Agro-Waste-Derived Biochar as an Efficient and Sustainable Material for Wastewater Treatment

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***Abstract*—Due to rapid growth rates of industrialization and urbanization, water resources are extensively contaminated, thus triggering the need to develop sustainable wastewater treatment materials at low costs. Biochar was produced from agro-waste orange peels using pyrolysis and tested as a prospective water treatment technology to separate heavy metals from wastewater. The surface morphological properties of the synthesized biochar were analyzed by FESEM, which clearly identified that the surface of the biochar had formed a heterogeneous structure post-pyrolysis, and the surface groups were identified by Fourier Transform Infrared Spectrometry (FTIR). Adsorption studies were performed to assess the efficiency of lead (Pb), cadmium (Cd), copper (Cu), and zinc (Zn) metal ion removal. The biochar sample obtained from 400°C showed considerable reduction in metal ion concentration, which removed 59.8% of Cu, 56.6% of Cd, 50.3% of Pb, and 63.9% of Zn metal ion from the solutions. Several factors like contact time, dosage, and pH of the solutions were found to affect the adsorption capacity. From these results, it can thus be concluded that biochar derived from orange peels is an effective, eco-friendly, and economically viable adsorbent. Through this study, the importance of agro-waste management is recognized.**

***Index Terms*—Agro-waste, Biochar, Wastewater treatment, Sustainable materials, Adsorption.**

I. Introduction

Freshwater scarcity and pollution have appeared on the horizon in the new century, becoming two of the major challenges of the twenty-first century [1]. Rapid population growth, industrialization, urbanization, and agricultural activities have contributed to this situation [2]. The growing problem of the unattended or incompletely treated effluent released into the river, lake, or groundwaters has caused serious pollution. Industrial effluent usually consists of numerous contaminants, including heavy metals, dyes, pesticides, medications, and various other toxic organic compounds. These contaminants include compounds that may be accumulated in organisms, threatening the environment or human health [3].

Heavy metals like lead, cadmium, chromium, and copper are a specific concern because of their toxicity, potential bioaccumulation, and persistence in the environment [4]. Similarly, dyes and other organic pollutants discharged from textile, pharmaceutical, and food-processing industries decrease the penetration of light through water bodies, disturb aquatic life, and may produce carcinogenic by-products [5]. A variety of conventional wastewater treatment technologies has been widely used to date, which involves coagulation–flocculation, membrane filtration, ion exchange, chemical precipitation, and advanced oxidation processes. However, these methods are usually characterized by significant capital and operational expenditures, high energy consumption, and sophisticated infrastructure besides generation of secondary sludge that needs further processing and disposal [6].

In developing as well as resource-limited countries, the application of the latest treatment technologies on a large scale may not be possible. This has led to increased research focus on the design of environmentally friendly and economic alternatives for wastewater treatment on a large scale [7]. Among the several alternatives available for wastewater treatment, adsorption has emerged as one of the promising approach owing to its ease of operation, efficiency, and suitability for the treatment of all types of pollutants. Adsorption processes are highly dependent on the adsorbents used in the adsorption techniques [8].

Biochar has been emerging as a viable sustainable adsorbent for environmental pollution removal. Biochar is a solid with a high carbon content that may be produced in large quantities by thermochemically converting biomass in low oxygen settings, typically through pyrolysis. Biochar possesses favorable properties, such as high porosity, large surface area, and functional groups that are present on the surface, which allow for its affinity to various inorganic and organic compounds. Biochar also has good chemical stability, non-toxicity, and environment-friendliness [9].

The physicochemical characteristics and adsorption efficiency of biochar are significantly affected by the choice of raw materias as biomass. The quantity, affordability, and regenerative nature of agro-waste products have drawn special attention. Large amounts of agricultural wastes, including rice husk, sugarcane bagasse, coconut shell, and fruit peels, are produced globally and are frequently burned or dumped in the open, which pollutes the environment and releases greenhouse gases. Converting these agro-wastes into biochar provides a dual benefit of waste management and the production of value-added materials for environmental applications [10].

Among the various agro-wastes,Orange peel waste is one of the important yet unexplored biomass materials. A large

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number of waste orange peels are available from the juice processing units, food industries, and also from the local markets. The waste materials contain high amounts of carbon-rich materials. In addition, the waste materials have oxygen-rich functional groups, which is considered to be highly beneficial for the production of biochar. The biochar prepared from waste orange peels is expected to have better surface properties [11].

