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EXPERIMENTAL SCRUTINIZATION ON THE TREATMENT OF SYNTHETIC WASTEWATER USING NEEM BARK AND DATE PALM FIBER AS AN ADSORBENT

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ABSTRACT

Industrial activities are the major causes of water contamination worldwide as they contain heavy metals with a high concentration leading to environmental threats and health issues. Neem bark and Date palm fiber were established in this research work as low-cost adsorbents to eliminate Copper (Cu) from synthetic wastewater. Batch studies were conducted for each adsorbent particle size of 1.18 mm and 0.6 mm. The influence of pH, contact time, adsorbent dosage, speed, temperature, and initial concentration were scrutinized. The smaller particle size (0.6 mm) was more efficient than the bigger particle size for both adsorbents. The optimum conditions for neem bark of size 0.6 mm were at an adsorbent dosage of 0.3 g, pH of 6, 30 minutes of contact time, initial concentration of 100 ppm, and stirring speed of 1000 rpm for a copper reduction of 97%. The date palm fiber of 0.6 mm resulted in a copper reduction of 91% at optimum pH 5.5, contact time of 45 minutes, stirring speed of 1200 rpm, and adsorbent dosage of 0.3 g. The adsorbents were characterized using Scanning Electron Microscope (SEM)-EDS and Fourier-transform infrared spectroscopy (FTIR). The SEM-EDS analysis displayed a carbon content of 64.1% in neem bark and 58.9% in date palm fiber. The FTIR analysis presented the functional groups in the adsorbent responsible for the adsorption of Copperas carboxyl and hydroxyl groups. In addition, the equilibrium adsorption data of Neem bark well fitted the Langmuir and Freundlich isotherm models having the correlation coefficients (R^2) respectively as 0.9815 and 0.9024. Experimental data with date palm fiber fitted the Langmuir isotherm model with an (R^2) value of 0.9601.

Keywords: Adsorption Isotherms, Copper, Date Palm Fiber, Neem Bark, Synthetic Wastewater.
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INTRODUCTION

Wastewater treatment is one of the most essential and conservational processes used to convert the no longer effluent water into that which can be either returned to the water cycle or reused. Conventional wastewater treatment plants comprise aeration, which is an energy-intensive process though nowadays, wastewater treatment plants sometimes contribute as an energy resource to the biogases and bio-solids involved. Refineries and manufacturing plants generate industrial wastewater treated at the onsite amenities before it can be released into the environment. This process should be encouraged worldwide to avoid pollution and hazards to human health. In simple terms, with the difficulty of obtaining conventional energy in remote areas and the high cost, it became necessary to have alternatives through access to renewable energy sources and exploitation in the operation of different technologies for the purification and treatment of groundwater. This paper is to create a logical model based on the conversion of solar energy and wind power to electric power, which operates a domestic reverse-watering system to flush out wells. Wastewater treatment is performed to generate aesthetically, chemically, and biologically adequate water. Fewer treatment stages are required if the raw water is uncontaminated, resulting in an overall low cost.[1] Industrial wastewater contains organic and inorganic substances such as Zn, Ni, Sb, Cu, Co, and Cr, nutrients like phosphorus and nitrogen, pathogens, and excess harmful liquids produced by mineral dispensation production or the finishing process of metal. These toxic and harmful contaminants must be removed to obey the environmental protection laws and reduce health issues such as cancer, kidney and liver disease, death, and environmental contamination before discharge into the aquatic ecosystem, land, or plant operations. There are several methods for wastewater treatment, such as biological treatment, physical

