Integration of Mechanical and Chemical Treatment in the Hydrological Cycle of the Paper and Pulp Industry

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Abstract

Today, the water crisis is growing overall in the world, not only in terms of the little amount of water but also in the misuse of water resources. The Paper and pulp industry is a major contributor to Egypt's water crisis and environmental pollution. It consumes a massive amount of water, approximately 17,000 gallons/ton of Paper. This project aims to develop efficient water treatment procedures in paper and pulp industries via the adsorption of lignocellulosic derivatives in wastewater and control the whole process using an automated mechanical unit for water consumption monitoring. Furthermore, a new Modified Activated Charcoal (MAC) was synthesized from Ficus Nitida tree branches and characterized by BET, BJH, and FTIR. During the activation of MAC, the carbon is impregnated in a basic alkaline solution using Magnesium hydroxide (Mg (OH)2) under a temperature of 340C for 1.35 hours. The results of multi-layer adsorption BET and BJH of one gram of charcoal revealed an average specific surface area (SSA) of 120.32 m^2/g, pore volume of 0.861 cc/g, and average pore radius of 0.26512 nm. At the same time, the maximum adsorption percentage was 84.13% and achieved by UV-Vis spectrophotometer after 20 minutes at 50 Celsius. These results could be considered promising solutions for worldwide water scarcity by minimizing the amount of water consumed in paper and pulp manufacture and treating the wastewater realized from the industrial process.

I. Introduction

Wastewater-related diseases kill a child every eight seconds and are responsible for 80 percent of all illnesses and deaths in the developing world [1]. 3900 children die every day from water borne diseases [2]. Industrial practices are responsible for water crisis and pollution especially paper and pulp industry. In 2015, paper industry released 174,000 tons of emissions to air, water, and land (or 5.3%) out of a total of 3.3 million tons of emissions released by all industries in Canada which are the third largest amount [3]. Moreover, In the United States the pulp and paper industry are the sixth largest in the industrial pollution, as it released about 79, 000 tons or about 5% of all industrial pollutant.

Paper and pulp wastewater is treated commonly using the activated sludge process, which depends on microorganisms to get rid most of lignocellulosic derivative’s biomasses. However, its inflexible in operation, large surface area required for sludge disposal, and high operation cost makes it not the needed appropriate method of treatment [4].

The reusing of treated paper wastewater will face water shortage and achieve water sustainability and can be considered as an additional value for environmental protection. An integration of the chemical treatment and mechanical system could offer an efficient solution for the water consumption and pollution of the paper and pulp industry. The paper wastewater could be chemically treated by the Modified Activated Charcoal, while the mechanical system would be serving as an automated control unit to address the water consumption, water treatment, and achieve the reusability concept.

II. Literature Review

Integrated Critical to environmental protection, drinking water safety, and industrial wastewater management, water purification plays an underappreciated role. The review investigates various cutting-edge approaches, including particle exclusion, electro-assisted processing, hybrid membranes, SR-AOPs, and biomimetic aquaporin-incorporated membranes. Through particle exclusion, water purification is revolutionized via an innovative approach involving hydrophilic surfaces. An intriguing concept has led to a new method of purifying water via a custom-made extractor, which captures clean water inside an Nafion tube's "exclusion zone". As confirmed by [5], this method exceeded expectations by achieving a removal rate of up to 99.6% for suspended particles. With particle exclusion, we can effectively remove organic and inorganic matter as well as pathogens. Whether it's pressure-driven membrane-based approaches that include reversed osmosis, ultrafiltration, microfiltration, or biological treatment, among other things, these are the conventional water treatment procedures. Electrochemical systems offer lesser-known alternatives in the field through electro-assisted methods. With its ability to cleanly and effectively purify water, electrochemistry has gained prominence in the field of scientific research. The flexibility to adjust electrode potential and tailor electrodes to suit distinct therapeutic requirements distinguishes electrochemistry. The latest breakthroughs and established methods in electrochemical technology for water treatment are discussed. Demanding efficient removal procedures are heavy metal ions and nuclear waste in water pollutants. The combination of protein amyloid fibrils and activated porous carbon leads to creative membrane design. These membranes showcase their effectiveness in removing heavy metal ions and radioactive waste from water sources. Heavy metal ion concentrations can decrease exponentially through repeat filtration, with each pass potentially lowering concentrations three to five orders of magnitude. The membrane's efficiency is unaffected when multiple ions filter simultaneously. The exceptional capabilities of these membranes originate from the selective absorption of heavy metal pollutants by amyloid fibrils, providing a revolutionary means for both water treatment and resourceful heavy metal recovery. SR-AOPs' capacity to oxidize makes them an appealing choice for water treatment, drawing notable interest. Field-specific, MOFs' potential becomes clear as catalysts for PMS activation. A considerable leap forward was made when in situ growth methods were applied to create MOF filters like ZIF-67/PAN composite fibers. PMS activation enables these advanced filters to remove organic pollutants with remarkable efficiency. Demonstrating their versatility, the manufacture of filtration devices displaying their suitability for diverse water treatment and separation purposes. With great promise, this innovative method could revolutionize water purification processes using MOFs [6].

