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STUDIES OF THE KINETIC PARAMETERS ON THE REMOVAL OF DYES FROM THE TEXTILE EFFLUENT USING PRE-TREATED SAWDUST

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ABSTRACT

In recent years, biosorption has been suggested as being cheaper and more effective than chemical or physical technologies. Low cost, high efficiency, minimization of chemical and biological sludge are the most important advantages of biosorption technique. Moreover, biosorbent regeneration and metal recovery is also possible. In this study, teakwood, neem and rosewood saw dusts were chosen for the adsorption of dyes from the textile effluents. In this work, the effect of contact time, pH, temperature and concentration of the sawdust towards the dyes present in the textile dye effluent were studied in detail. The equilibrium isotherms were analyzed by Langmuir and Freundlich adsorption isotherms. From the results obtained, the neem sawdust showed better adsorption, so it was taken for the analytical studies. The pre-treated neem sawdust and the dyes absorbed by this are investigated using Scanning Electron Microscope (SEM) and Fourier Transform Infra Red (FT-IR) spectroscopy for the surface morphology and surface functional groups. This study therefore shows that neem sawdust could be prescribed as bio-sorbent for the removal of dyes from the industrial effluents. The simplicity of the method may be significant for the treatment of dye waste waters that are difficult to deal with using chemical and biological methods.

INTRODUCTION

Generally, dyes are widely used in textile industry to color the textile and leather products. Dyes have many different and complex chemical structures, and there is a large range of products in commercial use. In recent years, water pollution with heavy metals and dyes has become an important environmental threat mainly because of the numerous industrial effluents containing various pollutants. The unaesthetic look of dyes in water streams and their toxicological effects have drawn considerable attention towards the contamination caused by textile and leather industry effluents. Most of the public's opinion is extremely sensitive to this kind of environmental impact and often becomes more intolerant with the type of colored waste water. Even, low concentration of dyes in water affects the aquatic life and food web, because of the presence of the high amount of heavy metals. Heavy metals such as lead, chromium, mercury, zinc, arsenic, cadmium, copper and nickel, etc., discharged into water resources leads to various severe health complications because of their non degradability and toxicity. Even if they are present in dilute, undetectable quantities, their recalcitrance and consequent persistence in water bodies imply that through natural process such as biomagnifications, concentration may become elevated to such an extent that they begin exhibiting toxic characteristics. The discharge of colored waste is not only damaging the aesthetic nature of receiving streams, but is also toxic to the aquatic life [1].

The inappropriate disposal of dyes in waste water constitutes an environmental problem and cause damage to

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the ecosystem. There has been increasing scientific concern about the hazardous effects of colored dyes which are widely used in leather industries because of their non biodegradable and polluting nature. Reactive dyes are most commonly used dyes due to their advantages such as bright colors, excellent color fastness and ease of application. They exhibit a wide range of different chemical structures primarily based on substituted aromatic and heterocyclic groups. A large number of reactive dyes are azo compounds and they are linked by azo bridge. Many reactive dyes are toxic to certain organisms and may cause direct destruction to creatures in water and even may be carcinogenic. In addition, since reactive dyes are highly soluble in water and their removal from effluent is difficult by conventional physiochemical methods. Some reactive dyes are recognized respiratory sensitizers and can cause occupational asthma. It was revealed that, when a person was sensitized, exposed to even very small amounts of the same dye may result in allergic symptoms such as a runny or stuffy nose, watery or prickly eyes, wheezing, chest tightness and breathlessness. A small number of dyes, based on the chemical benzidine, are thought to possibly cause cancer [2].

Nowadays, many environmental researchers have turned their interest on reduction of heavy metal ions in water resources, due to their known toxicity and carcinogenicity. Removal of heavy metal ions from water is a hard task, because of high cost in treatment methods. There are number of methods available for the removal of toxic metal ions from textile dye effluent. They are reverse osmosis, ion exchange, chemical precipitation, electro dialysis, nanofiltration and lime coagulation. These techniques are not only expensive but also suffer with incomplete removal, high reagent and energy requirements and generation of toxic sludge [3, 4, 5].