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treatment, and chemical treatment. Biological water treatment includes aerobic and anaerobic processes in which one utilizes oxygen, and the other utilizes the absence of oxygen during the process. In physical water treatment, neither chemicals nor biological processes are involved. Only processes like sedimentation, aeration, and filtration are applied. As the term shows, chemicals are used to neutralize and purify the water for chemical treatment. Heavy metals are the naturally occurring metallic components originating from the earth's crust water, and metals such as arsenic, lead, cadmium, and mercury are toxic even at lower levels of exposure. Nowadays, the availability of these metals has increased at a high rate due to their uses in several applications such as domestic, industrial, technological, and agricultural applications. However, these metals are toxicants resulting in antagonistic human health effects such as neurobehavioral and neurologic illness, deafness, heart disease, cancer, etc. Similarly, heavy metal accumulation can also occur from soil erosion and the leaching of heavy metals and metal ions. Natural marvels like volcanic explosions and weathering also contribute to this heavy metal contamination. Copper is released into the surrounding by human activities such as mining, wood production, metal production, etc. High levels of copper are detrimental to human health and the ecosystem. Exposure to copper in a work environment through dust, mists, etc., can cause brain damage. In contrast, long-term exposure can cause headaches, dizziness, diarrhea, stomach aches, and liver and kidney damage. The presence of copper in the soil leads to a strong negative influence on the growth of earthworms and microorganisms present in the soil. Adsorption is the technique chosen in this research article to remove copper from synthetic wastewater. Adsorption is a surface phenomenon where the adhesion of molecules, ions, or atoms occurs from a gas or liquid to a solid surface. This process forms a film of the adsorbate on the surface of the adsorbent. Adsorbents have a very high internal surface area that permits adsorption. Adsorption techniques include using chemical and physical methods for water treatment, like activated carbon as an adsorbent to adsorb the hazardous materials from the wastewater.[2] An experimental study has been conducted on the removal or reduction of copper and zinc from wastewater. The adsorption was carried out using low-cost natural adsorbents, namely neem bark and date palm fiber, due to their adsorption properties and availability in Oman. This study focused on decreasing the cost of wastewater treatment by using natural adsorbents, neem bark, and date palm bark for heavy metal degradation. Date sawdust and shimul sawdust were used to remove Cr (VI) from water in this study. The results of this study show that date and shimul sawdust can be excellent adsorbents for removing Cr (VI) from aqueous solutions. Date sawdust is more active than shimul sawdust in this experiment. Date and shimul sawdust as adsorbents can be compared to well-known adsorbents such as activated carbon and others in terms of cost. This adsorbent can be reused and regenerated. Furthermore, sawdust is a byproduct of the sawmill as well as an industrial waste that has been used to cleanse wastewater. In light of the current environmental crisis, a new channel for pollutant removal from wastewater could be opened.[3] The PAC from date seeds has been found to be effective for removing color from textile effluent as a low-cost adsorbent, with a high percentage of color removal obtained from batch trials for a wide range of beginning color concentrations. When it came to defining the adsorption process, it was discovered that both the Freundlich and Langmuir isotherms fairly well capture the adsorption process with date seeds PAC, with the Freundlich isotherm slightly better than the other. The pseudo-second-order kinetic model fits well with the entire range of contact time, demonstrating that chemisorption controls the adsorption process. Over the spectrum of contact periods evaluated, both external film and intraparticle pore diffusion mechanisms were engaged in the adsorption of color onto date seeds PAC, although film diffusion was determined to be rate-limiting in this case.

The process of removing color from date seeds PAC was discovered to be endothermic, and more color removal was linked to a rise in temperature. Date seeds offer high possibilities for being used for tertiary treatment of textile wastewater in Bangladesh as a polishing step before discharging into receiving water bodies, as they are abundant and a low-cost agricultural byproduct in Bangladesh, and they are also an efficient adsorbent.[4]

Batch and column tests were used to investigate lead adsorption on date seed-derived biochar. The biochar adsorption capacity for Pb^{2+} was positively and linearly connected with the pyrolysis temperature and heating time, according to regression analysis. The maximum Pb^{2+} adsorption capacity was found in biochar produced at 550°C for 3 hours. The amount of Pb^{2+} adsorbed varied dramatically depending on the initial Pb^{2+} concentration, solution pH, and contact time. For Pb^{2+} adsorption onto biochar, the Langmuir and