The potential of biomimetic membranes to upgrade water purification processes owing to their incorporation of aquaporins has generated excitement. Study participants considered thoughtfully integrating the purified aquaporins into the active layer of PBI nanofiltration membranes. By combining gum arabic and PVA-alkyl, aquaporins were distributed to produce stable

performance. Superior performance was displayed by PVA-alkyl-AqpZ membranes when compared to unmodified PBI membranes. Lowered flux decline, higher flux recovery, and superior rejections of both proteins and salt ions were the primary advantages. Integrating the remarkable properties of aquaporins and the robust structures of PVA-alkyl has led to a new pathway for improving membranes in water treatment and desalination procedures, resulting in exceptionally high flux and remarkably low rejection [7]. These water purification techniques encompass particle exclusion, electro-assisted methods, hybrid membranes, SR-AOPs, and biomimetic aquaporin-incorporated membranes. Approaches range from particle removal to improving membrane performance, spanning. Water quality and resource management priorities are set to benefit from the innovative techniques being developed, which aim to ensure access to clean and safe water.
According to the research topic, the global water crisis is further complicated by mismanagement and scarce water, not just water scarcity. The water usage of the paper and pulp industry, particularly in Egypt, is a significant worry. By tackling this pressing issue, the project looks to establish adapted water treatment method exclusively designed for the paper and pulp industry. Monitoring water consumption entails implementing an automated mechanical unit for lignocellulosic derivative - wastewater adsorption applications. The study presents a novel approach via the synthesis of Modified Activated Charcoal (MAC) derived from Ficus Nitida tree branches. The MAC, characterized by its distinct surface area and pore properties, offers a viable solution to the global water crisis by minimizing water use throughout paper and pulp manufacturing and treating industrial wastewater.

III. The purpose

The main objective of the present work is to introduce an integrated system for total recycling of the industrial wastewater from paper washing process using hybrid chemical treatment process with mechanical automation.

IV. Methods

200g of Ficus nitida tree branches were used as raw material for the new Modified Activated Charcoal (MAC). They were chopped and then burned at a temperature of 500°C in an oxygen isolated container for two and half hour. After that, the product was grinded into fine grains and impregnated with a solid-liquid ratio of 1:4 with 20g of Magnesium hydroxide in water solution during the activation stage of the charcoal at temperature of 340℃ for 1.35 hours under continues stirring until being completely dried. The final obtained carbon was washed in 2 Liter of distilled water then dried at temperature of 100 ℃ for one hour, as shown in figure 1.

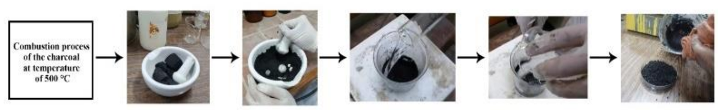

Figure 1 Schematic diagram of the charcoal activation from Ficus nitida.

i. Characterization of the MAC

i.i Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) analysis

The adsorption-desorption isotherm method in the Multi-point BET and BJH via liquid Nitrogen is used to determine the morphological structure comparison between before and after MAC modification besides the adsorption and desorption of MAC at relative pressures. The analysis of 0.1049g of MAC was adopted as an indicator of how the specific surface area of charcoal changed and the radius and pore volume. In addition, the BJH measured the mesopores of MAC and showed the pore size and the particle size distribution.

i.ii Fourier-transform infrared (FT-IR)

The FT-IR method was used with MAC before and after involvement in the treatment process to determine if there is a change of curve peaks to be an indicator of adsorption of the lignocellulosic derivatives according to its wavelength or other functional groups. The analysis was done with 1.319g of MAC via VERTEX 80/80v Spectrometer, as shown in figure 2.

