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Valorization of the Agriculture By-product of Palm Date Trees: Preparation of Activated Carbon for Organic Dyes Removal from Tanneries Waste Water.

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ABSTRACT

Leather industry consumes large amounts of chemicals for the processes of tanning and finishing of animal and skin hides. Therefore, tanneries generate great amounts of a polluted waste stream. In particular, they pump huge amounts of wastewater that is contaminated with toxic chemicals. Azo-dyes are among the most dangerous contaminants in this regard. This work has been devoted to producing an economic and low-cost nonconventional adsorbent, as alternative to high-priced adsorbents that have a high production cost, from agricultural by-products which are easily accessible from the local environment. Activated carbon has been produced from leafs of the palm date trees by-product to be used as an effective azo dye adsorbent to remove the dye from the tanneries waste stream. The biomass (palm tree leafs) has been carbonized at 450◦C for 60 minutes, the carbonized product has been treated with orthophosphoric acid (2:1, H_3PO_4 / carbonized material, v/w); followed by activation at 650 ◦C, and neutralization to pH 6-7. The surface studies of the prepared sample have been achieved by scanning electron microscope SEM. Surface morphology shows development of pores structure, and formation of regular size grooves that are deeply formed on the surface. Therefore, the activated carbon is expected to have great adsorption capacity to the organic dyes and other soluble impurities. The adsorption capacity of the prepared activated carbon for the azo day has been studied. The prepared activated sample shows a considerable adsorption uptake of the contaminated dyes. Therefore, the study successes to produce nonconventional and effective azo dye adsorbent from by-product waste which is available in abundance. The prepared activated carbon can be used to remove the azo dye from the industrial waste stream with acceptable removal efficiency.

Keywords: palm date tree, byproduct, dye, waste water.

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INTRODUCTION

The great progress in the leather industry led to the growth of the use of synthetic organic dyes. Synthetic dyes are aromatic compounds have delocalized electrons as a conjugated double bond which is called chromospheres. The mechanism of color is attributed to the presence of these chromophores. Azo days mainly have aryl rings and substituted azo groups as delocalized electrons center [1]. They have a desirable brittle color due to the presence of substituted azo groups (-N=N-), therefore they attract the attention of consumers. Due to the high demand and the need for large quantities, scientists are constantly developing new types of the organic dyes. Unfortunately, the dyes in the dyeing or tanning basin are not fully absorbed into the leather fibers, and not a small amount of them are discharged with wastewater stream into the eco-system, reaches to the rivers, and mix with irrigation water. They may also contaminate into the soil and consequently into the plant, reaching to the human food [2]. In general, organic dyes have a negative impact on human health. They are highly poisoned, non-biodegradable in the short term, as well as resist oxidizing agents, and are not affected by light and heat [3]. And what makes them even more dangerous is that they decompose in the water into highly toxic substances. Therefore, they have to be prevented to reach to the drainage. Considering that they are widely used and hundreds of thousands of these dyes are produced every year, there is a need for developing adsorbed materials that are able to prevent their way into the wastewater. Several methods are used in the removal of the contaminated chemicals from the industrial waste stream. Adsorption on activated carbon is one of the most common methods [4-5]. The high cost and the depletion of coal, which is used as raw material for the production of activated carbon, are the biggest challenges facing the production of the activated carbon. Therefore, there is need to develop innovative methods to produce low cost and economic activated carbon from economically feasible sources. It is important to look for an alternative cheap biomass for activated carbon manufacture. Agriculture by products are abundant supply and costly inexpensive. Date palm tree is an important source of food in desert areas; therefore it is a famous tree in the hot regions and cultivated on a large scale. Farms generate large amounts of agriculture byproducts of the palm trees, especially in the trim trees season, such agriculture byproducts are pods, stems, and leafs. Although these byproducts are rich in carbon content, they don't find the proper utilization. The disposal process of these biomasses involves discarding in the landfill or open-air burning which adversely affects the eco-system. Converting these by-products to products of value is a fine target. The recent work aimed to convert them into activated carbon as value - added product. Sustainability and decrease the cost of the product are also justifications for doing so. Porous carbon is well-known adsorbent, it basically uses to remove and reclaim the chemicals from gaseous and liquid flows. Its adsorption capacity results from the porosity and large internal surface area that is developed via activation and carbonization processes [6]. Activation process could be achieved through chemical or physical processing. The physical one involves carbonization in an inert gas followed by activation in a carbon dioxide stream. The chemical process is processed through impregnation of biomass into mineral acid or salt, and carbonization in nitrogen or an inert sphere. It has been reported that many local environmental byproducts have been used in this regard; sugarcane biogases, coconut shells, cassava peel, nut-shell, and apricot stones are good examples [6-9]. Toxic dyes and other pollutants find their way into wastewater stream from some industrial activities such as leather manufacture, paper industries, and metal plating. This work aimed to find an innovative method to make activated carbon from palm date trees by-products which are available in abundance in the local environment and to study the capability of using the prepared sample as a nonconventional adsorbent for the dye removal.

