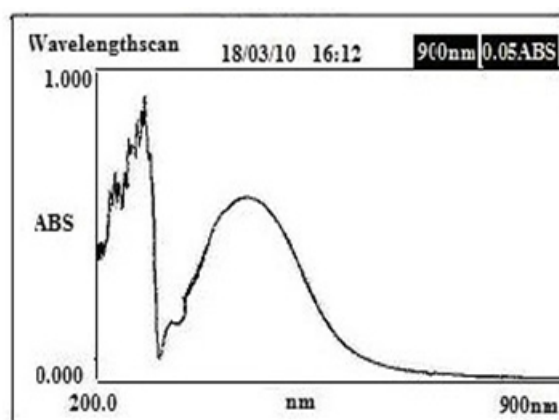


Figure 3: UV-visible spectra of Ag nanoparticles

Batch Adsorption Method

The effectiveness of the therapy was measured in a batch adsorption test using varying circumstances. As can be seen from the results of the experiment, calcium alginate beads are superior than silica gel and charcoal when it comes to purification. According to experiments using varying amounts of adsorbents and the same number of colony forming units in the sample water, 12 gms of calcium alginate beads was enough to significantly reduce the number of coliforms in a 500 ml sample. Experiments using water samples with varying CFU and the same amount of adsorbent indicated that 20 grammes of calcium alginate beads was adequate to completely purify the water. Comparing treated water samples with the same CFU count but varying contact times revealed that filtration was already complete within 5 minutes.

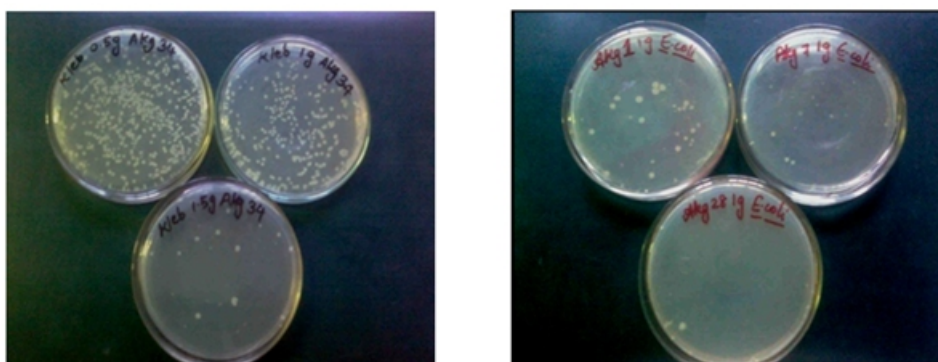


Figure 4: images of different microbial counts after water treatment

EDTA Titrimetric Method

Calcium concentrations in water samples were measured using a titration method. There is a possibility of calcium leaking into the treated water sample since calcium chloride was utilised in the manufacture of alginate beads. The findings rule out the possibility of any calcium leaching. Prior to and following treatment, the water's calcium hardness showed no change (Table:1).

Table 1: Calcium hardness concentration in untreated and treated water

Water sample	Calcium hardness before water treatment	Calcium hardness after treatment
Sample 1	8	8
Sample 2	24	24
Sample 3	20	20
Sample 4	12	12
Sample 5	88	88

Treatment Efficiency at Various Flow Rates

The treatment research found that if the filter's flow rate is kept at 150 ml/min, it is possible to effectively treat the subject. There is a significant reduction in coliforms and the filter is highly cost effective. Accordingly, the filter is a good choice for usage in the home (Table:2).

Table 2: Percentage of coliform removal at various flow rates of the filter

DIFFERENTFLOWRATE						
Flow rate/minute	25	50	75	100	150	200
Initial CFU	460	460	460	460	460	460
Final CFU	0	0	0	0	9	24
Percentage of Reduction (%)	99.99	99.99	99.99	99.99	98	95

Fe₂O₃ nanoparticles in Heavy Metal Removal

Effect of pH

One of the most crucial aspects of employing nanoparticles to remove heavy metals from drinking water is the water's pH. From a low starting point of 2.12 to a high of 12.6, the impact of pH on the elimination of chromium and arsenic was studied. Figure 5 depicts the change in chromium and arsenic adsorption capacity as a function of pH. As can be shown in Fig.4.5, with an initial As (III) concentration of 2.0 mg/L, almost 95% of the metal was adsorbed on the alginate surface in the pH range of 4.0-10. The proportion of removal drops down sharply as pH rises. The adsorption of As (III) on iron oxide loaded alginate beads was nearly pH independent between 4 and 10, with slightly increased adsorption in the acidic range. Chromium was shown to be removed most effectively at a pH of 2.5.