Figure 2 Identify FTIR spectra of MAC at the Egyptian National Research Centre central lab.

ii. Maximizing adsorption percentage of MAC Experimental Design

The adsorption percentage has been tested at three different parameters (weight of MAC, temperature, and time), as shown in table 1.

Table 1 The experimental design of the parameters involved in the adsorption process UV-VIS spectrophotometer.

Variable / No. of trials	Weight (gm)	Temperature (℃)	Time (min)
	4 (0.2, 0.5, 0.7, 1)	4 (25, 50, 75, 100)	4(10, 20, 30, 40)

Four trials were conducted for each parameter while using a 50 ml sample from real wastewater released from the paper and pulp washing phase. The adsorption percentage has been tested at three different parameters (weight of MAC, temperature, and time). All trials were performed in the same steps with a fixed amount of wastewater in the conical flask as shown in figure 3; the solution was put on the magnetic stirrer and filtered by a filter paper to be suitable for testing the residual concentration using a V-630 UV-VIS spectrophotometer. The initial wastewater has a high concentration of lignocellulosic derivatives presented at a wavelength of 305 nm.

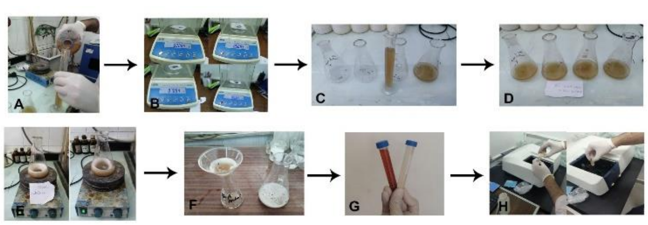

Figure 3 Schematic diagram of adsorption process under different conditions with fixed 50 ml of wastewater.

ii.i Water Quality

One liter of treated water and two liters of wastewater were tested within six days to know the adsorption of lignocellulosic derivatives that cause a high concentration of Biochemical oxygen demand (BOD) in the washing phase (wood or sugarcane bagasse) and the oxidizable organic causes also a high concentration of chemical oxygen demand (COD). Moreover, the water parameters such as pH, turbidity, and total dissolved solids (TDS) were tested with 20 ml of treated wastewater. All water parameters are essential indicators that make it pivotal for water reuse more times according to the standards and increase treatment efficiency, as shown in figure 4.

Figure 4 Testing the water parameters before and after in the Egyptian National Research Centre.

iii. The Automated Mechanical Unit (AMU) and the design of the phase

To make washing more realistic, use Arduino UNO connected with water pumps (12 vdc) and sensors (pH, turbidity, water level) with acrylic sheets 5mm thickness as constructed material. The prototype with dimensions of 60 cm length, 30 cm width, and 5 cm height. The surface platform forms two rectangles; one at the entrance and the other at the end, with dimensions of 16 cm in length and 2 cm used to return the water after treatment to be used in washing again. 13 pores at the center with diameter of 3 cm adhered to a 5mm pores mesh stainless steel used as a way of discharge.

The AMU controls the volumetric flow rate by making the pumps flow function as an analog of 136 (in coding) to be more efficient in water consumption than the standard washing water basin design. The AMU can automatically control the water flow by the readings coming from pH and Turbidity (model SEN0189), which can also be controlled manually as shown in figure 5.

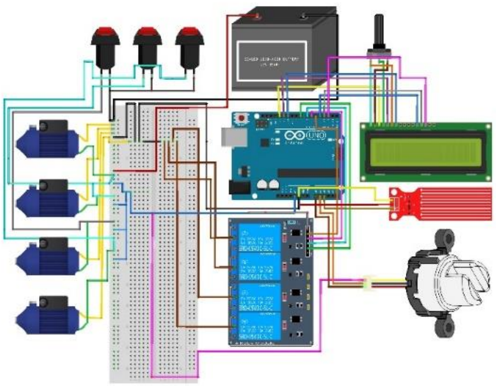

Figure 5 Circuit diagram of the mechanical automated system.