Freundlich isotherm models performed well (R2 0.97). At pH 6.0, the maximum adsorption capacity of 0.360 mmol g1 was obtained. The adsorption reaction reached equilibrium after 6 hours, according to adsorption kinetics. The pseudo-second-order kinetic reaction model and the experimental data were in good accord (R2 0.94). The projected results from the modified dose–response model were in good agreement with the breakthrough curve obtained from the column study (R^2 0.95). In the column experiment, the adsorption capacity was found to be 0.219 mmol/g. The adsorption reaction is a spontaneous process based on the negative adsorption standard free energy changes. Biochar has the potential to be an efficient sorbent for removing Pb^{2+} from aqueous solution, according to batch and column experiments.[5] Compared to various other low-cost and commercially accessible adsorbents, date palm fiber is found to be a better adsorbent for the removal of Cr(VI). The BET method was used to determine the specific surface area of DPF, which was found to be 128 m2/g. Different functional groups, such as amine, amide, alcohol, alkanes, carboxyl, and hydroxyl, are responsible for the chemical adsorption of Cr(VI) from aqueous solutions, according to a Fourier Transform Infrared (FTIR) analysis of the adsorbent. At pH = 2, the greatest percentage removal of Cr(VI) was achieved. At lower pH, the main form of Cr(VI) is HCrO4 - and the surface of the adsorbent is positively charged. The adsorption capacity rose rapidly when the starting concentration was increased up to a specific point, after which it became saturated. At a given Cr(VI) ion concentration, the percentage removal of Cr(VI) rose up to 98.75 percent with increasing adsorbent dosages. The Langmuir isotherm was used to fit the equilibrium adsorption data, which validated the monolayer adsorption of Cr(VI) onto the adsorbents. DPF's highest adsorption capacity was discovered to be 62.5 mg/g. The pseudo–second–order kinetic model better describes adsorption kinetics, and it was also used to predict a number of important sorption parameters.[5] A simple co-precipitation approach was used to successfully synthesize a novel natural substance-based magnetic nanocomposite (Fe_3O_4@date seeds powder) in one of the studies. The interaction between the functional groups of the date seeds organic framework and Fe_3O_4 nanoparticles demonstrated the development of magnetic nanocomposite in the FT-IR spectrum of the produced nanocomposite. Methylene blue dye was removed from water by adsorption using the Fe_3O_4@date seeds powder nanocomposite. The adsorption results indicated that magnetic nanocomposite had a good adsorption capacity for methylene blue dye. The Langmuir isotherm revealed that the greatest adsorption capacity was approximately 76.652 mg g1 at 27 °C. Freundlich is the best-fitting isotherm model, implying multilayer MB adsorption on the heterogeneous surface of Fe_3O_4@date seeds powder nanocomposite. The dye was removed due to an electrostatic contact between the functional groups on the adsorbent surface and the methylene blue. With a 50% loss in adsorption efficiency, the exhausted adsorbent could be re-used for the seventh cycle. All the findings were compared to previous research, indicating that the produced adsorbent is affordable and has a fast and high removal capability for MB removal. Mandake *et al*. proposed peanut and rice husks as adsorbents for the removal of methylene blue during wastewater treatment.[6] The authors investigated the reactive distillation of ethyl acetate utilizing the esterification process. The decanter is used to separate the wastewater from the product, and the methods for treating wastewater from the decanter were analyzed.[7–9] The authors investigated the methods for biogas from palm waste in Oman, and the biogas energy can be utilized for wastewater treatment[10]. Researchers group developed a noble fouling-resistant membrane made using copper oxide-graphene oxide (Cu2O-GO), and polyether sulfone. Membrane performance in terms of wastewater treatment and fouling resistance of the prepared mixed matrix membranes was also studied.[11] Author did an experimental study on removing organic and inorganic compounds using activated carbon prepared from waste tires, banana trunks, tea leaves, and date seeds.[12] An experimental study to treat subterranean water in distant areas of Oman using two renewable technologies to create enough electricity to run the reverse water purification ~~and water purification~~ system at the lowest cost.[13] Research group studied the isolation and characterization of cellulose nanofibers obtained from agricultural waste, which has emerged as an alternative to conventional wastewater treatment materials.[14] The author's group proposed that bloom energy as one of the major sources for wastewater treatment.[15]

EXPERIMENTAL

Preparation of the Bio-Adsorbents

Date Palm Fibers and Neem bark were collected from local, regional trees available in Muscat, Sultanate of Oman. The collected neem barks and date palm leaves were washed, dried in the oven, and crushed or cut into small pieces. Subsequently, they were washed using distilled water. Neem Bark and Date Palm Fiber were then again dried in an oven at 105^0C for 7 hours, then sieved into the appropriate sizes of 1.18mm and 0.6mm each. Figure-1 shows the adsorbents after preparation.