Although there has been an increase in the number of studies involving biochar-based materials, there is still a need for research work specifically focusing on the synthesis, characterization, and application of orange peel biochar, which is more relevant with regards to sustainability and wastewater treatment efficiency. In the contemporary scenario, the potential of agro-waste based biochar as an eco-friendly alternative remains unexplored for the treatment of wastewater. [12].

In the proposed study, biochar production was carried out from orange peel agricultural waste through pyrolysis, and the physicochemical properties of the produced biochar were analyzed. The adsorption capacity of produced biochar was also tested to examine its usability in water treatments. Results obtained from the proposed study will help in the development of water treatments through sustainable materials.

II. RELATED WORK

The utilisation of biochars obtained from agricultural waste for wastewater treatment has received attention in recent years because of their good adsorption properties, sustainability, and comparatively inexpensive preparation costs. Biochar is a carbonaceous substance that is produced when biomass is thermally broken down in an oxygen-limited environment. Its structure is inherently porous with large number functional groups on its surface, that can bind to contaminants. [13].

There are several reports on the utilization of various kinds of agro-waste-derived biochars as an adsorbent of heavy metals, dyes, and organic contaminants from water bodies. Rice husk, coconut shell, sugarcane bagasse, and fruit peels were some of the most common agro-wastes that have been pyrolyzed to generate biochar with excellent adsorption properties because of their higher surface area and porous morphology. Adsorption mechanisms reported were mainly electrostatic attraction, pore filling, hydrogen bonding, and surface complexation [14] [15] [16].

Orange peel biochars have gained considerable attention because they possess a higher amount of carbon along with the presence of natural oxygen functionalities. Past research work has demonstrated the higher affinity of Orange peel biochar toward pollutants like dyes and metallic ions, because of the presence of functional groups like hydroxyl and carbonyl. Yet, much research is conducted on a lab-scale synthesis, giving less emphasis on the perspective of efficient waste management [17].

There have been some attempts on the part of some researchers to chemically or physically activate biochar. The activation methods increase the surface area and the adsorption capacity of biochar. Although the current approach of activation is expensive for biochar production. Activation biochar might not be eco-friendly. Based on this point, the use of non-activation biochar from agro-wastes is a simpler and eco-friendlier option [18].

Although biochar material research has been conducted comprehensively, the scope of futher exploration exists for the evaluation of biochar from agro-waste that includes material fabrication and characterization, adsorption capacity, and sustainability. Furthermore, few works have been done to highlight the availability of local fruit waste material and its practical use in actual wastewater treatments.

As a consequence, the current research work emphasizes the preparation of biochar using orange skin agro-wastes and its utilization as a potential adsorbent for water treatment. This research work will fill existing research gaps and thoroughly investigate biochar preparation, characterization, adsorption capacities, and importance, thus addressing its potential utilization as an effective water treatment material.

III. MATERIALS AND METHODS

A. Materials and Chemicals

Agro-wastes in the form of orange peels were sourced from local vendors and fruit juice stalls. Raw material was preferred due to its wide availability, ease of biodegradability, and carbonaceous content, which qualifies it for biochar production. Orange peels were taken and given multiple washing sessions using tap water and then further distilled with distilled water to substitute dust and soluble contaminants present on their surfaces.

All the chemicals applied in the preparation of wastewaters as well as laboratory measurements were of analytical reagent grade. Distilled water was applied in solution preparation and washing. Sodium hydroxide and hydrochloric acid were applied as pH adjustment agents in the adsorption tests.

B. Pre-Treatment of Agro-Waste

Orange peel wastes were exposed in open atmosphere for 48 hours to remove any moisture content on their surfaces, and subsequently, they were oven-dried for at a temperature of 80°C for 24 hours .

A step of drying orange peel wastes cannot be overemphasized, as moisture content may result in inefficient performance of the process of pyrolysis and may also reduce the performance of the developed biochar.

The dried biomass was reduced in size in order to heat it evenly when undergoing thermal processing.