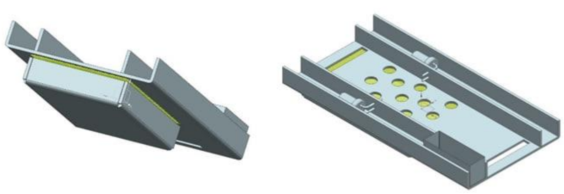

Figure 6 The 3D model of the new design of washing phase platform.

iii.i The pathway of the new design

The system pathway starts with entering the raw material and then is washed by two side pumps. The raw material is moved to the next stage, and the wastewater is discharged into the main container bottom via the 13 pores. The water is descended on a surface covered with MAC of 35 weight, deposited on the bottom of the container, and returned to wash more raw material after 18 min.

V. Data collection and Discussion

i. Charcoal Characterization

i.i BET Multi-point Results

Table 2 BET Multi-point results to determine the impact of the charcoal modification on its Morphological structure.

Test	Unit	Before activation	After activation
Surface Area	m²/g	63.131	120.32
Average Pore Radius	nm	0.1953e-000	0.26512e-000
Total Pore Volume	cc/g	2.377e+000	3.581e+000

The surface area of one gram MAC from Ficus nitida increased by 57.189 m²/g from a raw carbon to activated, while the average pore radius decreased by scale 0.06982 and total volume increased by scale of 1.204 due to the activation of mesopores and micropores through the addition of magnesium hydroxide.

ii. BJH Pore Size Distribution Adsorption results

Table 3 BJH Pore Size Distribution Adsorption results to determine the impact of the charcoal modification on its Morphological structure.

Test	Unit	Result	
		Before activation	After activation
Specific Surface Area	m²/g	32.782	58.351
Pore Radius Dv(r)	nm	1.92243	1.25671
Pore Volume	cc/g	0.24768	0.86133

As shown in table 3 both surface area and pore volume increased after the activation of charcoal. Moreover, the derivative of pore radius Dv(r) from the pore size distribution values getting a variation of how much loaded pollutants can be adsorbed in addition to the variation on pore radius indicates adsorbing different lignocellulosic biomasses and shapes as shown in figure 7.

The adsorption-desorption isotherm graph got a sharp hysteresis at relative pressure of 0.873 indicates that most of pores are from the conical pores of type C as shown in figure 8.

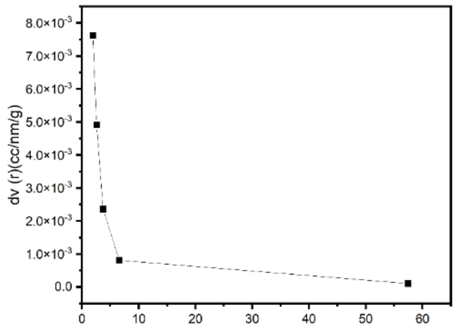

Figure 7 The derivative of pore radius and the pore radius in the surface after modification of the activation phase of charcoal.

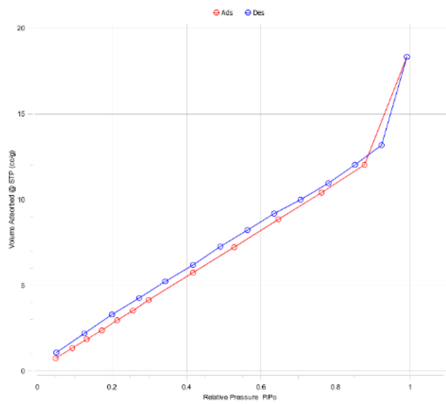

Figure 8 Adsorption-desorption isotherm graph of MAC to determine the pressure and the method of desorption with relative to time.

iv.iii FT-IR

The FT-IR of MAC after involving in the treatment process, there are two sharp peaks with a low transmittance of strong alcoholic stretching OH (3640.64 1/cm) and strong stretching aliphatic OH (2987.45 1/cm) which were adsorbed from the functional groups of lignocellulosic derivatives such as hydroxyl groups in lignin, cellulose, and hemicellulose as shown in figure 10.