Fig.-1: Date Palm Fiber

Fig.-2: Neem Bark Fiber

Preparation of Stock Solution for Copper

The stock solution was prepared from any hydrous Copper Sulphate. The required concentration was prepared by adding the calculated dose of salt in distilled water. The concentrations ranged from 10-100 mg/l. The solution was stirred for 5 minutes to dissolve the salt completely. The prepared solution was then stored in closed bottles for practical use.[16] One of the studies revealed that ADS could be used as an adsorbent for removing reactive green dye from the solution. The optimum model for describing dispersing green dye adsorption on ADS was found to be the pseudo-second-order kinetic model equation. The Freundlich isotherm equation likewise produced the greatest match for the experimental data, according to the findings. Finally, the application of ADS to remove reactive green dye demonstrated a high removal efficiency of 72.5 percent, suggesting that it might be used in industrial wastewater treatment.[17] The powder of Ajwa date seeds (PADS) was transformed into an adsorbent and successfully used in this work to recover copper (ii) ions, lead (ii) ions, cadmium (ii) ions, cobalt (ii) ions, chromium (ii) ions, chromium (iii) ions, and manganese (ii) ions from aqueous solution. The removal experimental studies and mechanisms are also influenced by a number of parameters, including the initial metal ion concentration, metal-metal ion competition for binding sites, temperature, metal ion characteristics, ion size, and metal ion solubility. The study's findings revealed that PADS had a remarkable adsorption efficiency. With the exception of manganese, the highest metal ion removal efficiency with PADS was extremely high. It is thus possible that adsorbent (PADS) might be utilized to remove metal ions from an aqueous solution due to its high adsorption effectiveness.[18] The use of DP waste material for heavy metal adsorption is a widespread and efficient wastewater treatment approach. Studies have demonstrated that both the raw and processed forms of DP waste are effective at extracting Cu^{2+} from aqueous solutions. However, because of the cost-effectiveness, stability concerns, availability, and highly large-scale required for DP waste, the use of raw or even modified DP waste for wastewater treatment on large sizes, such as industrial scale, remains a worry. The raw material effect of starting metal concentrations on the adsorption capacity and percentage removal of Cu^{2+} shows a comparison of the adsorption capacity and percentage removal of Cu^{2+} in the raw and modified forms of DP waste. The adsorption capability of DP is lower than that of chemically or physically activated versions. Chemical activation of biosorbents, on the other hand, is unfavorable because it makes the technique less environmentally friendly and more expensive. As a result, more research should be done to improve the adsorption potential of the DP raw material utilizing simple and low-cost procedures, such as using DP waste in the form of dehydrated carbon or media filters. DP waste leaves could be a source for producing dehydrated carbon, a greener alternative to AC that can be used in industrial wastewater treatment. AC manufacture is a harmful process because it is typically made from charcoal and requires high temperatures. Dehydrated carbon, on the other hand, can be made simply by treating DP leaves with sulfuric acid at 170°C before using it to clean wastewater. This technology could be particularly valuable in places where DP is widely farmed, such as Saudi Arabia, which produces 480,000 tons of DP waste each year, the majority of which is made up of leaves. For the elimination of dyes, hospital waste, and heavy metals, dehydrated carbon generated from DP leaves is as effective as AC and can be reused multiple times.[19] Batch and column experiments were used to investigate lead adsorption on date seed-derived biochar. The adsorption capacity of biochar for Pb^{2+} was positively and linearly correlated with the pyrolysis temperature and heating time, according to regression analysis. The highest Pb^{2+} adsorption capacity was found in biochar prepared at 550 °C for 3 hours. The amount of Pb^{2+} adsorbed varied significantly depending on the initial Pb^{2+} concentration, solution pH, and contact time. For Pb^{2+} adsorption onto biochar, the Langmuir and Freundlich isotherm models performed well (R^2 0.97). At pH 6.0, the maximum adsorption capacity was 0.360 mmol/g. The adsorption reaction reached equilibrium after 6 hours, according to adsorption kinetics. The experimental data agreed well with the pseudo-second-order kinetic reaction model (R^2 0.94). The breakthrough curve from the column study agreed well with the predicted results from the modified dose–response model (R^2 0.95). In the column experiment, the adsorption capacity was determined to be 0.219 mmol/g. Adsorption standard free energy changes that are negative indicate that the adsorption reaction is a spontaneous process. Based on batch and column studies, biochar has the potential to be an effective sorbent for removing Pb^{2+} from aqueous solutions.[5] The surface of activated carbon (AC) was improved with CaO and magnetic nanoparticles after it was calcined for 2 hours at 700 °C from date seeds. After that, an AC/CaO/Fe_3O_4 nanocomposite was used to remove formaldehyde ions from the aqueous media. The structural properties of the materials were thoroughly investigated using FT-IR, XRD, SEM, EDX, Map, VSM, BET, and TEM analyses. The results revealed that the nanocomposite has a mesoporous structure (average pore diameter 13 nm) and a high sorption capacity. Furthermore, the maximum removal efficiency of formaldehyde using AC, AC/ Fe_3O_4, CaO/ Fe_3O_4, and AC/ Fe_3O_4/CaO nanocomposite was 94.73, 95.67, 95.14, and 98.22 percent, respectively, indicating that improving the surface properties of the AC increases the removal efficiency. Furthermore, formaldehyde uptake by an AC/ Fe_3O_4/CaO nanocomposite follows the Freundlich isotherm and pseudo-2nd-order kinetic models. Furthermore, using the Langmuir model, the highest sorption capacity of AC, AC/ Fe_3O_4, CaO/ Fe_3O_4, and AC/ Fe_3O_4/CaO nanocomposite was 19.86, 24.21, 21.28, and 24.01 mg/g, respectively. The thermodynamic study revealed that formaldehyde sorption is exothermic and spontaneous when all four adsorbents are used. The adsorbents' reusability was also evaluated after ten reuse cycles, and the results showed that these four adsorbents have significant reusability. Furthermore, the effect of interfering ions (e.g., carbonate, sulfate, phosphate, nitrate, and chloride) revealed that, except for nitrate, all these compounds had little competition with formaldehyde ions for adsorption on the nanocomposite surface.[20]

Design Expert Software

The software inserted three parameters: pH, adsorbent dosage, and contact time. The parameters were given specific ranges of values, and corresponding to the input ranges, the optimum number of runs was 17 runs for each size.

