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Research Article

STUDIES ON ADSORPTION OF DYES USING AGRO-WASTE MATERIALS

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ABSTRACT

Agricultural wastes products are quite commonly distributed as the result of agricultural practices. They are inexpensive and subject to biodegradable. This paper presents a review of dye adsorption using activated carbon prepared from different sources and environmental implications. Also, its major challenges together with future prospects are summarized and discussed. Conclusively, the production of activated carbon from waste biomass for adsorption of these dyes is of great importance in pollution control and environmental conservation. Agricultural waste is a good source for the adsorption of the dyes generated during the textile processing. For the process of adsorption, agricultural waste products are used as natural or in the modified form through activation process. This review article focuses on the various sources of the agricultural waste products and its adsorption capacity of the different dyes. Signifying the potential of the use of agricultural wastes products for removing off the toxic dye substances from the effluent discharging into the water bodies.

INTRODUCTION

Waste water from the textile industries mainly contains moderate concentration of dyestuffs which contributes significant contamination of aquatic ecosystem. The demand of synthetic dyes has experienced the significant growth in the past decades and it is reported that more than 7×10^5 metric tonnes of various dyes are produced worldwide annually. Effluent discharged from dyeing industries is highly coloured and prove toxic to the aquatic ecosystem. Dyes are persistent in nature and strongly absorb sunlight which decreases the intensity of light absorbed by the water, plants and reduces photosynthesis, dissolved oxygen of the aquatic ecosystem and results in increase of COD. Dye effluents exhibit toxic and carcinogenic effects towards microbial population, human beings and animals. [1]

Therefore many methods such as activated carbon adsorption, chemical coagulation, ion exchange, electrolysis, ultra filtration, photo oxidation were studied to decolourize dye solution. Among them adsorption technique is generally considered to be an effective method for quickly lowering the concentration of dissolved dyes.

REVIEW OF LITRATURE

Srinivasa kannan *et al* (2004) carried out a two-stage process for the preparation of activated carbon from rubber wood saw dust. The two-stage process with semi-carbonization up to 200 C for 15 min followed by activation at 400 and 500 C for 30, 45, 60 and 90 min. Phosphoric acid was used as an activating agent with various impregnation ratio (dry wt. of H3PO4/ dry wt. of rubber wood saw dust) of 1, 1.5, and 2. At the optimal conditions of activation, activated carbon with iodine number and surface area of 1096 mg g-1 and 1496 m2 g-1 respectively were obtained.

Corcho *et al* (2006) prepared activated carbon from vineyard shoot using phosphoric acid as the activating agent. They found the activated carbons porosity was better when the raw material was impregnated and heated at intermediate temperatures.

Haimour & Emeish (2006) reported phosphoric acid activated date pit carbon, the iodine number increased with increasing activation temperature. Impregnation increases caused an oscillation in the iodine number.

Senthilkumaar *et al* (2006) prepared activated carbon from male flowers of coconut tree and jute fibre using 15%

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phosphoric acid in the ratio 1:3. They found a porosity of 72.36% and 76.14%, surface area of 328 and 680 m2/g and pHzpc of 6.23 and 4.56 for coconut flower carbon and jute fibre carbon respectively indicating that the fibrous materials gave a higher surface area than the other cellulosic materials. The porosity of the carbon varied based on the activating agent, activated carbon prepared from coconut male flower using phosphoric acid and sulphuric acid (Senthilkumaar *et al* 2006b) yielded carbons with 72.36% and 65% porosity respectively.

Baccar *et al* (2009) prepared activated carbon from olive-waste cake using phosphoric acid as a activating agent, carbon preparation parameters such as concentration of the activating agent, impregnation ratio 19 and activation time were optimized. They found the surface area of the sorbent increased rapidly from 716 to 1020 m2/g with an increase of acid concentration from 35 to 65% phosphoric acid, and further increase in the acid concentration (85%) did not show an appreciable increase in the surface area. Chan *et al* (2009) prepared activated carbon from bamboo waste scaffolding using phosphoric acid. They found the surface area up to 2500 m2/g of the activated carbon increased with impregnation ratio (2.4) and activation temperature (400 or 600ºC).