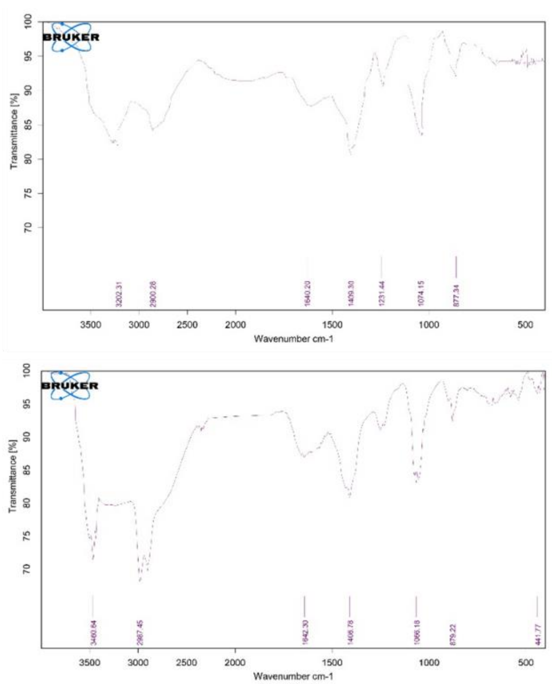

Figure 10 FT-IR results after and before the adsorption process of lignocellulosic derivatives

ii. Maximization of Adsorption Percentage

After analysing the wastewater sample, the lignocellulosic derivatives appeared clearly within 305 nm wavelength range with initial absorbance lambda max of 3.72789 as shown in figure 10. According to UV-Vis Spectra, a fixed 0.5 g in 50 ml of wastewater within 10, 20, 30, 40 mins as shown in figure 11, gets adsorption percentage of 46.2%, 53.58%, 47.45%, and 36.75% respectively. get the highest percentage of 53.58% within 20 min. During fixed 20 min with a 0.2, 0.5, 0.7, 1.0 grams get adsorption percentage of 27.48%, 31.56%, 48.08%, and 12.71% respectively. Getting the highest percentage using 0.7 grams of MAC. The last testing parameter with 0.7 of MAC and fixed 20 min get through a 25 °C, 50 °C, 75 °C, and 100 °C. resulted in 73.10%, 84.13%, 75.25%, and 80.78% respectively as shown in figures 12 to 17.

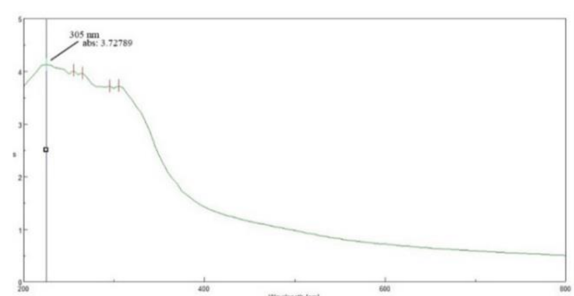

Figure 9 UV-Vis Spectra of the 50 ml initial wastewater

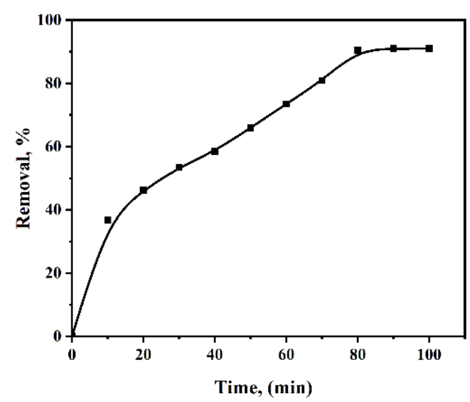

Figure 11 The removal percentage and time relation of adsorption process in maximum of 100 minutes and break line in range of 40 to 45 percent.

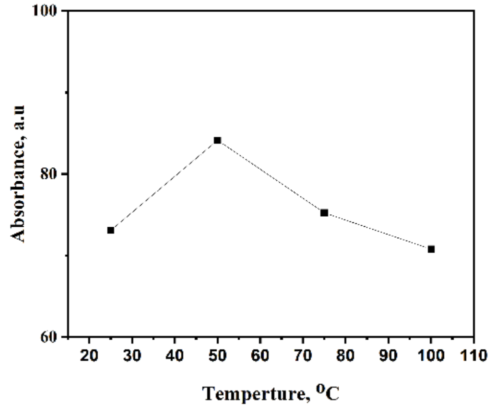

Figure 12 The removal percentage and temperature relation of adsorption process by 0.7 of MAC within 20 min