MATERIAL

Leafs of palm date trees, as an agriculture by-product wastes, have been collected from local farms. Methyl orange has been used in the recent study as an anionic azo dye. A stock solution of 500 ppm of the methyl orange was prepared. Further, dilute solutions of concentration range from 10 ppm to 50 ppm have been prepared. The chemicals used in this work are analytical grade.

METHODS

The pre-treatment of the by-product

The palm tree leafs have been washed with tap water to remove dust and other impurities, and dried in open air for several days. The dried leafs have been milled using a blender machine for a particle size 1-2 mm. The milled goods has been dried into an electric oven for 4-5 hours at temperature105^{o} C, and stored in sealed containers for further treatment. The milled raw biomass of palm tree leafs was examined by thermo

gravimetric analysis [TGA] as shown in figure 1. TGA analysis has been achieved at 10° C/min heating rate, with a heating range from 5- -600° C

Activated carbon preparation

The milled samples were carbonized in an inert atmosphere at temperature 450 ° C for 60 minutes; the obtained char has been cooled to room temperature. After complete cooling, the char has been treated with twice quantity of orthophosphoric acid (2: 1, phosphoric acid to char, v/w) for 24 hours. The substance has been washed with deionized water for several times to remove excess acid. After that, the substance was dried at 200 for 4 hours, and the dried mixture has been activated in an inert atmosphere, at 650° C for 40 minutes [11]. The produced active carbon has been rewashed several times by using a suitable amount of deionized water and neutralized to pH6-7. The neutralized samples have been dried in an electric oven at 105°C for 2 hours and preserved into a sealed container for further use. The porosity and surface structure of the prepared active carbon has been studied using Scanning Electron Microscopy [SEM]. A JEOL scanning microscope (Japan) JSM-T20 has been used to achieve the surface study of the prepared samples.

Adsorption studies

The adsorption studies have been achieved at room temperature. The process has been carried out in 250 ml Erlenmeyer flask, the desired amount of the adsorbent dose was added to 50 ml volume of the solution, and the adsorption has been studied at different parameters of initial concentration, contact time, and adsorbent dose. The flask was shaken at 150 rotate/minute for the desired time. The contents of the flask were filtered using a double layer of filter papers. The filtrate was analyzed to evaluate the remaining methyl orange MO by using UV spectrophotometer, at maximum absorption (λ max) 465 nm. The percentage of removal equal $[C_o - C_f]/ C_o$ x100 .The effect of initial concentration was studied from 10-50 mg/L, using adsorbent dose from 10-50g/L. The parameters have been varied showing the best removal of MO under the given conditions. The contact time has been varied from 20 – 100 minutes.

RESULTS AND DISCUSSION

Thermal analysis of the by-products biomass

The thermal properties of the raw material of the palm trees leafs were investigated by thermo gravimetric analysis TGA. Figure 1 shows the TGA curves of the palm tree leafs. The TGA of the materials was carried out at a heating rate of 10°C/min with a temperature range of 25°C to 600°C. The weight loss at the beginning of the process 200°C was due to evaporation of free moisture content. As the temperature increase, the bound water is evaporated. A major weight loss occurs in the temperature range of 200 to 400°C that is attributed to the release of volatile matter and decomposition of the main components of the biomass (cellulose, hemicelluloses, and lignin). These results are in a good accordance with the data cited in the references [12]. As lignin decomposes at a low temperature with a low rate, however, its decomposition continues until the end of the heating process (900◦C). hemicellulose and cellulose decompose at a temperature range from 200-360◦C and 400oC respectively. Above 400◦C the final decomposition takes place, where the lignin fraction aromatizes and the weight loss, as well as, decomposition becomes very low.