Lim *et al* (2010) prepared activated carbon from palm shells by phosphoric acid impregnation. They prepared carbon at low activation temperature (425ºC) and activation time (30 min), while varying the impregnation ratio of phosphoric acid from 0.5 to 3. The yield of activated carbon was not vary with the impregnation ratio and was found to be about 50%. The textural characteristics were found to improve with increase in the impregnation ratio, up to 2 and further increase in IR the textural character decreased. The BET surface area of activated carbon corresponding to an impregnation ratio of 3, with an iodine number of 1035 mg/g was found to be 1109m2/g with a pore volume of 0.903cm3/g and an average pore diameter of 3.2 nm. The textural characteristics of activated carbon reveal that the pore size is widely distributed with the contribution of micropores around 50%.

Fabiana *et al* (2010) prepared activated carbon from piassava fibres using chemical activation with zinc chloride and phosphoric acid and physical activation with carbon dioxide or water vapour. Zinc chloride gave the highest surface area of 1190 m2/g and phosphoric acid activated carbon gave largest pore volume of 0.543 cm3/g. Li *et al* (2010) reported that activated carbon prepared from polygonum orientale Linn by phosphoric acid activation gave a surface area of 1398 m2/g.

Bhari *et al* (2012) prepared activated carbon from grape seeds using chemical activation with phosphoric acid. Grape seeds were pre-treated with sulfuric acid to improve its wettability. Microporous activated carbons with some contribution of mesoporosity were obtained. The best results in terms of surface area (1139 m2/g) and mesopore volume (0.24cm3/g) development were observed for a grape seeds to phosphoric acid ratio of 1:3 and a carbonization temperature of 500°C. They found the activated carbon morphology had an egg shell structure that favored applications in liquid phase.

Mohamad & Paul (2012) studied the pore characteristics of activated carbons obtained from the phosphoric acid activation of cotton stalks. They concluded that the textural characteristics of the derived activated carbons were found to be strongly dependent on the impregnation ratio and activation temperature. The mesopore volume attained a maximum value (0.61cm3/g) in the case of activated carbons produced at the highest impregnation ratio and activation temperature.

Aghdas *et al* (2014) revealed the impregnation ratio of the activating agent highly influenced the surface area and the porosity development during activated carbon preparation. They prepared highly microporous activated carbon from Eucalyptus camaldulensis wood by chemical activation with H3PO4, ZnCl2 at different impregnation ratios as well as by pyrolysis, followed by activation with KOH. Varying the H3PO4/biomass ratio from 1.5 to 2.5, the prepared activated carbon displayed BET surface areas in the range of 1875–2117 m2/g with micropores content of 69-97%. For the ZnCl2 activated carbon, BET surface areas varyied from 1274.8 to 2107.9 m2/g with micropores content of 93-100% for impregnation ratios of 0.75–2.0. The activated carbon obtained by KOH activation had the largest BET surface area of 2594 m2/g and a high micropore of 98%. From the above they found that the activating agent and its concentration strongly influenced the textural characteristics of the eucalyptus wood based activated carbon.

Alicia *et al* (2014) studied the influence of activation atmosphere used in the chemical activation of almond shell on the carbon characteristics. They found activated carbons prepared at low and intermediate impregnation ratios showed higher yields. This could be attributed to the decomposition of the polymeric structures of the activated carbons during the activation stage that release most elements different from carbon (N, H and O). Activating agent employed permits the dehydration, depolymerization and redistribution of the constituent polymers, and the conversion of aliphatic groups to aromatics, increasing the yield of the activated carbons. Higher impregnation ratios produce a higher elimination of tars of the pores decreasing the yield.