The mechanism of binding of metal ions by adsorbents may depend on the chemical nature of metal ions viz. species size and ionic charge, the type of biomass, environmental conditions like pH, temperature, ionic strength and existence of competing organic or inorganic metal chelators [6]. Natural materials that are available in large quantities or certain waste products from agricultural operation may have the potential as inexpensive sorbents [7,8].

Many industries, such as dyestuffs, textile, paper and plastics, use dyes in order to color their products and also consume substantial volumes of water. As a result, they generate a considerable amount of colored wastewater. It is recognized that public perception of water quality is greatly influenced by the color. Color is the first contaminant to be recognized in wastewater [9]. It was shown that the presence of very small amounts of dyes in water (less than 1 ppm for some dyes) was highly visible and undesirable [5] and [9]. Over 100,000 commercially available dyes exist and more than 7×10^5tonnes per year are produced annually [10]. Due to their good solubility, synthetic dyes are common water pollutants and they may frequently be found in industrial wastewater. It was an indication of the scale of the problem which was given by the fact that 2% of dyes that are produced are discharged directly in aqueous effluent [5]. Due to increasingly stringent restrictions on the organic content of industrial effluents, it is necessary to eliminate dyes from wastewater before it is discharged. Many of these dyes are also toxic and even carcinogenic and this poses a serious hazard to aquatic living organisms [11, 12]. However, it was confirmed that wastewater containing dyes was very difficult to treat, since the dyes were recalcitrant organic molecules, resistant to aerobic digestion, and were stable to light, heat and oxidizing agents [13,14]. During the past three decades, several physical, chemical and biological decolorization methods have been reported; few, however, have been accepted by the paper and textile industries [15]. Amongst the numerous techniques of dye removal, adsorption is the procedure of choice and gives the best results as it can be used to remove different types of coloring materials [16-18]. It was studied that the right design of the adsorption system would produce a high-quality treated effluent [19].

Adsorption is the most commonly used method for color removal. Adsorption onto activated carbon is widely practiced for removal of dissolved dyes from wastewater. However, adsorbent-grade activated carbon is cost prohibitive. So it is necessary to seek some alternative low cost adsorbents that do not need pretreatment to replace activated carbon [20]. Recently, a number of low-cost adsorbents for dye removal from agricultural wastes, microbial biomass [21] and higher plant biomass [22] were reported in the literature. Most commercial systems currently use activated carbon as sorbent to remove dyes in wastewater because of its excellent adsorption ability. Activated carbon adsorption has been cited by the US Environmental Protection Agency as one of the best available control technologies [18].

However, although activated carbon is a preferred sorbent, its widespread use is restricted due to high cost. In order to decrease the cost of treatment, attempts have been made to find inexpensive alternative adsorbents. The Textile industry is in the forefront in the use of dyes in its operations [23] with more than 9,000 types of dyes are incorporated in the color index [24]. It was reported that more than 70000 tons of approximately 10000 different types of dyes and pigments are produced annually worldwide, of which 20-30% are wasted in industrial effluents during dyeing and finishing processes in the textiles industries. As a result of the low biodegradability of dyes, the conventional biological treatment process is not very effective in treating dye wastewater [23]. Some of the physicochemical methods that have been employed to remove dye from wastewater include chemical precipitation, coagulation and oxidation. However these methods are not economical [24, 25].

Among them, biomaterials from higher plants seem to be one type of popular low-cost adsorbents because they usually have higher biomass compared with microbes and are easily available. For example, tree fern [22], orange peel [26], date pits [9], palm kernel fiber, sawdust [23], neem sawdust [27], husk based active carbon [28], neem leaf [29], groundnut shell [30] and dead macro fungus [31] were tested for treatment of dye-bearing wastewaters with different success.

Technologies available for color removal

The industrial effluent from the paper and pulp industry was treated with a white rot fungi and the organic matters were degraded also the color was removed [32]. Microbial bioremediation is an alternative treatment option available other than the commonly employed physicochemical and biological methods to treat these toxic effluents, with the use of non adaptive bacteria the textile effluent was decolorized [5]. It was reported that degradation of dyes in aqueous solutions by the Fenton process [23] and degradation of dyes using immobilized fungi [34,35] was promising methods for the removal of dyes from the effluent.