Activated carbon investigation

Surface morphology of the prepared active carbon is shown in figures 2. The images of the Scanning Electron Microscopy [SEM] describe the morphology of the surface, they show good porosity and grooves formation inside the surface of the sample. Regular distribution of the grooves confirms that the prepared activated carbon sample has a great adsorption capacity and it is possible to use as a high absorption nonconventional surface. This emphasizes that the orthophosphoric acid activation of the carbonized biomass was effectual to make well pores with identical distribution on the precursor surface. Therefore, the prepared activated carbon of a great surface area and uniform porous structure has been successfully attended.

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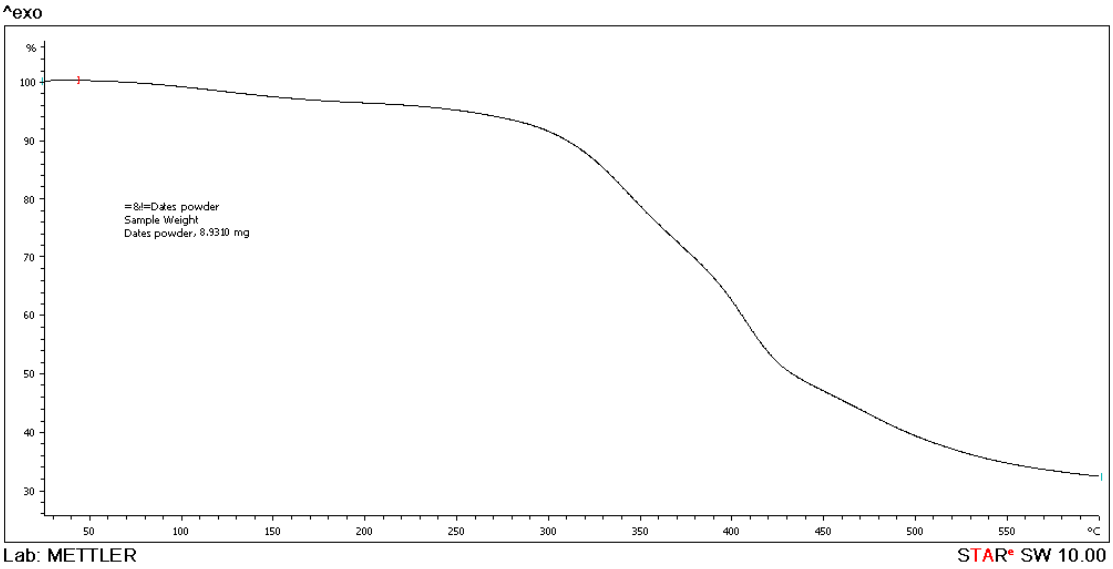

Figure 1: TGA curve of palm trees leafs as a by-product raw material.