Advantages of Adsorption over Other Methods

Colour in dye house effluents has always been a difficult problem to solve and the utilization of dyes has made it even more serious. Cooper (1993) summarized the technologies used until then in order to remove or atleast reduce colour, mentioning that some them have certain efficiency: Coagulation and/or flocculation, membrane technologies, chemical oxidation technologies, biochemical oxidation and adsorbent utilization. Among various treatment technologies, adsorption onto activated carbon has proven to be one of the most effective and reliable physicochemical treatment methodology

Research Hypothesis

Adsorption

Adsorption is the most used method in physicochemical wastewater treatment, which can mix the wastewater and the porous material powder or granules, such as activated carbon and clay, or let the wastewater through its filter bed composed of granular materials. Through this method, pollutants in the wastewater are adsorbed and removed on the surface of the porous material or filter. Commonly used adsorbents are activated carbon, silicon polymers and kaolin. Different adsorbents have selective adsorption of dyes. But, so far, activated carbon is still the best adsorbent for dye wastewater.

The chroma can be removed to 92.17% and COD can be reduced to 91.15% in series adsorption reactors, which meet the wastewater standard in the textile industry and can be reused as the washing water. Because activated carbon has selection to adsorb dyes, it can effectively remove the water-soluble dyes in wastewater, such as reactive dyes, basic dyes and azo dyes, but it cannot adsorb the suspended solids and insoluble dyes. Moreover, the activated carbon cannot be directly used in the original textile dyeing wastewater treatment, while generally used in lower concentration of dye wastewater treatment or advanced treatment because of the high cost of regeneration.

As discussed earlier, adsorption has emerged out as effective, economical and ecofriendly treatment technique. It is a process potent enough to fulfill water reuse obligation and high effluent standards in the industries. Adsorption is basically a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and/or chemical interactions [5]. It is a partition process in which few components of the liquid phase are relocated to the surface of the solid adsorbents. All adsorption methods are reliant on solid-liquid equilibrium and on mass transfer rates. The adsorption procedure can be batch, semi-batch and continuous. At molecular level, adsorption is mainly due to attractive interfaces between a surface and the group being absorbed. Depending upon the types of intermolecular attractive forces adsorption could be of following types:

Physical adsorption It is a general incident and occurs in any solid/liquid or solid/gas system. Physical adsorption is a process in which binding of adsorbate on the adsorbent surface is caused by van der Waals forces of attraction. The electronic structure of the atom or molecule is hardly disturbed Dyes are widely used in industries such as textiles, rubber, plastics, printing, leather, cosmetics, etc., to color their products. As a result, they generate a considerable amount of colored wastewater. There are more than 10,000 commercially available dyes with over 7×10^5 tonnes of dye stuff produced annually. It is estimated that 2 % of dyes produced annually is discharged in effluents from associated industries. Among various industries, textile industry ranks first in usage of dyes for coloration of fiber. The total dye consumption of the textile industry worldwide is in excess of 107 kg/year and an estimated 90 % of this ends up on fabrics. Consequently, 1,000 tones/year or more of dyes are discharged into waste streams by the textile industry worldwide. Discharge of dye-bearing wastewater into natural streams and rivers poses severe problems to the aquatic life, food web and causes damage to the aesthetic nature of the environment.

Dyes absorb and reflect sunlight entering water and so can interfere with the growth of bacteria and hinder photosynthesis in aquatic plants. The problems become graver due to the fact that the complex aromatic structures of the dyes render them ineffective in the presence of heat, light, microbes, and even oxidizing agents and degradation of the dyes become difficult. Hence, these pose a serious threat to human health and water quality, thereby becoming a matter of vital concern. Keeping the essentiality of color removal, concerned industries are required to treat the dye-bearing effluents before dumping into the water bodies. Thus, the scientific community shoulders the responsibility of contributing to the waste treatment by developing effective dye removal technique.

Dyes can have acute and/or chronic effects on exposed organisms depending on the exposure time and dye concentration. Dyes can cause allergic dermatitis, skin irritation, cancer, mutation, etc. Dyes can be classified as anionic (direct, acid and reactive dyes), cationic (basic dyes) and non-ionic (dispersive dyes).

Among treatment technologies, adsorption is rapidly gaining prominence as a method of treating aqueous effluent. Some of the advantages of adsorption process are possible regeneration at low cost, availability of known process equipment, sludge-free operation and recovery of the sorbate (Kapdan and Kargi 2002). Activated carbon is the most widely used adsorbent for dye removal because of its extended surface area, micro-pore structures, high adsorption capacity and high degree of surface reactivity. However, commercially available activated carbon is very expensive and has high regeneration cost while being exhausted. Furthermore, generation using solution produces a small additional effluent while regeneration by refractory technique results in a 10–15 % loss of adsorbent and its uptake capacity. This has lead to search for cheaper substances. Researchers are always in a hunt for developing more suitable, efficient and cheap and easily available types of adsorbents, particularly from the waste materials.

