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Silica Interfaced Biocarbon Technology for Decolourization and Removal of Pollutants from Distillery Wastewater and its Safe Use in Farming Practice – a Green Concept

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Abstract: Distillery industries are responsible for the generation of ecotoxic wastewater called spent wash. They discharge their untreated wastes directly into the natural environments which cause various adverse effects on soil, water, air and health. It contains caramel, melanoidin and much more toxic chemicals. Melanoidin is a recalcitrant pigment responsible to give brownish colour to spent wash. The level of Biochemical oxygen demand (BOD) and chemical oxygen demand (COD) are key indicators of wastewater characteristics and treatment. In the current investigation, we introduced a new biocarbon is generated using a novel medicinal plant Garland daisy (*Glebionis coronia* – Asteraceae). The removal capacity of the biocarbon is significantly enhanced by interfacing with inert silica as support material. The dirt free distillery wastewater was introduced into the batch reactor system and biosorption process is carried out at room temperature of 30 ±2°C.The results indicated that, 98.5% of organic load is removed with biocarbon dose rate of 2.5g/100 mL at 180 min equilibrium time. The higher growth of fodder grass and leafy vegetables such as *Coriandrum sativum* L. and *Amaranthus caudatus* in a pilot project are observed.

Key words: Distillery wastewater · Detoxification · Garland daisy · Biocarbon · Reuse

INTRODUCTION

Water, food and energy securities are emerging as increasingly important and vital issues for the sustainable development. The quality of water is of vital concern for mankind since it is directly linked with human welfare. Water quality, characteristics of aquatic environments arise from a multitude of physical, chemical and biological interactions. This dynamic balance in the aquatic ecosystem is upset by various man-made activities and industrial modernization is resulting in severe water pollution. Current and future fresh water demand could be met by enhancing water reuse efficiency and demand management. Thus, wastewater or low quality water is emerging as potential source for demand management after essential treatment [1, 2].

Toxic organic pollutants cause several environmental problems to our environment. The most common organic pollutants are generally named as persistent organic pollutants (POPs).Since they are persistent, long way transported and highly toxic in nature. During the decomposition process of organic pollutants the dissolved oxygen in the receiving water may be consumed at a greater rate than it can be replenished, causing oxygen depletion and having severe consequences for the stream biota [3].

Wastewater with organic pollutants contains large quantities of suspended solids which reduce the light available to photosynthetic organisms and, on settling out, alter the characteristics of the water bodies, rendering it an unsuitable habitat for many aquatic lives [4, 5].

The removal of organic pollutants from wastewater is a very important challenge aspects in industrial wastewater treatment and environmental management [6]. Efficient techniques for the removal of highly toxic organic compounds from water have drawn significant interest. Most of the conventional methods are not economically viable or environmentally unfriendly and

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also technically complicated processes. In comparison, adsorption is simple and widely used in wastewater treatment due to the simplicity, versatility and efficiency in extracting a variety of chemical compounds in wastewater treatment. Adsorption can remove both soluble and insoluble organic pollutants with a high removal capacity [7, 8].

It has been generally agreed that the most important factor for successful adsorption is the selection of adsorbent. The adsorption process is widely used for treatment of industrial wastewater from organic and inorganic pollutants and meets the great attention from the researchers [9].

It is well known that commercial activated carbons have unique characteristics owned to their high surface area, surface acid groups, micro and mesoporous structure and large sorption capacities [10, 11]. It has been successfully used as adsorbent for the removal of synthetic and naturally occurring organic pollutants from water and wastewater [12]. Unfortunately, the high cost of activated carbon production hinders its extensive use in wastewater treatment practices [13]. Hence, new search for cheap adsorbents are essential in wastewater treatment.

Distillery spent wash is perceived as one of the serious pollution problems of the countries producing alcohol from the fermentation and subsequent distillation of sugar cane molasses. Molasses is the dark brown, putrid, viscous liquid and is the most common feed stock for industrial fermentation processes and diluted 1 – 3 fold for effective fermentation process and purification of spirit. Spent wash is highly acidic, having strong odour, variety of recalcitrant colouring pigment as melanoidins, metal sulfides and phenolics are responsible for dark brown colour of spent wash. Spent wash is daily generated with large quantity during the ethanol production in distillery industry [14]. The post methanation distillery effluent (PME) produced from the treatment is characterized by high biological oxygen demand (BOD) and chemical oxygen demand (COD), intense brown colour and high salt levels apart from being rich in plant nutrients [15].

