COMPARISON OF FOOD WASTE, *PONGAMIA* SEED COATS AND COMMERCIAL ACTIVATED CARBON AS EFFECTIVE ADSORBENTS IN DAIRY EFFLUENT TREATMENT

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ABSTRACT

Activated carbons are widely used as adsorbents for the removal of organic chemicals and metal ions of environmental or economic concern from air, gases, potable water, and wastewater. The economic drawback of hard wood and bituminous coal has stimulated the interest to utilize cheaper raw materials for the production of activated carbon. Consequently, a wide variety of wastes have been investigated as cellulosic precursors for the production of activated carbon. Dairy industry is one of the major agro-based industries, which involve processing of raw milk into consumer products. Adsorption technique for the treatment of dairy waste water can reduce impurities namely protein, fat, carbohydrates, lactose, milk solids and whey along with the removal odor considerably. The objective of the present work is to synthesize and characterize activated carbon adsorbents from the selected raw materials, through pyrolysis assisted by chemical activation, for odor removal by adsorption of organic matter from dairy waste water. For this purpose, *Pongamia* seeds and food waste were selected as precursor materials. Commercial charcoal was also used as a reference adsorbent. The carbon produced by pyrolysis of *Pongamia* seeds and food waste are chemically activated with various activating agents, namely, zinc chloride and potassium hydroxide. Characterization tests were carried out for the activated carbon as well as for the effluent treatment plant inlet dairy effluent sample. Adsorption studies for biological oxygen demand and chemical oxygen demand control of the dairy effluent samples were carried out using the prepared activated carbon.

Keywords: Dairy waste water, Chemical oxygen demand, Biological oxygen demand, Food waste, *Pongamia pinnata*, Activated carbon, Adsorption, Odour removal.

INTRODUCTION

Activated carbon

Activated carbon has been processed to make it extremely porous, to have a very large surface area available for adsorption or chemical reactions. Under an electron microscope, the high surface-area structures of activated carbon are revealed [1]. Individual particles display various kinds of porosity; there may be many areas where flat surfaces of graphite-like material run parallel to each other, separated by only a few nanometres [2]. These micropores provide excellent conditions for adsorption to occur since adsorbing material can interact with many surfaces simultaneously. Tests of adsorption behavior are usually done with nitrogen gas at 77 K under high vacuum, but in convention, activated carbon is found to be perfectly capable of producing the equivalent, by adsorption from its environment, liquid water from steam at 100°C and a pressure of 1/10,000 of an atmosphere [3]. Physically, activated carbon binds materials by van der Waals force or London dispersion force. Activated carbon does not bind well to certain chemicals, metals and most inorganic [4]. Activated carbon is classified based on their physical characteristics.

1. Powdered activated carbon
2. Granular activated carbon
3. Impregnated carbons
4. Polymer coated carbon
5. Extruded activated carbon.

Preparation of activated carbon

Activated carbon is nothing but carbon produced from carbonaceous source materials like nutshells, peat, wood, coir, lignite, coal and petroleum pitch [5-7]. It can be produced by any one of the following described processes:

Physical reactivation
By this process the precursor is developed into activated carbons using gases. This is generally done by using one or a combination of the following processes: Carbonization-material having appreciable carbon content are pyrolyzed at temperature ranging between 600 and 900°C, in the absence of oxygen [8]. Oxidation-in this process carbonized material are exposed to oxidizing atmospheres at temperatures above 250°C, usually in the temperature range of 600-1200°C.

Chemical activation
Before carbonization, the raw material can be impregnated with an acid, strong base, or a salt. After impregnation, the raw material needs to be carbonized at lower temperatures (450-900°C) [9,10]. Chemical activation is preferred over physical activation owing to the lower temperatures and shorter time needed for activating material [11].

Applications of activated carbon

Activated carbon is used in gas purification, gold purification, metal extraction, water purification, medicine, sewage treatment, air filters in gas masks and respirators, filters in compressed air and many other applications [12].

One major industrial application involves the use of activated carbon in the metal finishing field. It is very widely employed for purification of electroplating solutions. For example, it is a main purification technique for removing organic impurities from bright nickel plating solutions. A variety of organic chemicals are added to plating solutions for improving their deposit qualities and for enhancing properties such as brightness, smoothness, ductility, etc [13]. Due to passage of direct current and electrolytic reactions of anodic oxidation and catholic reduction, organic additives generate unwanted break down products in solution [14,15]. Their excessive build up can adversely affect the plating quality and physical properties of deposited metal. Activated carbon treatment removes such impurities and restores plating performance to the desired level.