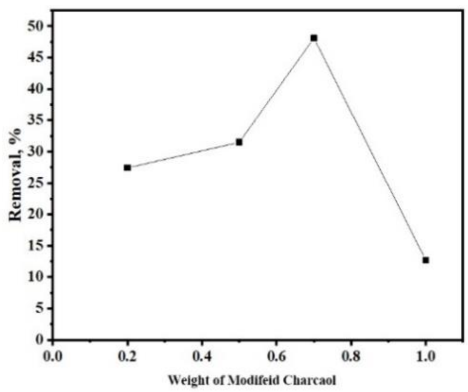

Figure 13 The removal percentage and charcoal weight relation within fixed 20 min

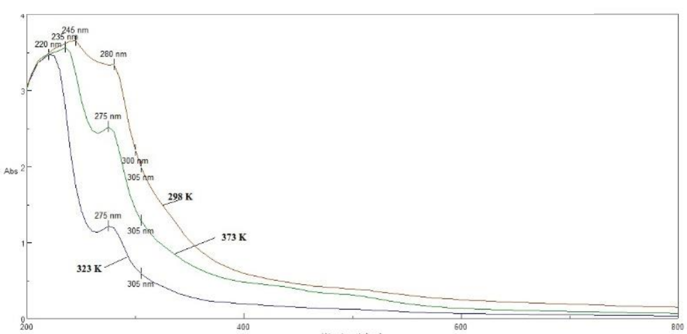

Figure 14 UV-Vis Spectra graph shows the removing in different temperature values.

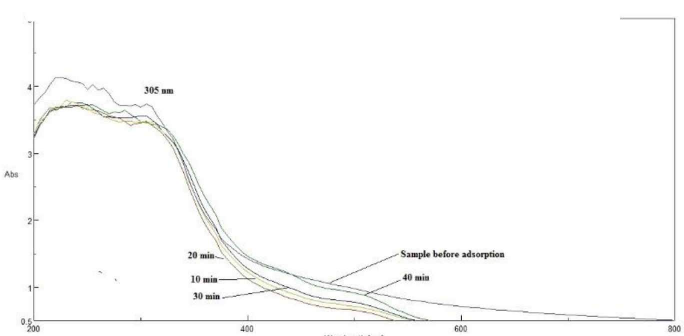

Figure 15 UV-Vis Spectra graph shows the removing within different time periods.

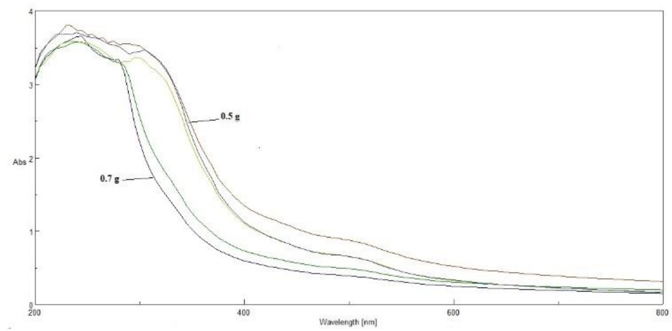

Figure 16 UV-Vis Spectra graph shows the removing using different weights of the MAC.

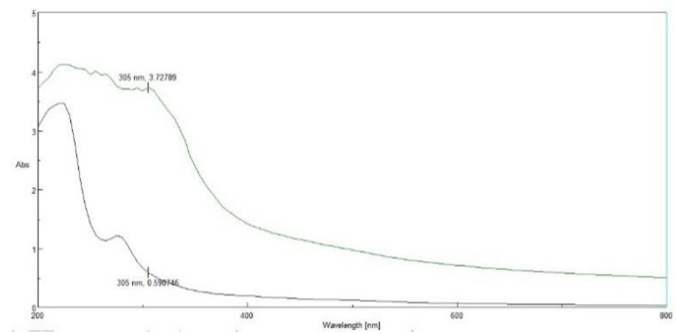

Figure 17 Illustration of initial and residual concentrations of lignocellulosic derivatives curves.

The adsorption percentage was calculated using the following equation:

$$Removal\ percentage = \frac{Intial\ value - Final\ value}{Intial\ value} \times 100$$

The maximum adsorption percentage was 84.13% by weight of 0.7 at temperature of 50 °C within 20 min under stirring condition.

v.1 Water quality analysis

The removal percentages of the BOD, COD, turbidity, and TDS was 84.4 %, 85.49%, 56.22% and 23.18%, respectively, were reduced due to adsorption of oxidizable organic matter present in wastewater as shown in table 4. As a result, the watercolour became more transparent as well as the total dissolved solids decreased which make the water suitable more for reuse again in the same process.