C. Synthesis of Agro-Waste-Derived Biochar

Biochar was produced using a pyrolysis method at a low oxygen atmosphere. Dried orange fruit biomass was loaded into a pyrolyser. The pyrolysis temperature for the production of biochar was set at 400°C for 2 hours, based on optimization as per existing literature.

After the completion of pyrolysis process, it was left untouched till it attains the ambient temperature. The resulting black carbon-rich material was crushed with a mortar and pestle followed by screening, ensuring uniformity in the particle size. The biochar was stored in a sealed container to prevent moisture absorption.

D. Characterization Techniques

1. Surface Morphology Analysis

The surface morphology and porous structure of the prepared biochar was analyzed by FESEM. These images show surface roughness, pores distribution, and adsorption-active sites, which are very important for pollutant removal. 2. Functional Group Analysis

Functional groups on the surface such as hydroxyl, carboxyl, and aromatic groups were identified using Fourier Transform Infrared Spectroscopy (FTIR) in the wavenumber range of 4000-400 cm^{1}.The identified surface functional groups are involved in adsorption process due to electrostatic attraction, H-bonding, and surface complexation.

E. Adsorption Experiments

A known mass of the biochar was added to a fixed volume wastewater solution in conical flasks. The mixture was agitated using a mechanical shaker at constant speed in order to ensure good contact between biochar and the pollutants. This exercise was done to investigate the efficiency of agro-waste-derived biochar as an adsorbent for heavy metals.

The samples were withdrawn at predetermined time intervals, filtered for the separation of the biochar, and analyzed for the residual pollutant concentration. Key parameters like contact time, dosages of the used biochar, and pH value have been systematically explored on adsorption performance.

F. Adsorption Efficiency Calculation

The adsorption efficiency of orange peel biochar (OPBC) to eliminate heavy metals present in the polluted wastewater was calculated using the standard concentration difference method. The metal ion concentration in the wastewater before adsorption (C_0) and the concentration after adsorption (C_e) were experimentally determined. The percentage removal efficiency was calculated by taking the ratio of difference between the magnitude of initial and final concentrations of metal ion and the concentration of metal ion present in wastewater before adsorption. This approach provides a reliable estimation of the efficiency of the adsorbent material in reducing pollutant concentrations in aqueous solutions. The calculated removal efficiencies indicate the adsorption performance of OPBC.

$$\text{Removal efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100$$

where C_0 is the initial concentration (mg/L) and C_e is the equilibrium concentration (mg/L).

G. Sustainability and Environmental Perspective

The waste orange peel was used as a raw material for biochar synthesis, is a circular economy based approach of recycling waste into eco-friendly useful product. The biochar synthesis strategy selected for this research is cost-effective and eco-friendly, which requires little use of chemical reagents. The produced biochar has great potential as a means for treating wastewater in resource-poor settings.

IV. Results and Discussion

A. Surface Morphology Analysis

Fig. 1 and Fig. 2 shows the surface morphology of raw orange peel and orange peel biochar (OPBC) respectively, through FESEM images.

The FESEM image of crude orange peel shown in Fig. 1 indicates that it has relatively compact and irregular surface structure with limited porosity upon observation. Its surface is rather fibrous, similar to other untreated lignocellulosic biomasses, hence dense. This morphology provides fewer accessible adsorption sites and limited surface area for effective interaction with pollutants.

Contrasting with that, the FESEM of the orange peel biochar (Fig. 2) presents a very heterogeneous and porous surface morphology. There are a lot of cavities, channels, and pores in different sizes on the surface of the biochar. These were created by the thermal decomposition of cellulose, hemicellulose, and lignin during the pyrolysis process. The formed porous structure develops well as a result of the volatile components' release during the carbonization process. The transformation of the compact structure in raw orange peel to a porous morphology in OPBC is, therefore, representative of the effectiveness of the pyrolysis process. The rough and porous surface of OPBC enhances adsorption performance by increasing surface area and facilitating pore filling, mechanical entrapment, and intimate contact between the adsorbent and contaminants.

These observations from FESEM strongly support the improved efficiency of adsorption obtained in the case of OPBC during experiments on wastewater treatment.