Batch Studies

The copper stock solution was prepared in a 1000 ml volumetric flask by dissolving 2.48 g of copper sulfate in distilled water. The adsorbents were weighed according to the condition given for each run. 100 ppm concentration of synthetic wastewater was prepared in a 100 ml conical flask. The weighed adsorbent was added to the synthetic wastewater solution, and the desired pH adjustment was made using 0.1N of HCl and NaOH. The solution was stirred at a speed of 1200 rpm for a specific time and allowed to settle for a minute. The Atomic absorption spectrophotometer (AAS) was calibrated using 2 - 8 ppm standards, and sample concentration was measured.
The percentage removal of copper was calculated as shown in eqn.-1.

$$\text{Copper percentage reduction (\%)} = Co - Ce \,/\, Co * 100 \tag{1}$$

Equation 1, Co is the initial concentration, and Ce is the final equilibrium concentration. The amount of metal adsorbed was calculated based on the mass balance for the bio-sorbent in the system, which is given by the following expression in eqn.-2;

$$Qe = (Ce - Co)\, V / M \tag{2}$$

Qe is the adsorbent phase concentration after equilibrium in mg/g, M is the mass of adsorbent in grams, V is the volume of solution, and Ce is the final equilibrium concentration in mg/l.

Analytical Instruments and Techniques

Atomic Absorption Spectrophotometer (AAS)

Atomic absorption spectrophotometer is a systematic method that measures the concentrations of components by referring to the wavelengths of the amount of light absorbed by the elements.

Scanning Electron Microscope (SEM)

A scanning electron microscope scans the sample with a high-energy beam of electrons that produces images. The electrons and the sample interact and produce representative X-rays, secondary and backscattered electrons. The X-ray detector performs the Energy Dispersive X-Ray Spectroscopy (EDS), which semi-quantitatively and qualitatively determines the essential compositions present in the sample.

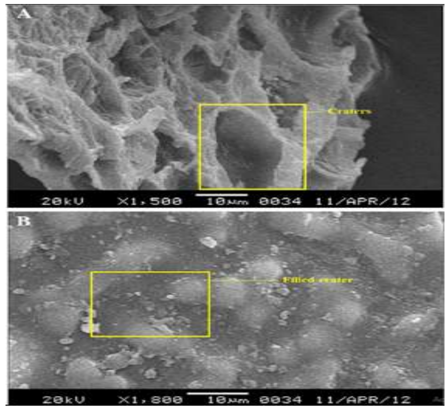

Fig.-3: SEM Images for Neem Bark Before and After Use as an Adsorbnet[21]

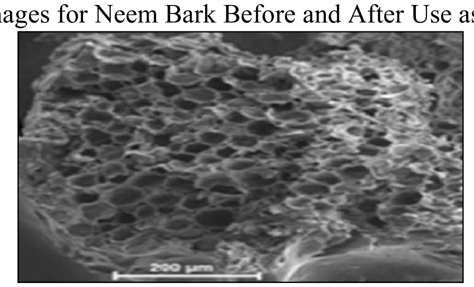

Fig.-4: SEM Images of Date Palm Fiber After Use as Adsorbent[22-23]

Fourier Transform Infrared spectroscopy (FTIR)

Fourier Transform Infrared spectroscopy is a device that passes infrared radiations through the sample where the sample absorbs some, and some are transmitted. IR spectrum of neem bark and date palm fiber before adsorption is shown Fig.-5 and Fig.-6 respectively.