Wastewater is also a rich source of plant nutrients, therefore soils irrigated with wastewater are enriched in nutrients. The spent wash is useful as a fertilizer for production of crops like wheat, maize, sugarcane and rape seed. However, the problem of directly using distillery spent wash in agriculture practice increases the quantity of salts in soil [16]. Various physical, chemical and biological techniques are used for the treatment of distillery spent wash before its discharge into the aqueous ecosystem [17].

In the current investigation, we introduced a new biocarbon is generated using a novel medicinal plant Garland daisy (*Glebionis coronia* – Asteraceae). The characteristics of the biocarbon is unique and having good potential for the removal of salts and organic components in water and wastewater. Further, the removal capacity of the biocarbon is significantly enhanced by interfacing with inert silica as support material. The pretreated distillery wastewater with specific dilution is introduced into the batch reactor system and the biosorption properties of SiO_2 interfaced biocarbon is evaluated and presented in this paper. The treated water is safely used for the growth of fodder grass and selected leafy vegetables in a pilot project and its performance is evaluated and discussed.

MATERIALS AND METHODS

Preparation of Silica Interfaced Biocarbon: Garland daisy (*Glebionis coronia* – Asteraceae) is an important medicinal plant widely distributed in agricultural fields. A model procedure for the preparation of pure biocarbon is found in the literature [18]. According to the established protocol, the shade dried leaves are crushed and made into fine powder by using grinding system. The biocarbon was prepared by treating the leaves powder with the concentrated sulphuric acid (Sp. gr.1.84) in a weight ratio of 1:1.8 (biomaterial: acid). The resulting black product was kept in an air-free oven, maintained at 160±2°C for 6h followed by washing with distilled water until free of excess acid and then dried at 105±2°C. Then pure form of silica gel is used for interfacing with biocarbon. Pure silica gel and biocarbon was taken in 2:1 ratio in a 500 mL beaker and enough distilled water is added and warmed at 60°C for 30 min. The resulting mass was filtered and dried at air oven for 2 hours. The dried material is granulated at the size range of 100 to 120 μm and used for further biosorption process.

Collection and Analysis of Distillery Wastewater: The reliability of laboratory analysis and tests depends upon the method of sampling. Hence, Suspended solids and slit free wastewater samples were collected in 5 L capacity clean polythene containers and transported to the laboratory and incubated at 4°C for analysis of essential wastewater quality parameters. The essential

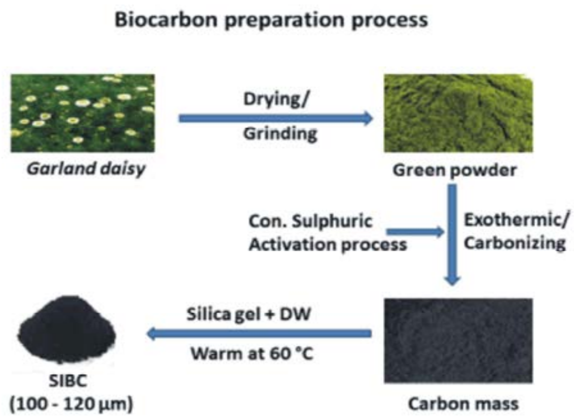

Fig. 1: Preparation of silica interfaced biocarbon

physico-chemical characteristics and selected heavy metals such as Cd, Cu, Cr and Pb were determined as per the procedures given by American Public Health Association (APHA) manual [19]. Heavy metals like cadmium, copper, chromium and lead were analyzed by using atomic absorption spectrometer.

Treatment of Distillery Wastewater

Sample Preparation: The original distillery wastewater was passed through different screening system, whereby visible materials and dirt are removed. Then it is filtered using cotton cloths for the removal of any coagulants. The clean wastewater sample was stored in polythene containers as stock feed wastewater. The initial pH of the feed stock is measured using Hanna pH meter. The feed water was diluted to 10 times and kept for biosorption process.

Biosorption Process: Optimization of the amount of adsorbent dose is very important in the removal of pollutants in wastewater. For this purpose, the biosorption experiments were carried out in series of six 250 mL Erlenmeyer flask using 100mL of diluted feed wastewater. The initial pH of the feed wastewater is 4.4. The silica interfaced biocarbon (SIBC) was added in the flasks at dosage ranging from 1 to 5 g. The flasks with mixture of wastewater and SIBC were placed on the rotatory shaker system and agitated at the speed of 250rpm. The biosorption system was kept in contact with 180 min. At the end of the experiments, all the flask was removed and the contents was filtered and analyzed for the parameters such as COD, TDS, colour and heavy metals were measured using AAS. Similarly the effects of contact time and solution pH were optimized by changing one parameter at a time and keeping the others constant. The pH of feed wastewater was adjusted using 0.1N H_2SO_4 or 0.1N NaOH. The biosorption process is carried out at room temperature of 30 ±2°C.