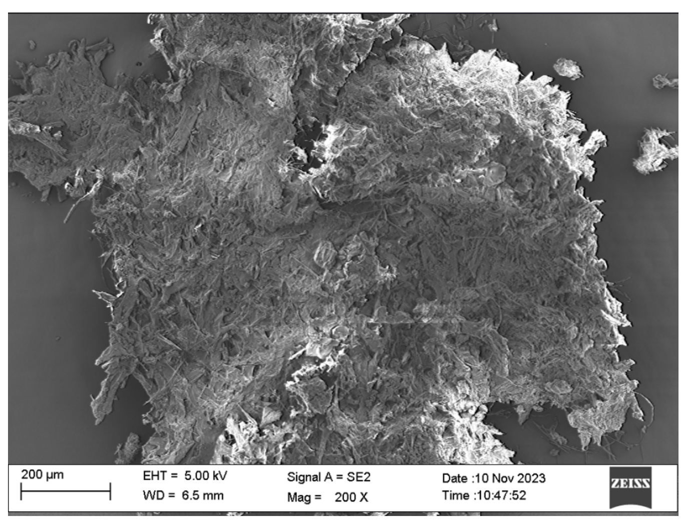

Fig. 1. FESEM image of raw orange peel showing compact and fibrous surface morphology.

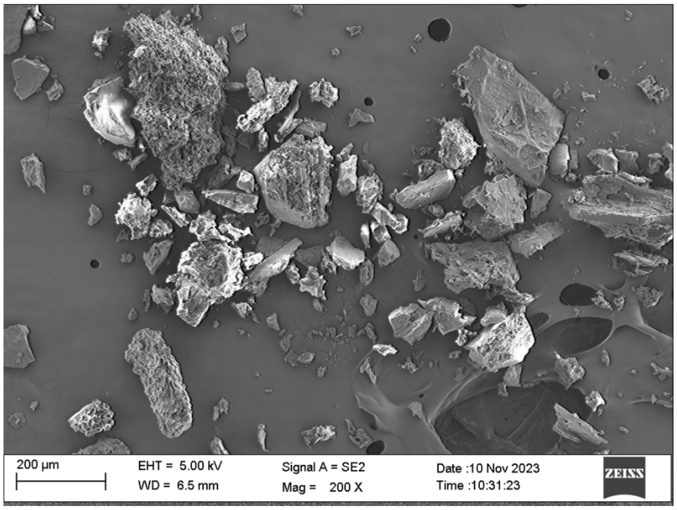

Fig. 2. FESEM image of orange peel biochar (OPBC) prepared at 400 °C showing porous and heterogeneous surface structure.

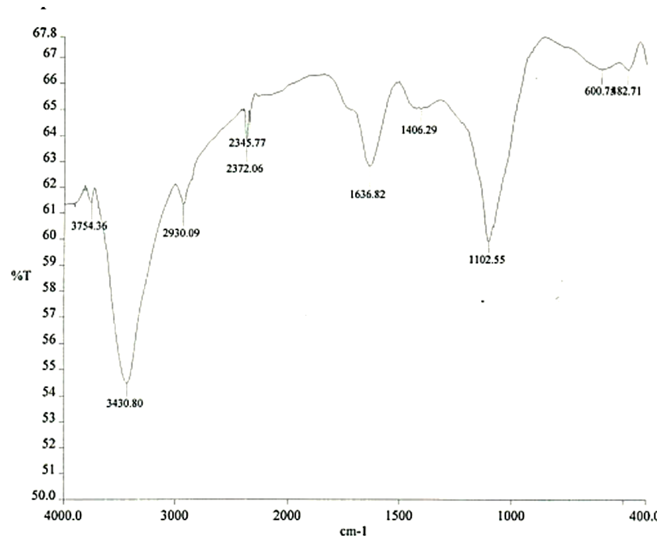

Fig. 3. FTIR spectrum of raw orange peel indicating characteristic functional groups of lignocellulosic biomass.