Biological decolorization using potential microorganisms capable of decolorizing and detoxifying the synthetic dyes has been considered as a promising and eco-friendly method [36, 37]. There are several reported methods for the removal of pollutants from effluents. The technologies can be divided into three categories: biological, chemical and physical [5]. All of them have advantages and drawbacks. Because of the high cost and disposal problems, many of these conventional methods for treating dye wastewater have not been widely applied at large scale in the textile and paper industries [15].

` At the present time, there is no single process capable of adequate treatment, mainly due to the complex nature of the effluents [38,38. In practice, a combination of different processes is often used to achieve the desired water quality in the most economical way. A literature survey shows that research has been and continues to be conducted in the areas of combined adsorption-biological treatments in order to improve the biodegradation of dyestuffs and minimize the sludge production.

Biological treatments

Biological treatment is often the most economical alternative when compared with other physical and chemical processes. Biodegradation methods such as fungal decolorization, microbial degradation, adsorption by (living or dead) microbial biomass and bioremediation systems are commonly applied to the treatment of industrial effluents because many microorganisms such as bacteria, yeasts, algae and fungi are able to accumulate and degrade different pollutants [9, 10]. However, their application is often restricted because of technical constraints. Biological treatment requires a large land area and is constrained by sensitivity toward diurnal variation as well as toxicity of some chemicals, and less flexibility in design and operation [29]. Biological treatment is incapable of obtaining satisfactory color elimination with current conventional biodegradation processes [5]. Moreover, although many organic molecules are degraded, many others are recalcitrant due to their complex chemical structure and synthetic organic origin [14]. In particular, due to their xenobiotic nature, azo dyes are not totally degraded.

Chemical methods

Chemical methods include coagulation or flocculation combined with flotation and filtration, precipitation–flocculation with Fe (II)/$Ca(OH)_2$, electro flotation, electro kinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), irradiation or electrochemical processes. These chemical techniques are often expensive, and although the dyes are removed, accumulation of concentrated sludge creates a disposal problem. There is also the possibility that a secondary pollution problem will arise because of excessive chemical use. Recently, other emerging techniques, known as advanced oxidation processes, which are based on the generation of very powerful oxidizing agents such as hydroxyl radicals, have been applied with success for pollutant degradation. Although these methods are efficient for the treatment of waters contaminated with pollutants, they are very costly and commercially unattractive. The high electrical energy demand and the consumption of chemical reagents are common problem

Physical methods

Different physical methods are also widely used, such as membrane-filtration processes (nano filtration, reverse osmosis and electro dialysis) and adsorption techniques. The major disadvantage of the membrane processes is that they have a limited lifetime before membrane fouling occurs and the cost of periodic replacement must thus be included in any analysis of their economic viability. In accordance with the very abundant literature data, liquid-phase adsorption is one of the most popular methods for the removal of pollutants from wastewater since proper design of the adsorption process will produce a high-quality treated effluent. This process provides an attractive alternative for the treatment of contaminated waters, especially if the sorbent is inexpensive and does not require an additional pre-treatment step before its application. Adsorption is a well known equilibrium separation process and an effective method for water decontamination applications [10]. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances.

Color removal using commercial activated carbon

Adsorption techniques employing solid sorbents are widely used to remove certain classes of chemical pollutants from waters, especially those that are practically unaffected by conventional biological wastewater treatments. However, amongst all the sorbent materials proposed, activated carbon is the most popular for the removal of pollutants from wastewater [41,42,18]. In particular, the effectiveness of adsorption on commercial activated carbons (CAC) for removal of a wide variety of dyes from wastewaters has made it an ideal alternative to other expensive treatment options [42]. It shows a non-exhaustive list of examples of CAC used in wastewater treatment. Because of their great capacity to adsorb dyes, CAC are the most effective adsorbents. This capacity is mainly due to their structural characteristics and their porous texture which gives them a large surface area, and their chemical nature which can be easily modified by chemical treatment in order to increase their properties. However, activated carbon presents several disadvantages [41].It is quite expensive, the higher the quality, the greater the cost, non-selective and ineffective against disperse and vat dyes. The regeneration of saturated carbon is also expensive, not straightforward, and results in loss of the adsorbent. The use of carbons based on relatively expensive starting materials is also unjustified for most pollution control applications [43]. This has led many workers to search for more economic adsorbents.