In environment field activated carbon is used in removing pollutants from air or water streams both in the field and in industrial processes such as spill cleanup, groundwater remediation, drinking water

filtration, air purification, volatile organic compounds capture from painting, dry cleaning, gasoline dispensing operations, and other processes [16].

In medical applications activated carbon is used to treat poisonings and overdoses following oral ingestion. It is thought to bind to poison and prevent its absorption by the gastrointestinal tract. Dosing is usually empirical at 1 g/kg of body mass (for adolescents or adults, give 50-100 g), usually given only once, but depending on the drug taken, it may be given more than once. In rare situations activated charcoal is used in intensive care to filter out harmful drugs from the blood stream of poisoned patients.

Dairy waste water treatment techniques
The dairy waste water contains the following contaminants:

Milk solids, whey, dissolved sugars, acids, alkalis, detergents, disinfectants, microbiological load, pathogenic viruses, and bacteria. Due to the high organic content of the dairy effluents, the chemical oxygen demand (COD)/biological oxygen demand (BOD) analysis is chosen as a measure of the activated carbon treatment. Dairy industries discharge wastewater, which is characterized by high COD, BOD, nutrients, and organic and inorganic contents. Such wastewaters, if discharged without proper treatment, severely pollute receiving water bodies [17-19]. Common techniques for treating dairy industry wastewaters include grease traps, oil water separators for separation of floatable solids, equalization of flow, and clarifiers to remove suspended solids. Dairy wastewaters are generally treated using biological methods.

Biological methods
Aerobic process
Aerobic biological treatment involves microbial degradation and oxidation of waste in the presence of oxygen that includes processes such as:

- Activated sludge
- Trickling filters
- Sequencing batch reactor

All compounds of dairy wastewater are biodegradable except protein and fats, which are not easily degraded. However, the presence of fats shows the inhibitory action during anaerobic treatment of dairy wastewaters. This inhibition is due to the presence of long-chain fatty acids formed during the hydrolysis of lipids, which causes retardation in methane production. Long-chain fatty acids were reported to be inhibitory to methanogenic bacteria, but lipids do not cause serious problems in aerobic processes.

Anaerobic process
The up flow anaerobic sludge blanket reactor is a single tank process. Wastewater enters the reactor from the bottom and flows upward. A suspended sludge blanket filter treats the wastewater as the wastewater flows through it. The sludge blanket is comprised of microbial granules, because of their weight, resist being washed out in the up flows [20]. As a result, gases (methane and carbon dioxide) are released. The rising bubbles mix the sludge without the assistance of any mechanical parts. Sloped walls deflect material that reaches the top of the tank downwards. The clarified effluent is extracted from the top of the tank in an area above the sloped walls [21,22]. After several weeks of use, larger granules of sludge are formed which in turn act as filters for smaller particles as the effluent rises through the cushion of sludge. Because of the up flow regime, granule-forming organisms are preferentially accumulated as the others are washed out. The gas that rises to the top is collected in a gas collection dome and can be used as energy (biogas). An up flow velocity of 0.6-0.9 minute/hrs must be maintained to keep the sludge blanket in suspension.

Physico-chemical treatment method
The physico-chemical treatment methods consist of coagulation/ flocculation by various inorganic and organic natural coagulants and membrane processes. Membrane processes produce purified water without milk proteins and lactose and which could be recycled. Coagulation using chemical coagulants consists of combining insoluble particles and/or dissolved organic matter present in dairy wastewater into large aggregates, thereby facilitating their removal in subsequent sedimentation, floatation, and filtration stages [23,24].

METHODS

The effluent treatment process for dairy waste water adopts physico-chemical methods with adsorption playing a significant role in removing organic chemical contaminants that may indirectly contribute to secondary pollutants like odor [25,26]. In the present study, an attempt has been taken to study economic and eco-friendly activated carbon alternatives for effective organic contaminant removal. The entire investigation has been focused with the monitoring of COD, BOD and dissolved oxygen (DO) all directly related to the organic chemical content and indirect measure of odor.