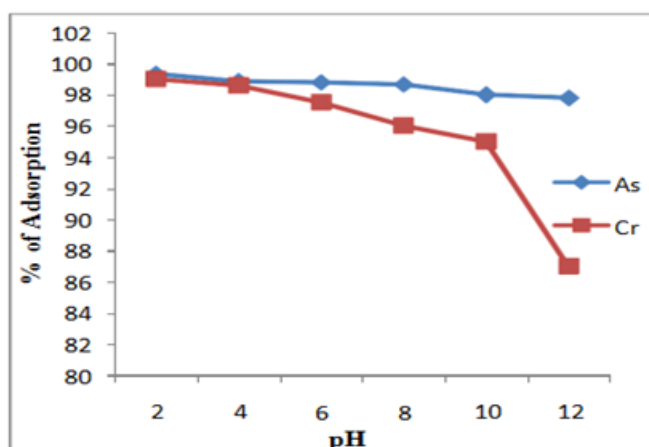


Figure 5: Percentage adsorption as a function of pH

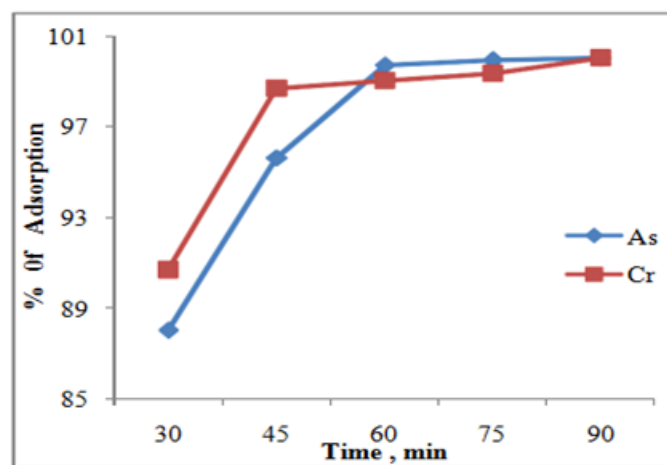


Figure 6: Percentage adsorption as a function time

The adsorption of 1.5mg/L of metals at pH=4.5 with a dose of 25g of adsorbent was used to conduct a kinetic investigation of the adsorption process. Contact times ranged from 30 minutes to 90 minutes. Initially, adsorption was higher, as shown in Fig. 6; however, after 75 minutes, the maximum clearance percentage of 99.33% was achieved. When the chromium contact duration was prolonged to 90 minutes, no additional change was seen.

Effect of Adsorbent Dosage

Adsorbent's impact on the process is seen in Fig. 7. A larger dosage of adsorbent increases the rate of removal. One possible explanation is the presence of additional adsorption sites. With an adsorbent dose of 25 grammes at 2 milligrammes per litre of arsenic, arsenic removal increases to 97.5% from 75.0% for 10 grammes of alginate beads containing 1.5 grammes of iron. Adsorbent dose that was increased significantly enhanced Cr(VI) removal. The adsorbent's efficiency at removing Cr(VI) was 90.66 percent at a dosage of 10 grammes. In the experiment, a removal efficiency of 100% was obtained at a dosage of 25g of adsorbent. Up to a certain point, the removal efficiency was found to increase in direct proportion to the amount of the adsorbent; beyond that point, the removal efficiency was found to remain constant regardless of the amount of adsorbent added. As the adsorbent dose is increased, more adsorption sites per unit area become available, leading to a higher percentage of removal.

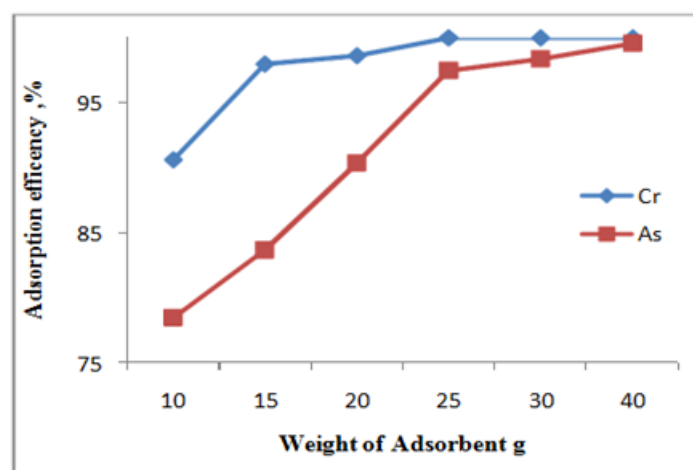


Figure 7: Percentage adsorption as a function of adsorbent dose

CONCLUSION

Wastewater treatment by electrochemical oxidation process was established in a laboratory scale for many years. However, electrochemical oxidation technologies have not reached real application maturity in commercial scale perhaps due to the limitation of comparatively high capital investment and the cost of electricity supply. Consequently, operating cost reduction and efficient electrode materials manufacturing are the main problems need to be overcome before the site-scale accomplishment of electrochemical oxidation in wastewater treatment. Microbial contamination was the major water quality problem reported in the selected ground water sources. Pathogenic contamination is the primary health concern in drinking-water samples, requiring disinfection to inactivate the microbes. On the basis of preliminary investigations, nano silver disinfection technology can be used as an appropriate technology for disinfection. Biosynthetically prepared silver nanoparticles were used in this study. The study has established the viable feature of nano silver disinfection at a very economical price, which can be affordable by common man.

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