Non-conventional low-cost adsorbents and removal of dyes

Due to the problems mentioned above, research interest into the production of alternative sorbents to replace the costly activated carbon has intensified in recent years. Attention has focused on various natural solid supports, which are able to remove pollutants from contaminated water at low cost. Cost is actually an important parameter for comparing the adsorbent materials. It was reported that a sorbent could be considered low-cost if it requires little processing, is abundant in nature or is a by-product or waste material from another industry. Certain waste products from industrial and agricultural operations, natural materials and biosorbents represent potentially economical alternative sorbents [44].

This study explores the viability of sawdust of teakwood, rosewood and neem wood powders as natural biosorbents for the removal of heavy metals from textile dye effluent.

MATERIALS AND METHODS

Collection of adsorbents and the industrial effluents

The three different saw dust (SD) such as of teak wood, neem wood and rose wood were collected from the saw mill at Pallavaram. The industrial effluent was collected from a textile industry near Erode. All the chemicals used are analytical grade.

Experimental procedure

Chemical treatment of adsorbents

The adsorbents was treated to a mixture of 37% formaldehyde and 0.2N sulphuric acid in the ratio of 5:20(v/v). The ratio of adsorbents to the chemical mixture was 2:5 (g/ml). The percentage of dye removal from the effluent was calculated by using the formulae:

% of dye removal = $(C_o-C_e)/C_o \times 100$

Where C_o is the initial concentration of the dye and C_e is the solution concentration after adsorption.

Effect of contact time on the adsorption of dye sawdust

The saw dust and effluents were taken in the ratio of 2:5 (gm/ml). The saw dust and the effluent were taken in a conical flask and the mixture was shaken in a shaker with regular time intervals of 90-450 minutes. The studies were done at constant room temperature. Samples were analyzed for reduction of absorbance at different time intervals of 90,180,270,360 and 450 minutes using UV / VIS spectrophotometer at 480nm after filtration of the samples using Whattman filter paper.

Effect of pH on the adsorption of dye sawdust

For each experimental run, the pH of initial solution was adjusted between 2.0 and 8.0 in four different conical flasks by the addition of dilute 0.1N HCl or 0.1N NaOH using a pH meter. The mixture was shaken in a shaker for 450 minutes and the liquid was filtered through Whatmann filter paper and the samples were analyzed for reduction in absorbance using UV / Visible Spectrophotometer at 480 nm.

Effect of temperature on the adsorption of dye sawdust

The mixture of the saw dust and effluent were taken in four different conical flasks and were shaken for 450 minutes. The samples were then transferred to test tubes for heating in the water bath. Then these samples were then transferred to a 2ml eppendrof and then centrifuged at 10,000rpm for 10 minutes. The samples were then analyzed for reduction in absorbance using UV / Visible Spectrophotometer at 480 nm.

Effect of adsorbent dosage

The effect of quantity of the saw dust on the amount of color adsorbed was studied. The saw dust was taken with different amounts of addition such as (2.0, 4.0, 6.0, 8.0) g. The above procedure was followed for each of the dosage to the effluent and the samples were then analyzed for reduction in absorbance using UV / Visible Spectrophotometer at 480 nm.

Characterization of the adsorbent

Fourier Transform Infra red Spectroscopy (FT-IR)

The FT-IR spectra of the neem wood sawdust of pre-treated and their absorption of dyes were taken using a Niclet Impact 400 Fourier Transform Infra Red spectrometer. For measuring IR spectra, 5mg of powdered pre treated sawdust and dye absorbed sawdust are encapsulated in 400mg of KBr. A translucent disk was made by pressing the ground mixed material with a hydraulic pellet press for 1 min. The spectra was recorded in a FT-IR with the range of 500-6000 cm^{-1}.

RESULTS AND DISCUSSION

Table 1. Effect of time with different saw dusts

Time (mins)	Percentage of dye removal		
	Teak wood sawdust	Rosewood sawdust	Neem wood sawdust
90	40.9	35.2	30.1
180	45.4	37.1	32.0
270	52.0	44.5	37.6
360	56.5	49.9	42.0
450	57.1	51.7	42.8
540	57.1	57.1	57.1

Table 2. Effect of temperature on dye removal.