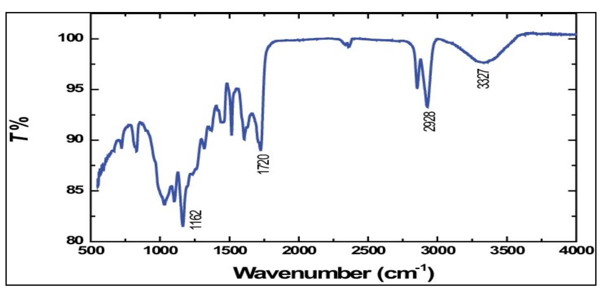

Fig.-5: IR Spectrum of Neem Bark Before Adsorption[24]

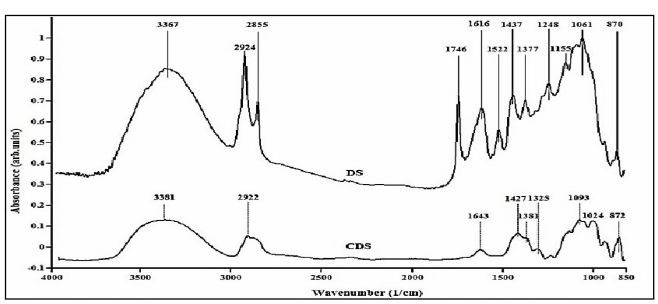

Fig.-6: IR Spectrum for Date Palm Fiber Before Adsorption[25]

RESULTS AND DISCUSSION

The effects of various parameters for a particle size of 0.6 mm are discussed in this section.

Effect of Initial Concentration

The initial concentration varied from 20 ppm to 100 ppm. As shown in Fig.-7, as the initial concentration increases, the percentage reduction decreases for both the adsorbents. The optimum initial concentration for both was at 40 ppm, which is due to less availability of binding sites (occupied sites) in which there will be no space for the other copper metals to bind.

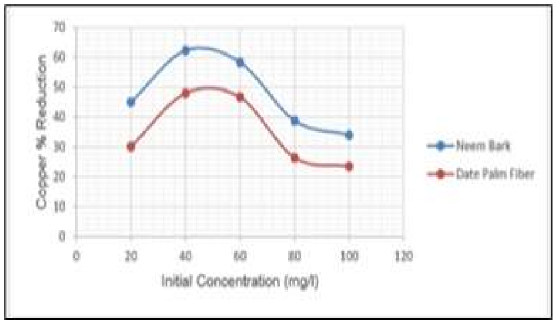

Fig.-7: Initial Concentration versus Copper % Reduction

Effect of Initial pH

The pH value varied from 1 to 7. It was observed that at a lower pH (acidic), the reduction percentage is low as shown in Fig.-8. However, as there is an increment in the pH towards the neutral region, the reduction percentage increases to a pH of 6 and then drops again. This means the optimum pH is 6 for the reduction of copper from the water solution for both the bio-adsorbents resulting in a reduction percentage of 97% for neem bark and 91% for DPF.

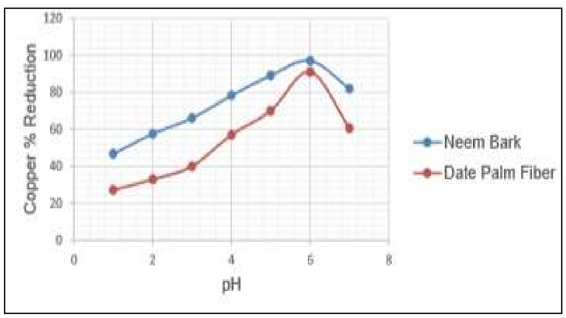

Fig.-8: pH versus Copper % Reduction

Effect of Contact Time

The concentration, pH, and speed were kept constant at 100 ppm, pH of 6, and stirring speed of 1200 rpm. As the contact time of the process increases, the reduction percentage also increases until the reduction percentage becomes almost constant as shown in Fig.-9. The optimum time for neem bark was at 30 minutes and 45 minutes for date palm fiber.

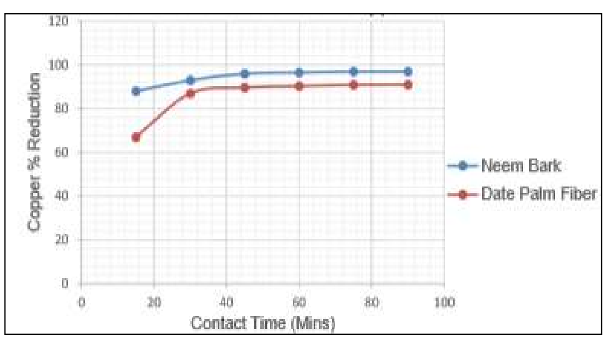

Fig.-9: Contact Time Versus the Copper % Reduction

Effect of Adsorbent Dosage

A smooth increase in copper percentage reduction with an increase in adsorbent dosage results in an optimum adsorbent dosage of 0.3g for neem bark and date palm fiber, which has a reduction of 97% and 91% as shown in Fig.-10. A similar result was observed and explained in the researchers study [19] where the more the number of adsorbent particles, the more are the surface areas that allow greater availability of exchangeable sites for metal attachment.