Research Hypothesis

Activated carbons (commercial) with large surface area have shown high adsorption capacity for many adsorbates containing dyes but they are composed of pores less than 2nm and hence are not effective for large size synthetic dyes[2]. Furthermore the commercial Activated carbon has also disadvantages such as high price, high cost of regeneration. In order to overcome this problem researchers are trying to develop low cost adsorbents as viable substitute for activated carbon.

Agricultural wastes are of low economic value, so inexpensive and abundantly available. They are mainly composed of cellulose, hemicelluloses and lignin which make them effective adsorbent due to presence of functional groups like hydroxyl, carboxyl ,methoxy, phenol etc, that participate in binding with pollutants.

There are two basic processes to activate carbon materials – physical, chemical the temperatures used in chemical activation are lower than that used in the physical process. As a result the development of a porous structure is better in the case of chemical activation processes. Chemical activation can be accomplished in a single step by carrying out thermal decomposition of raw material with chemical reagents. Chemical activation processes have been carried out with acidic reagents namely $ZnCl_2$ [3], H_3PO_4 [4], HCl[5] ,H_2SO_4[6],or with basic reagents like KOH[6], K_2CO_3[7], NaOH[8], Na_2CO_3[9]

Aims and Objectives

In the present study adsorbents will be prepared from different agricultural waste like coconut coir, cotton seeds, peanut hull, ground nut hull, sugarcane bagasse coconut shell, and jackfruit seeds. The agricultural waste will be cleaned and dried first in sunlight and then in oven. The dried material will be pulverised to get powder form of various size. Raw material obtained from agricultural waste will be given chemical treatment to produce activated carbon material as mentioned above. The adsorbents(raw and activated) obtained will be characterised by techniques like X- ray Diffraction, Scanning Electron Microscope(SEM),Transmission Electron Microscope (TEM) , Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), Fourier Transform Infrared Spectroscopy (FTIR) before and after adsorption. Following parameters of adsorbents (raw and activated) will be studied.

- pH
- Conductivity
- Moisture Content
- Ash Content
- Bulk Density
- Specific Gravity
- Water Soluble Matter
- Acid Soluble Matter
- Iodine Number
- Surface Area
- Phenol-adsorption Capacity
- Decolorizing Power

Study of adsorption of different dyes using different adsorbents prepared from different agricultural wastes will be done. From this dye and corresponding adsorbent can be fixed.

Once dye and particular adsorbent is selected, effect of various parameters like initial concentration of dye, particle size of adsorbate, adsorption dosage, contact time, effect of pH of solution etc will be studied.

The mechanism of adsorption will be studied by various adsorption isotherms like Langmuir, Freundlich, and Temkin adsorption isotherm [10]

Kinetics of dye adsorption on activated charcoal prepared from agricultural waste will be analyzed using three different kinetic models namely Pseudo second order model, Intraparticle model, Pseudo first order model [11]

Various Thermodynamic parameters like Gibbs free energy change, enthalpy change, entropy change will be evaluated.

Decolourization of dye solution using raw as well as activated carbon material will be done. This decolourization is due to adsorption process.

Uptake capacity (adsorption capacity) of dye and various adsorbents will be studied.

Desorption –After completing the study of adsorbent and dye, desorption study will be done.

MATERIALS AND METHODS

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Desorption –After completing the study of adsorbent and dye, desorption study will be done.

For the entire experimental work AR grade chemicals, deionised distilled water will be used.

Spectrophotometer, digital balance, centrifuge machine, water bath, pH meter, muffle furnace, shaker bath, vacuum desiccators and various instruments as required for characterisation of adsorbent will be used.

EXPECTED RESULTS

This study will be done to elucidate the nature of adsorption, recycling of the adsorbant and the dye. This desorption study will make dying process economical, used to design process in pollution amendments and control.

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