Temp (°C)	Percentage of dye removal		
	Teakwood sawdust	Rosewood sawdust	Neem wood sawdust
30	41.2	37.1	30.8
50	47.4	39.9	33.6
70	49.8	41.7	37.8
90	54.0	43.1	39.8

Table 3. Effect of pH on the adsorption of dye from the effluent using Sawdust.

pH	Percentage of dye removal		
	Teak wood sawdust	Rosewood sawdust	Neem wood sawdust
2	63.7	45.7	42.0
4	61.1	42.8	40.0
6	58.2	40.0	34.2
8	58.0	39.5	34.0

Table 4. Effect of concentration of adsorbent on the uptake of dye from the effluent.

Conc (gm/ml)	Percentage of dye removal		
	Teak wood sawdust	Rosewood sawdust	Neem wood sawdust
0.2	45.9	35.2	31.5
0.4	47.1	40.1	33.1
0.6	54.4	48.1	39.3
0.8	59.9	53.4	43.4
1.0	61.1	55.1	45.1

Table 5. Langmuir isotherm

Initial concentration Co (mg)	Final concentration Ce (mg)	Qe=(Co-Ce)v/w	Ce/Qe
5	0.86	1.04	0.72
0	1.90	2.03	0.97
5	3.61	2.85	1.26
20	5.10	3.72	1.36
25	6.60	4.60	1.43
30	8.60	5.40	1.59
35	10.60	6.11	1.74
40	13.08	6.73	1.93
45	16.30	7.17	2.17
50	18.56	7.86	2.35

Table 6. Freundlich isotherm

Ce	Qe	logCe	logQe
1.9	2.03	0.278	0.307
3.61	2.85	0.557	0.5705

5.0	3.72	0.707	0.662
6.6	4.6	0.815	0.732
8.6	5.4	0.934	0.785
10.6	6.1	1.025	0.828
13.08	6.73	1.116	0.856
16.3	7.17	1.212	0.895

Fig.1a. Percentage of dye removal from the effluent by the pre-treated sawdust with effect of contact time.

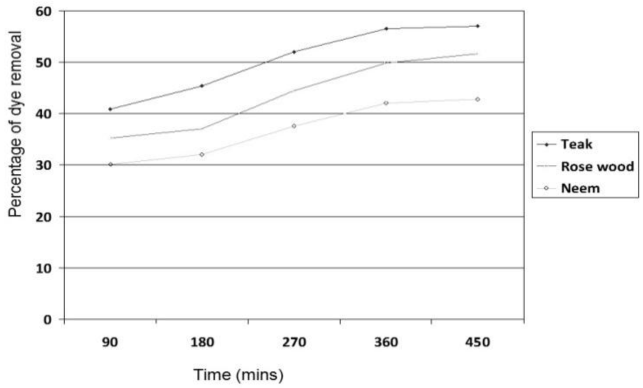


Fig. 1b. Comparison of treated and untreated sawdust with the effect of time on the uptake of dye from the effluent

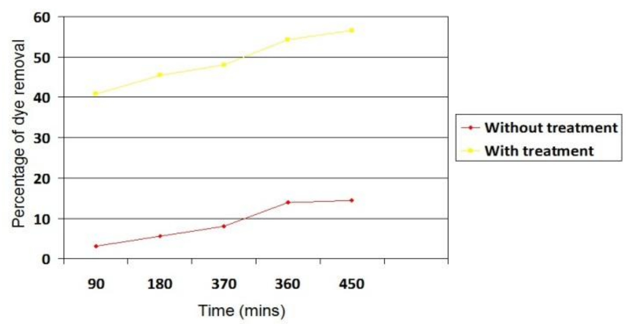


Fig. 2. Percentage of dye removal from effluent by sawdust with effect of temperature.