Preparation of activated carbon
The composite food waste sample was collected, and dried in an oven (105°C) for 2 hrs. The dried material was then crushed to uniform powder and subjected to sieve analysis was done on the powdered feed (mesh size 44, 60, 85). The smallest mesh size having the largest percentage weight of feed was selected, and that particular uniform powder was used for further experiments [24,27]. The powdered food waste samples were soaked in 1 N solution of zinc chloride in the ratio 1 g:2 ml. The mixture was put on the magnetic stirrer for 2 hrs at 80°C and left overnight for the proper impregnation. The sample mixture was dried in an oven (110°C) for 3-4 hrs [28,29]. The dried and chemically impregnated sample was now crushed again using a mortar and pestle. The muffle furnace was set up and the sample was placed in an open crucible at 500°C for 60 minutes. The activated carbon was crushed using a mortar and pestle. It was washed with distilled water till the pH showed 7. The washed activated carbon was now dried in an oven (110°C, 2 hrs). The final product (carbon from food waste activated with $ZnCl_2$) was crushed and stored in an air tight container [30,31]. The procedure was repeated for *Pongamia pinnata* seed coats with KOH used as an activating agent instead of $ZnCl_2$. The two activated carbon samples were characterized and tested for organic chemical contaminant removal from dairy effluents (Fig. 1).

Characterization tests for synthesized activated carbon and dairy effluent
The characterization tests for activated carbon which includes sieve analysis for the separation of a mixture of various sizes of grains was done to achieve the specific size requirements (1-150 μm) for activation using a screening surface [32]. Bulk density of the activated carbon was also checked to meet the specifications (0.2-0.75 g/cc) prior to activation. Volatile matter content and moisture content were evaluated to determine the gas or vapor and moisture released from the synthesized activated adsorbent. Ash content was checked to identify the inorganic residue remaining after the water and organic matter have been removed by heating the activated samples in the presence of oxidizing agents [10,33].

The dairy effluent subjected to adsorption was primarily characterized to evaluate certain preliminary parameters using standard procedures.

pH conforms the acidity and basicity of the sample. Inorganic chloride, which can corrode metals and affect the taste of food products was measured to test the quality of water. Conductivity was measured to monitor the salt content and to check the ability of water to conduct electricity. COD, a measure of the amount of oxygen used to oxidize the organic matter in a sample of waste water by using a strong oxidizing agents like potassium dichromate, where carbon and hydrogen present in the waste water is oxidized to carbon dioxide and water. COD is an
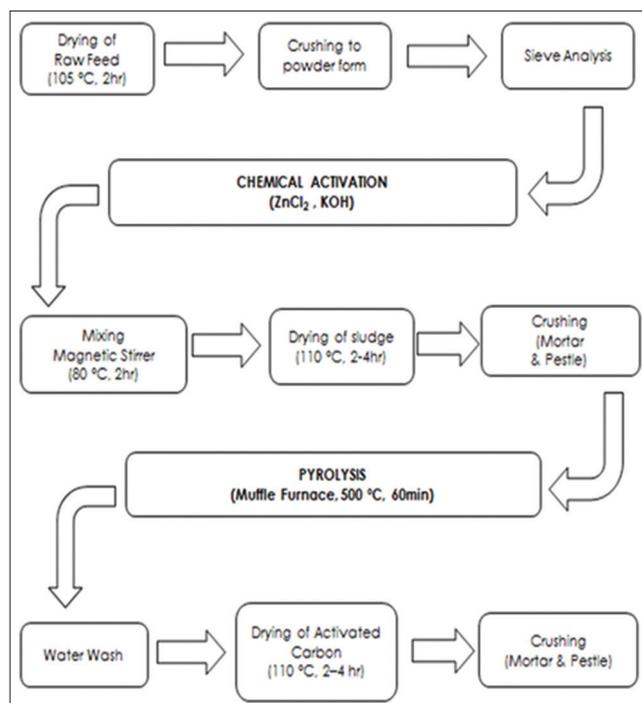
Fig. 1: Preparation of activated carbon

Fig. 2: Schemes of experiments

Table 1: Comparison of activated carbon characteristics

Characteristics	Food waste $ZnCl_2$ activated	*Pongamia* seed coats KOH activated	AC [8]
Db (g/cc)	0.458	0.561	0.2-0.75
Vc (%)	43	37	37.5±0.03
Mc (%)	14.4	16.1	16.67±0.07
Ac (%)	12	17	17.1±0.01

Table 2: A comparison of activated carbon characteristics

Characteristics	Effluent before adsorption studies	Effluent treated with activated carbon		
		A	B	AC
pH	8.53	7.25	7.29	7.18
Chloride (mg/L)	350.24	195.3	200.4	185.23
Conductivity (μs/cm)	1.875	1.62	1.65	1.58
COD (mg/L)	244	92	96	89
BOD (mg/L)	115.2	41.4	47.4	40.8
DO (mg/L)	0.49	3.84	3.35	3.92