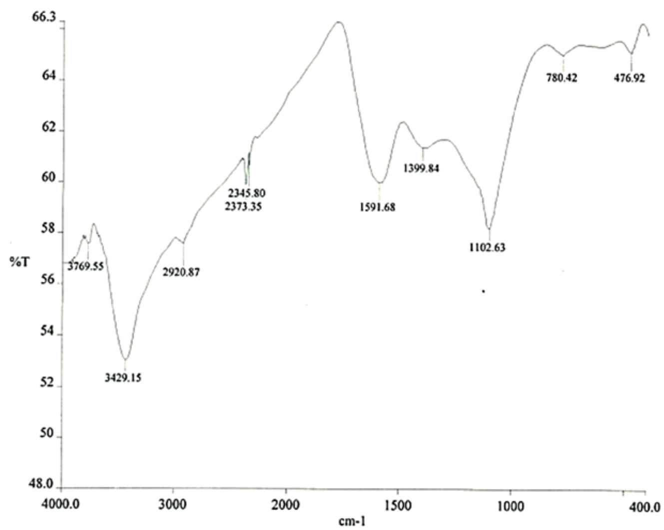

Fig. 4. FTIR spectrum of orange peel biochar (OPBC) prepared at 400 °C showing surface functional groups involved in adsorption.

B. Functional Group Analysis (FTIR)

Fourier Transform Infrared (FTIR) spectroscopy was used to determine the surface functional groups found on the raw orange peel samples and the OPBC samples, shown in Fig. 3 and Fig. 4, respectively.

The FTIR spectrograph of the raw orange peel (Fig. 3) has strong absorption peaks corresponding to natural functional groups found in the lignocellulosic material. The broad spectral range of 3200-3500 cm^1 reveals the presence of hydroxyl (–OH) functional groups from the cellulose and hemicellulose fractions. The spectral range of 1700-1730 cm^1 is characteristic of the C=O bonds of carboxyl and ester groups, whereas the spectral range of 1000-1200 cm^1 is due to the C-O bonds of alcohols and ethers.

After the pyrolysis, the FTIR spectrum of the orange peel biochar undergoes substantial alterations, as shown in Fig. 4. The fall in the peaks associated to hydroxyl groups is indicative of the dehydration of the sample. However, biochar still retains oxygen-containing functional groups, for instance, carboxylic, carbonylic, and phenolic. In addition, the occurrence and intensification of peaks at 1400 – 1600 cm^1 are due to aromatic C=C stretching, verifying aromatic carbonaceous compounds found in biochar. Func¬tical groups of biochars are essential for adsorption due to electrostatic, H-bond, and surface complexation interactions of biochar surfaces and metal ions.

This FTIR analysis further justifies the successful processing of orange peel to biochar that is chemically active in nature. The functional groups containing oxygen present in the OPBC surface, it is significant for the removal of heavy metals present in the wastewater.

C. Effect of Contact Time on Adsorption Efficiency

The influence of contact time on the pollutant removal efficiency was also considered to interpret the process of pollutant adsorption. It was found that the process involved a fast increase in the uptake of the pollutant, followed by a consequent gradual reduction in the rate of pollutant adsorption until reaching equilibrium. The fast increase in the pollutant adsorption rate may be ascribed to the abundance of unoccupied sites for the adsorption process on the outer surface of the biochar.

As the contact time enhanced, the rate of adsorption gradually reduced owing to the progressive saturation of active sites along with the resistance to the mass transfer process. The later stages of the process involve the principal mechanisms of intra-particle diffusion, where the pollutants diffuse into the biochar pores.

The reaching of the adsorption equilibrium implies that the biochar has a high affinity towards the wastewater pollutants.

This adsorption capacity is beneficial when considering effective wastewater treatment systems, which require fast removal of pollutants.

D. Heavy Metal Adsorption Performance

The adsorption capacity of orange peel biochar (OPBC) produced at 400°C in the removal of selected heavy metals from water has been evaluated. Initial and final concentrations of Cu, Cd, Pb, and Zn in water before and after adsorption are given in Table I.

A marked reduction in heavy metal content was noticed in OPBC treatment. Copper values decreased from 4.50 mg/L to 1.81 mg/L, demonstrating a removal efficiency of 59.8

The differences in the removal efficiency for the various metals might be due to differences in ionic radius, electronegativity, and affinity for surface functional groups of the biochar. The higher removal of the latter two metals indicated a better affinity with the oxygen-containing functional groups, whereas Pb exhibited lower adsorption due to the competitive adsorption phenomenon.

The above findings confirm that the moderate to high adsorption efficiency of heavy metal ions without chemical activation can be attained by using the OPBC prepared at 400 °C.