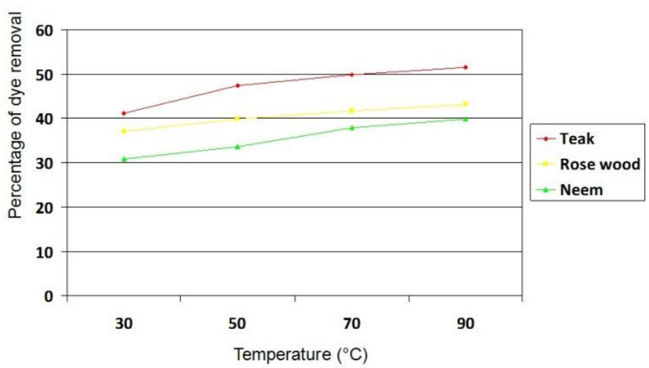


Fig. 3. Percentage of dye removal from effluent by sawdust with effect of Ph

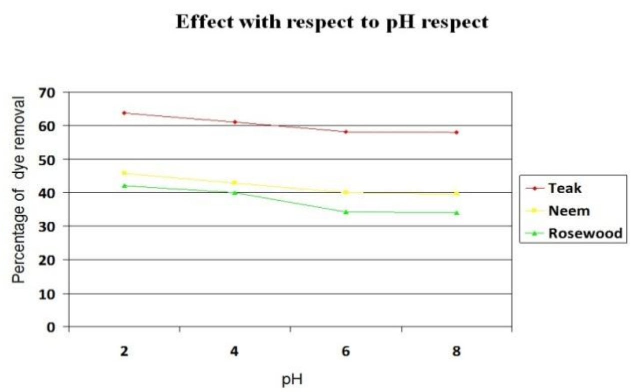


Fig. 4. Percentage of removal of dye from effluent by sawdust with effect of adsorbent dosage.

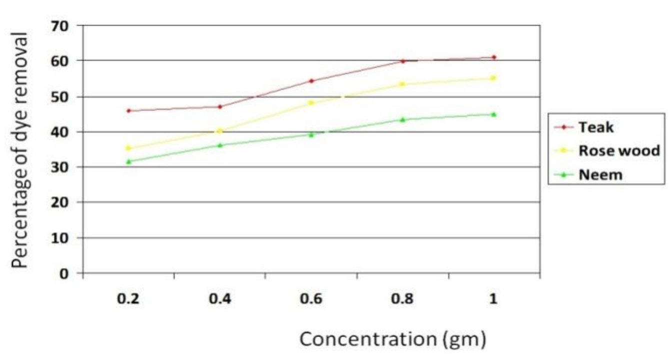


Fig. 5. Langmuir isotherm model

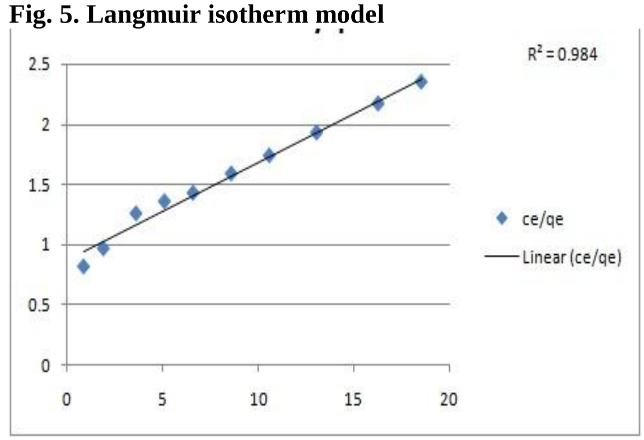
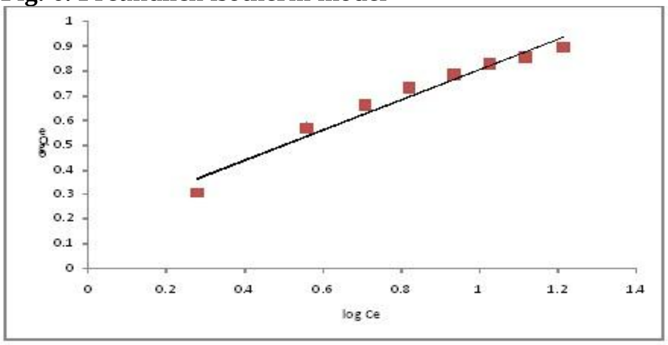