COD: Chemical oxygen demand, BOD: Biological oxygen demand, DO: Dissolved oxygen

indirect measurement of determining the amount of pollutants in waste water. DO is the amount of oxygen dissolved in waste water [26,34]. Fish and other aquatic animals depend on DO to live. DO is determined by titrimetric method and found immediately whereas BOD takes five days. BOD is a measure of the amount of oxygen consumed by the bacteria to decompose the organic matter under aerobic conditions. BOD is determined by incubating a sealed sample of water for 5 days and measuring the loss of oxygen from the beginning to the end of the test. If effluent with high BOD level is discharged into a stream or river, it will accelerate bacterial growth in the river. The oxygen may diminish to levels that are lethal for most fish and many aquatic insects.

Adsorption studies using activated carbon synthesized from food waste and *Pongamia* seed coats

The effluent after characterization was subjected to batch adsorption studies using the synthesized activated carbon from food waste, *Pongamia* seed coats and the effluent after adsorption was characterized for COD and BOD specifically as detailed in Fig. 2. The results were then compared with that obtained using commercially available activated carbon [35,36].

RESULTS AND DISCUSSION

Activated carbon was synthesized from the given precursor materials (food waste and *Pongamia* seed coats). The activating agents used were zinc chloride and potassium hydroxide. 85 mesh size powdered precursor material was activated with 1N solution of the activating agent. Single step pyrolysis method was used for activating. The dairy effluent samples were collected from Jeppiaar dairy, Thiruvannamalai. Adsorption studies were done on the effluent treatment plant (ETP) inlet sample, and the drop in organic content was compared with the ETP outlet sample. Activated carbon prepared from food waste activated by zinc chloride (A) showed favourable characterization results over activated carbon prepared from *Pongamia* seed coats activated by potassium hydroxide (B) in comparison with commercial grade activated carbon (AC), showing lower density (D_b), higher volatile matter content (V_c), lower ash content (A_c) and lower moisture content (M_c) as shown in Table 1.

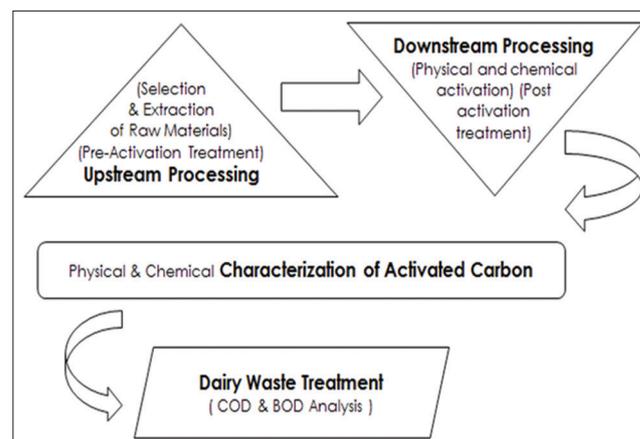Food waste (activated by zinc chloride) and *Pongamia* seed coats (activated by potassium hydroxide) showed considerate decrease in COD, BOD levels of the ETP inlet samples. The COD and BOD values, initially, were found to be 244 mg/L and 115.2 mg/L respectively which exceeded the limitations of 200 mg/L and 100 mg/L set by the central pollution control board (CPCB) for dairy effluents. Post adsorption, the COD value showed a minimum of 92 mg/L while the BOD came down to 41.4 mg/L. The characteristics of dairy waste water were also analyzed before and after adsorption to further understand and analyze the effect of the adsorptive properties of the synthesized activated carbon. The pH of the ETP inlet samples came down to 7.25 from 8.53. The permissible pH of the effluent waters set by the CPCB for dairy effluents is 8.5. The chloride content drastically reduced from 350.24 mg/L to 195.32 mg/L. The conductivity declined from 1.875 μs/cm to 1.623 μs/cm. The evaluated effluent characteristics are represented in Table 2 respectively.

CONCLUSION

Activated carbon was synthesized from the given precursor materials (food waste and *Pongamia* seed coats) using zinc chloride and potassium hydroxide as activating agents. It was successfully used to treat dairy waste water (ETP inlet) to lower the organic content and hence reduce odor. COD, BOD of the dairy effluent showed a decline of over 60%. Furthermore, there was a considerable decrease in chlorides content, pH and conductivity of the dairy effluents. Hence, it is concluded that food waste and *Pongamia* seeds can be considered

as effective replacements for commercial charcoal for dairy waste treatment because they show good adsorptive results, are cost-effective and environment friendly.

ACKNOWLEDGMENTS

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