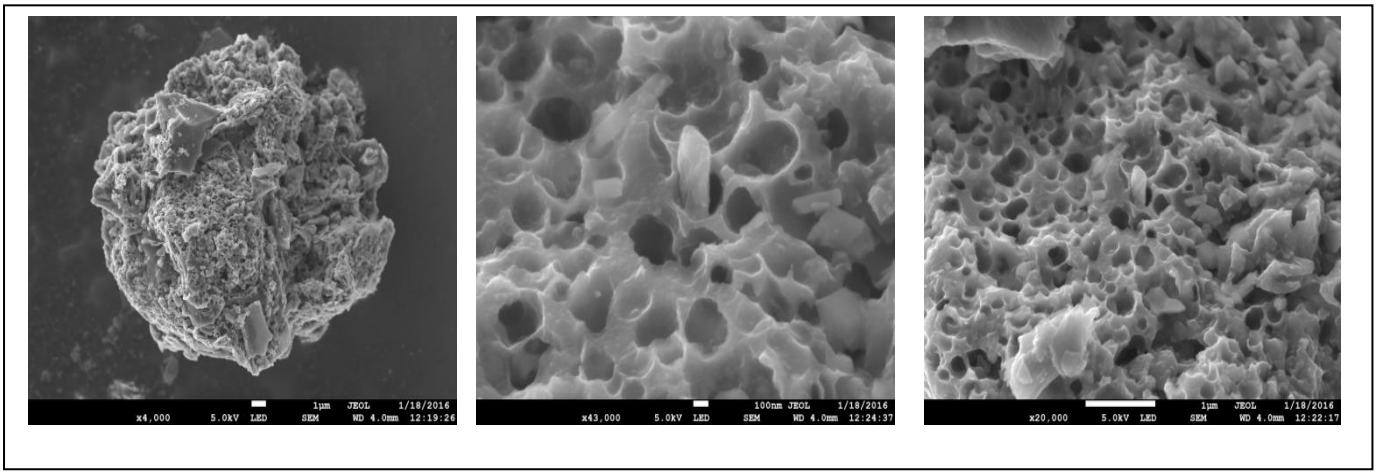

Figure 2: SEM micrograph of prepared activated carbon

Adsorption capacity of the prepared activated carbon

Effect of initial concentration

The effect of initial concentration into the uptake of the dye has been illustrated in figure 3; the efficiency of removal was studied via varying the initial concentration of the dye (10mg/L - 50 mg/L), at optimum pH 6-7, 60 minutes contact time and room temperature. The data into the figure well shows that the dye uptake increase, as the initial concentration increase. Therefore, increasing the initial concentration facilitate the mass transfer from the bulk of the solution towards the adsorbent because the high concentration offers a driving force to overcome the mass transfer resistance [13]. The graph shows that the efficiency of removal increases from 71.10% to maximum value 82.60 as the initial concentration increases from 10 mg/L to 50 mg/L. However, there was no significant increase in the dye uptake at a higher rate of initial concentration, this may attribute to the increase of competition on the surface of adsorbent and the saturation of the adsorption sits that takes place on the surface at higher concentration [14].

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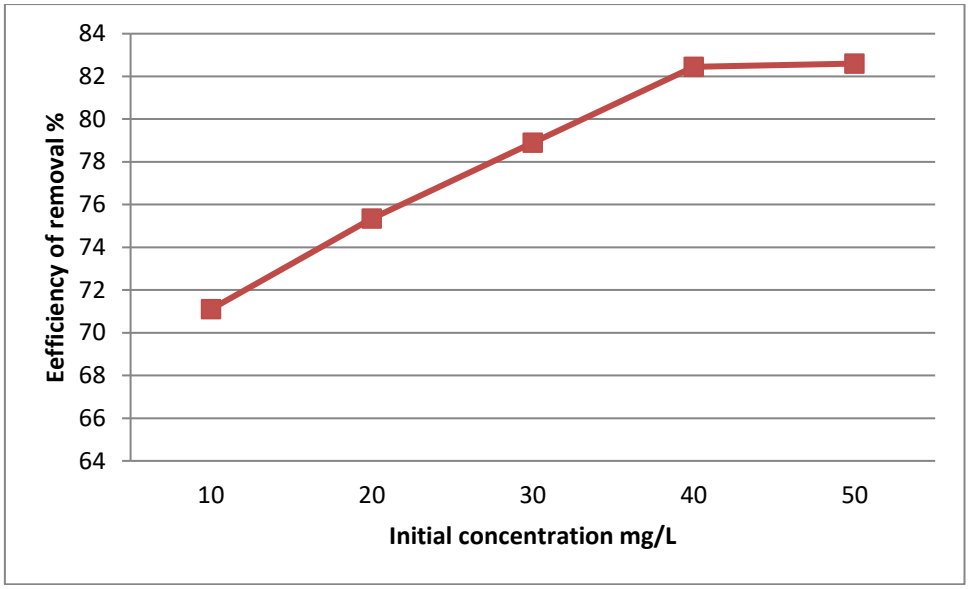

Figure 3: Effect of initial concentration on the removal efficiency

Effect of contact time

The effect of the contact time on the efficiency of removal has been investigated at different contact time 20, 40, 60, 80, and 100 minutes and initial concentration 40mg/L, without varying other parameters. The results have been illustrated in graph 4; it is obvious from the graph that the efficiency of the removal increases as the contact time increase. It is clear that the efficiency of removal is so fast initially up to 80 minutes, after that the removal rate decrease with the time; this can be explained based on the limiting available number of sorption sites at higher contact time. The adsorption capability is fast initially due to the plenty of adsorption sites at the start, with progress at the time, these sites become more saturated and their ability to attract the dye is almost non-existent. The data in the figure confirm that the maximum uptake can be achieved after 80 minutes contact time and no significant removal after that time.