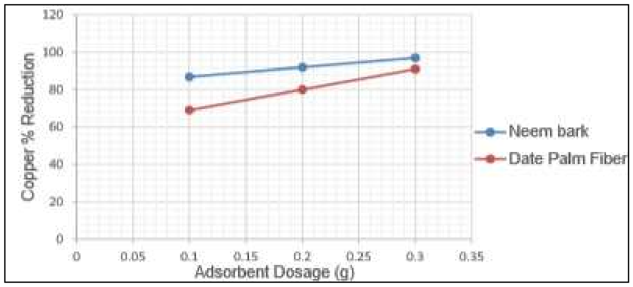

Fig.-10: Adsorbent Dosage versus Copper % Reduction

Effect of Stirring Speed

The speed was varied in the range from 200 to 1200 rpm as shown in Fig.-11. It was observed that as the speed increases, the copper reduction percentage increases to a specific turbulence limit where no change is noticed in the reduction level. At a particle size of 0.6 mm, the turbulence speed for neem bark was found to be 1000 rpm, while for the date palm fiber, it was found to be 1200 rpm. Exceeding this stirring speed level will lead to the adsorbent particle disruption and damage its function.

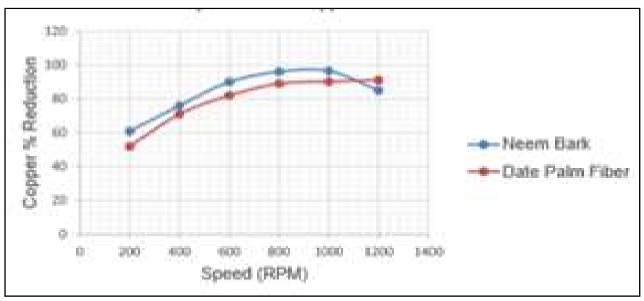

Fig.-11: Stirring speed versus Copper % Reduction

Effect of Temperature

The temperature varied in the range from 25 to 55 ^{0}C. As the temperature increases, the reduction percentage decreases, resulting in the adsorption process being exothermic as depicted in Fig.-12.

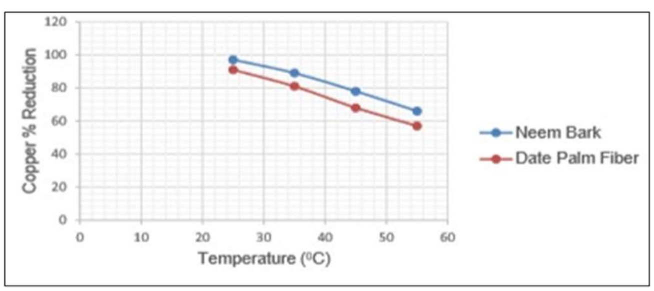

Fig.-12: Temperature Versus Copper % Reduction

Adsorption Isotherms

Langmuir Isotherm

The model assumes unvarying energies and nonmoving adsorbates onto the surface. Based on the assumptions made, the Langmuir model is denoted by equation (3).[21-22]

$$q_e = (C_o - C_e)V\ m \qquad (3)$$

where, q_e = Amount of metal adsorbed on the surface (mg/g)

C_o = Initial Concentration (mg/l)

C_e = Equilibrium Concentration (mg/l)
V = Volume of solution (liter)
m = Mass of the adsorbent (g)
Slope, m = 1 q_e
Intercept, C = 1 bq_{max}
b = Adsorption equilibrium constant related to the energy of adsorption

The Langmuir constants were calculated and the results are shown in Table-1 and Fig.-13.

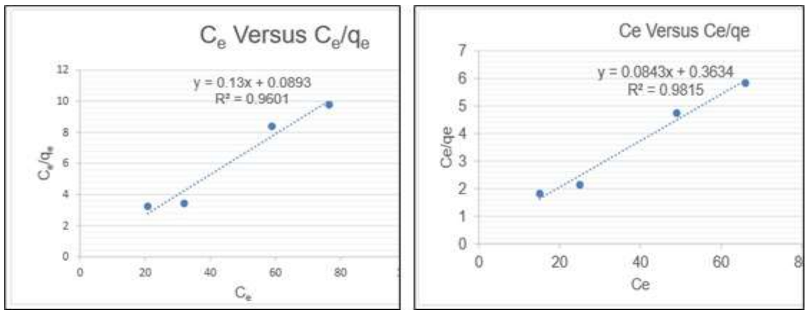

Fig.-13: Langmuir Isotherm Plot for Neem Bark and Date Palm Fiber

Table-1: Langmuir Constant Values of Neem Bark and Date Palm Fiber

Adsorbents	Langmuir Constants	
Neem Bark	b	0.232
	q_e	11.86
	R^2	0.9815
Date Palm Fiber	b	1.45
	q_e	7.69
	R^2	0.9601