TABLE I
HEAVY METAL CONCENTRATION BEFORE AND AFTER TREATMENT USING OPBC AT 400 $^{\circ}C$

Metal	Initial (mg/L)	Final (mg/L)	Removal (%)
Cu	4.50	1.81	59.8
Cd	3.20	1.39	56.6
Pb	3.90	1.94	50.3
Zn	2.80	1.01	63.9

E. Effect of pH on Adsorption Performance

Solution pH is an important factor in the adsorption process, which can impact the charge of the biochar surface as well as the species of the pollutants. The efficiency of the adsorption process of the biochar can vary greatly with the change in the pH of the solution. At lower pH solutions, the electrostatic attraction between the biochar and the pollutants can get reduced due to protonation.

An increase in pH leads to the deprotonation of functional groups, resulting in stronger surface charge, hence favoring adsorption. The optimum pH range obtained in this study suggests that adsorption of pollutants occurs favorably due to the ion exchange and surface complexation processes.

The pH-dependent phenomena clearly indicate the involvement of oxygen-functional groups on the activated carbon and the necessity for pH regulation in wastewater treatment applications.

F. Adsorption Mechanism

The adsorption of pollutants on orange peel biochar is determined by the combination of physical and chemical processes. In physical adsorption, pore filling and van der Waals interactions dominate due to the porous carbon structure. In the latter, electrostatic interactions, hydrogen bonds, and surface complexation are the main factors that influence the adsorption of pollutants.

The aromatic properties of biochar also promote - bond interactions with organic pollutants. These mechanisms work in synergy to ensure effective removal of the pollutants from the wastewater.

G. Sustainability and Comparative Performance

The adsorption ability of the biochar synthesized can be considered excellent when compared with biochars produced from other agricultural wastes under similar conditions, as presented in the literature. The advantage of using orange peel as the precursor is its abundance, cost-effectiveness, and the fact that it is a waste material. Turning fruit wastage into valuable biochar is a positive step toward waste management.

Additionally, the low energy demands, together with the environmentally friendly synthesis procedure, ensure that this technique is sustainable for large-scale wastewater treatment.

V. CONCLUSION AND FUTURE SCOPE

A. Conclusion

The current work has shown the efficacy of using biochar derived from agro-wastes as a effective, eco-friendly, and economical alternative material in the field of wastewater treatment. Biochar derived from orange peel waste had a well-defined porous structure with a heterogeneous surface morphology. The existence of a high quantity of oxygen-containing functional groups played a crucial role in improving the adsorption capacity using electrostatic attraction, hydrogen bonding, or surface complexation.

Adsorption experiments showed that certain operating factors such as contact time, biochar concentrations, and solution pH are significant in the process of adsorptive efficiency for removing pollutants. The rapid adsorption process in the initial stage and then reaching equilibrium Indicates the great affinity adsorption relationship that biochar holds for wastewater contaminants. The result of adsorption validates the synergetic effect of pore filling and surface chemical adsorption.

On the whole, the findings showed the effectiveness of biochar derived from orange peel, declaring its potential for wastewater treatment, equalled to the other conventional methods, but, in addition, environment benefits like resource valorization and cheaper cost. The utilization of agricultural wastage is a successful way for sustainable goals and the circular economy.

B. Future Scope

Although the promising results are seen in the present study, there are many research avenues that could be explored to increase the effectiveness of biochar produced using agro-waste to remove wastewater. Focus could be laid on how to optimize the process of pyrolysis with respect to temperature and time to increase the effectiveness of the adsorption process.

The possibility of modifying biochar using chemical activation or biological methods could be explored in order to improve its selectivity towards a target pollutant that includes heavy metals, pharmaceuticals, dyes, and emerging contaminants. Furthermore, adsorption kinetics and adsorption isotherm data analysis based on sophisticated models could help in understanding adsorption mechanisms and scalability better.

It is necessary to carry out more research with actual samples of industrial and municipal wastewater to assess the efficacy of biochar under more complex and real-world environments. Regeneration and reuse of biochar should also be studied to help determine the economic sustainability of biochar-based systems.

In application development, the integration of biochar into fixed-bed columns, filtration systems, or combined systems has great application potential. Techniques such as life cycle assessments and technoeconomic analyses will also help in the commercialization and adoption of biochar derived from agricultural waste in water management practices.

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