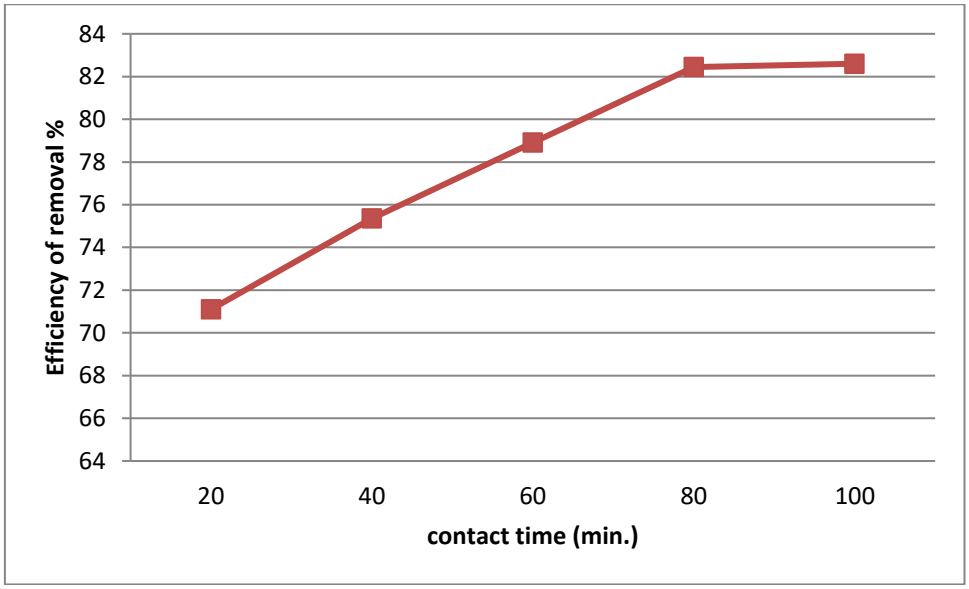

Figure 4: Effect of contact time on the removal efficiency

Effect of adsorbent dose

The effect of adsorbent dose on the removal efficiency of the dye has been studied at varying amounts of sorbent of (10, 20, 30, 40, 50 g/L), the equilibrium conditions were 80 minutes contact time and 80mg/L initial concentration, without varying other parameters. The results have been presented in figure 5. It

appears that the adsorbent dose has a significant effect in the removal efficiency, The dye concentration in the bulk of the solution decrease with the increase the adsorbent dose for a given initial dye concentration and contact time. This fact can be attributed to the effect of a specific area which is the actual area that is available for adsorption [15]. Therefore, the surface adsorption area increase leading to higher adsorption capacity and removal efficiency. The figure shows clearly that the maximum adsorption has been recognized at 40mg/L and no significant change after this dose.

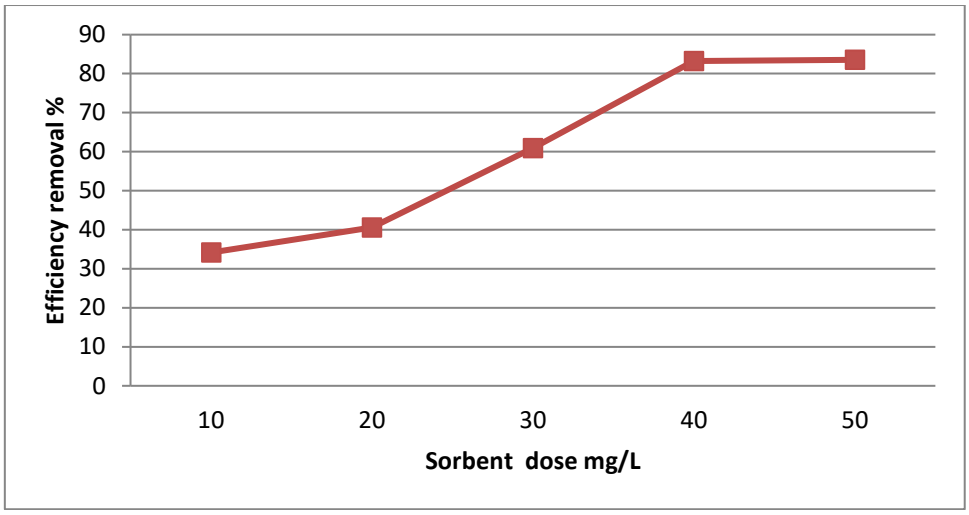

Figure 5: Effect of sorbent dose on the removal efficiency %

CONCLUSION

The palm date tree is a famous tree in hot areas where it is cultivated to a large extent. It generates great amounts of byproducts which are rich in carbon content and are an abundant supply. Active carbon has been prepared from the by-product via orthophosphoric acid activation. The surface morphology study of the prepared activated carbon shows regular porous and grooves formation fixed onto the surface, therefore it can be used as a nonconventional adsorbent. The active carbon shows a significant effect of azo dye removal from the industrial waste stream. Therefore, a product of value has been prepared from by-product waste that is available in abundance.

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