Freundlich Isotherm

The Freundlich equation is expressed in a linear relation of ln x/m versus ln C. The Freundlich equation (4) is as follows:

$$\text{Ln } x/m = \ln K_f + 1/n \ln C \tag{4}$$

Where, K_f = Freundlich constant
x = Amount adsorbed on the surface (mg/g)
C = Final concentration (mg/l)
m = Mass of the adsorbent
Slope, m = $1/n$
Intercept, C = ln K_f [6]

The Freundlich constants were calculated based on the plot equation as shown in Fig.-14, and the results are shown in Table-2.

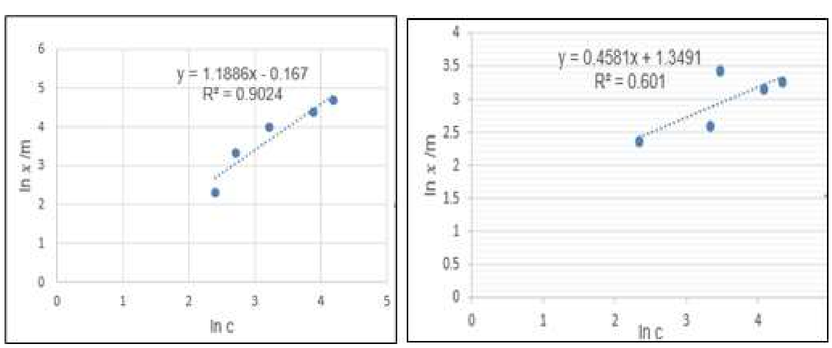

Fig.-14: Freundlich Isotherm Plot for Neem Bark and Date Palm Fiber

Table-2: Freundlich Constant Values of Neem Bark and Date Palm Fiber

Adsorbents	Freundlich Constants	
Neem Bark	n	0.841
	K_r	0.846
	R^2	0.9024
Date Palm Fiber	n	1.65
	K_r	2.30
	R^2	0.601

CONCLUSION

The present work carried out batch experimental studies for the adsorption of copper from synthetic industrial wastewater using natural adsorbents, neem bark, and date palm fiber. The adsorbents were characterized using Scanning Electron Microscope (SEM)-EDS and Fourier-transform infrared spectroscopy (FTIR), in which the SEM-EDS analysis showed that the adsorption process was poured dependent. The EDS showed a carbon content of 64.1% in neem bark and 58.9% in date palm fiber resulting in a better adsorption property in neem bark. The SEM analysis showed that the adsorption process is pore-dependent. The FTIR analysis presented the functional groups in the adsorbent responsible for the adsorption process. The main functional groups for the adsorption of copper were carboxyl and hydroxyl groups. The design expert software showed that the neem bark was more efficient in performing the adsorption of a copper process than date palm fiber. Comparing the particle size of 1.18 mm and 0.6 mm for both the adsorbents, the 0.6 mm particle size showed a better result in removing the copper from the aqueous solution due to its more significant surface area. Neem bark of size 1.18 mm at a constant pH of 6, initial concentration of 100 ppm, contact time of 45 mins, speed of 1200 rpm, and adsorbent dosage of 0.2 g at a room temperature of 250ºC resulted in a reduction percentage of 92% while at a size of 0.6 mm following the same conditions. The optimum adsorbent dosage was at 0.3 g, contact time of 30 minutes, speed of 1000 rpm, and a reduction percentage of 97%. Similarly, date palm fiber sizes 1.18 mm and 0.6 mm resulted in an optimum pH of 5.5, contact time of 45 minutes, speed of 1200 rpm, and adsorbent dosage of 0.3 g. The copper percentage reduction was found to be 87% and 91%. In addition, the equilibrium adsorption data of neem bark well fitted the Langmuir and Freundlich isotherm models having the correlation coefficients (R^2) respectively as 0.9815 and 0.9024. On the other hand, date palm fiber well fitted the Langmuir isotherm model resulting in an R^2 value of 0.9601 and an R^2 of 0.601 in Freundlich, which expresses the data not fitting the model. The best-fitting model for this research was the Langmuir adsorption isotherm model, as it indicated a higher correlation coefficient (R^2) value. Hence, the neem bark and date palm fiber worked well in copper adsorption from synthetic industrial wastewater as natural, low-cost adsorbents without the need for activation, which leads to a reduction in pollution.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

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All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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