Table 4 Water quality analysis to indicate the removal percentage.

Parameter	Unit	Result	
		Before treatment	After treatment
pH	= =	7.8	8.3
Turbidity	NTU	29.7	13
COD	mgO2/l	1275	185
BOD	mgO2/l	405	63
TDS	mg/l	6900	5300

VI. Discussion

The global water crisis, with its escalating concerns over both water scarcity and resource management, poses a pressing challenge. Linked to the paper and pulp industry, an alarming rate of water consumption is estimated to be around 17,000 gallons per ton of paper produced. Environmental pollution, fueled by the industry in Egypt, adds to the complexity of water scarcity challenges. Underway is an exhaustive endeavor to create tailored water treatment approaches for the paper and pulp industry through this research project. The proposed solution incorporates both the absorption of lignocellulosic derivatives into wastewater and the automated mechanism to monitor and manage water consumption throughout the manufacturing process. The innovative aspect of this study is the use of Mac derived from Ficus Nitida tree branches called Modified Activated Charcoal (MAC). Properties analyzed meticulously, this novel form of activated charcoal proves highly effective across diverse water treatment applications, marking a substantial innovation. Fusing together Ficus Nitida branches through high-temperature burning and subsequent impregnation with Magnesium hydroxide (Mg(OH)2) in basic alkaline solution constitute(s) the process of MAC synthesis. Notable qualities were found in the resulting MAC, including an SSA of 120.32 m², a pore volume of 0.861 cc/g, and an average pore radius of 0.26512 nm. With its expansive surface area, MAC is well-suited for water treatment via adsorption.

The adsorption process was optimized by experimenting with MAC weight, temperature, and contact time, a thorough approach undertaken. Experiments provided essential knowledge about MAC's performance, culminating in an adsorption percentage of 84.13% as the most notable achievement. With just 0.7 grams of novel material at 50°C for 20 minutes, impressive results were achieved, showcasing its effectiveness in water treatment applications. Key parameters like BOD, COD, turbidity, and TDS exhibited substantial decreases following water quality assessment. Given the reduction, it is evident that MAC is powerful in removing lignocellulosic derivatives and other organic matter, yielding clearer and more environmentally friendly water. Greater efficiency in the water treatment process is achieved with the addition of an AMU within the system used by the paper and pulp sector. Meticulously crafted with Arduino UNO technology, water pumps, and sensors, this AMU was built with precision in mind. The AMU's key duty is to manage and govern the volumetric flow rate during the treatment process, which is its primary role. Sensor readings enable the AMU to dynamically adjust water flow, thereby optimizing treatment efficiency. Along with optimizing the water treatment process, this automated control unit also decreases the time required for treatment, rendering it more proficient and economical. Addressing the water crisis demands innovation, particularly within the context of the paper and pulp sector, and this project offers a significant step forward. By integrating MAC adsorbents and AMU process controls, a total and lasting answer is provided for wastewater treatment in this segment. A noteworthy improvement in adsorption efficiency and water quality has been observed through this approach, emphasizing its ability to effectively tackle the environmental consequences of the paper and pulp industry and complement international attempts to fight water scarcity. Achieving greater sustainability and shrinking the ecological footprint of industrial activities, this research represents a major stride toward global water security.

VII. Conclusion

After considering the results, it was found that the integration of the chemical treatment and the mechanical design is such an efficient solution to the problem of wastewater pollution, specifically in the processes involved in paper and pulp industries. Regarding the chemical treatment part, it was found that the addition of magnesium hydroxide in the activation of the charcoal has increased both adsorption and removal percentage which resulted in reduction of water consumption and pollution. In the mechanical part, the used control unit within the system could make the water reusable up to 6. In addition, through developing an automated system of water pumps and sensors, the control unit efficiently reduces the total time of the process. From these finding, the integration of the chemical treatment and the mechanical design is offering an efficient solution to the problem of wastewater form paper and pulp industries, which in turn will have a significant positive effect on the water scarcity worldwide challenge.

VIII. References

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