Fig. 6. Freundlich isotherm model



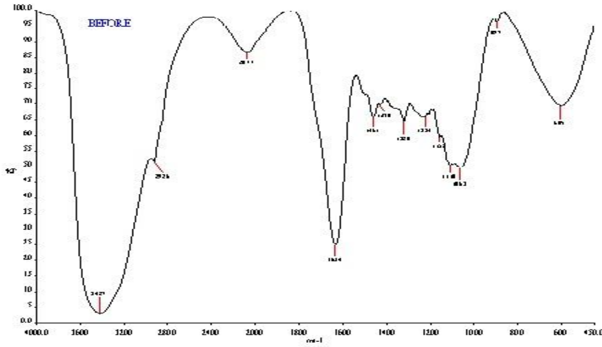


Fig.9 FT-IR of pretreated Teak wood sawdust

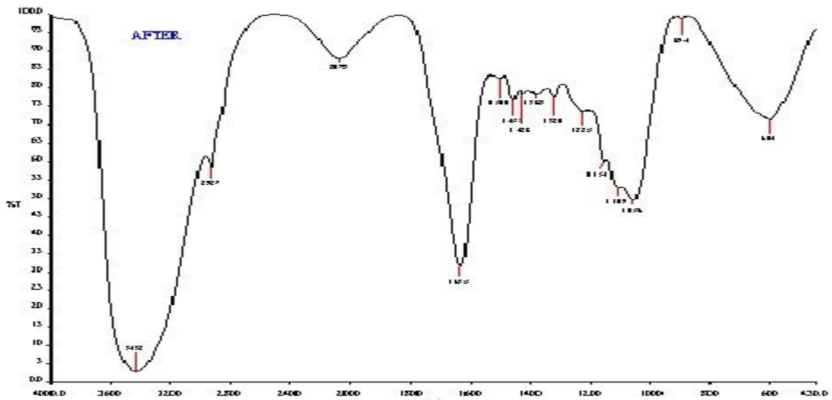


Fig. 10 FTIR of dye adsortpion og pretreated teak wook sawdust

DISCUSSION

Adsorption of dye from industrial effluent

Effect of pH

Acidity of the solution is one of the most important parameter controlling the uptake of dye from waste water and aqueous solution. The uptake of dye decrease as the pH increases from 2 to 10. Identically it was found that as pH increases from 1 to 11, adsorption decreases. The optimum pH was found to be 2.

Effect of adsorbent dosage

It was observed that the amount of dye absorbed varied with varying concentration. The amount of dye absorbed was found to be significant when the adsorbent concentration was increased from 0.2 to 1g. It was found that the maximum adsorption is at the concentration of 1g/ml.

Effect of contact time

The data obtained showed that the contact time of 450 minutes was sufficient to achieve equilibrium and adsorption doesn't change significantly for further increase in contact time.

Effect of temperature

By increase in the temperature from 30-60ºC percentage adsorption was found to be up by 55%. The studies have shown that increase in temperature is known to increase the rate of diffusion of the adsorbent molecules across the external boundary layer owing to decrease in viscosity of the effluent.

Bio-sorption equilibrium

The equilibrium isotherm is of fundamental importance in the design of adsorption. The isotherm expresses the relation between the mass of dye adsorbed at constant temperature per unit mass of the adsorbent and liquid phase concentration. In order to access the adsorption of the effluent over three different saw dust, both Langmuir and Freundlich isotherm models were applied in the entire concentration range from 5mg/l to 50mg/l at room temperature, the data obtained was correlated with the well known linear forms of Langmuir and Freundlich adsorption models.

FT-IR Analysis

In the FT- IR spectra of the teak wood sawdust exhibited in the Fig.9 and fig.10 show absorptions at 3445 cm^{-1} due to the OH (inter molecular hydrogen bonding), 2880-2950 cm^{-1} for C-H stretching, 1614 cm^{-1} for carbonyl group (CO), 1109 cm^{-1} for asymmetrical C-O-C stretching and 518-875 cm^{-1} indicative of aromatic ring.

CONCLUSION

The sawdust were used successfully as an adsorbent for the removal of dye from the industrial effluent among which the saw dust of the teak proved to be much efficient in adsorbing the dye. The different operational parameters observed during the process of investigation revealed that the pH, adsorbent dosage, contact time and temperature govern the overall process of adsorption. The equilibrium isotherms were analyzed for Langmuir and Freundlich adsorption isotherms. The FTIR results showed that the main functional groups present in the sawdust are phenol and alcohol. The SEM analysis reveals that there are changes in the characteristics of the sawdust. This study therefore shows that neem wood sawdust could be prescribed as bio-sorbent for the removal of dyes from the industrial effluents. The simplicity of the method may be significant for the treatment of dye waste waters that are difficult to deal with using chemical and biological methods.

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