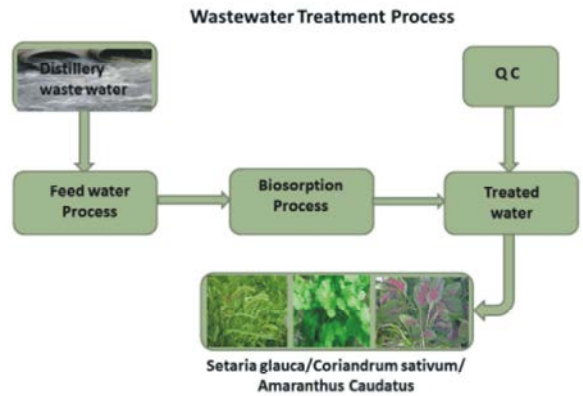

Fig. 2: Treatment of distillery wastewater

Pilot Scale Farming Practice: This is one of the ultimate aim in this research work as part of green concept. Hence, we planned a pilot project for farming of fodder grass and leafy vegetables using the treated wastewater. In 12 × 12 Sq. ft fields, the farming practice is carried out in normal atmospheric condition. In the farming application, *Setaria glauca, Coriandrum sativum* L. and *Amaranthus caudatus* are selected and grown in the experimental field. The quality seed are spiked in soil and treated water is allowed to wet the soil regularly. Mainly, length of shoot and leaves of crops was observed at the end of 120 days. The soil quality (mainly essential nutritional aspects) was also taken care during the growth of crops.

RESULTS AND DISCUSSION

Characteristics of Biocarbon: The nature and the characteristics of the biocarbon are essential to understand the adsorptive behavior on the surface of the biocarbon. The detailed characteristics of the biocarbon of Garland daisy (*Glebionis coronia*) are shown in Table 1. It is observed that, the surface and particle size is relatively high and is responsible for potential removal of metal ions and organic molecules from wastewater system. The results indicated that, the biocarbon has high capacity for metal ion adsorption and it is regenerative in nature.

Characteristics of the Distillery Wastewater: The analytical results of physico-chemical parameters of the raw distillery wastewater are presented in Table 2.

Table 1: Characteristics of the biocarbon

S.No.	Parameters	Values for BC
1.	Moisture content	0.40%
2.	Ash content	8.75%
3.	Total carbon	92.5%
4.	Bulk density	1.35/mL
5.	Matter soluble in water	0.60%
6.	Matter soluble in acid	1.5%
7.	pH	7.30
8.	Ion exchange capacity	0.95 meq/mg
9.	Methylene blue value	35
10.	Phenol number	48.5
11.	Decolorizing power	1.50 mg/g
12.	Iron	0.82%
13.	Surface area	385m^2/g

Table 2: The initial characteristics of the distillery wastewater

Parameters	Values (mg/L)	Parameters	Values (mg/L)
pH	4.4	Chloride	3450
EC (μmhos/cm)	3250	Sulphate	1800
Color	Dark brown	Nitrogen	850
Turbidity (NTU)	3070	Phosphorus	13
TDS	2120	Calcium	1200
TSS	650	Magnesium	175
BOD	3850	Potassium	530
COD	8700	Sodium	1120
DO	2.30	Iron	85
Copper	8.5	Cadmium	7.8
Chromium	12.4	Lead	2.6

The results indicated that, acidic nature. The color of effluent was very dark brown, the COD and BOD level is also very high. It also containing alarming level of heavy metals. The concentration of nitrogen higher that phosphorous. It is imperative that, effluents released from the distillery industry discharge in to the agricultural land certainly deteriorates the quality of productive soil. It well observed that, in the present investigation, the physico-chemical characteristics were much beyond the permissible limit. When this effluent is disposed into waters, it might cause severe depletion of oxygen and leads to the deterioration in water quality.

Because of the higher concentration of pollutants present in the distillery wastewater, it not directly suitable for the treatment and evaluation of performance of the biosorption process on the SIBC under predetermined equilibrium conditions. Hence, from the raw distillery wastewater, feed water is prepared by 10 fold dilution. This feed water is subjected to biosorption process and the selective physico – chemical parameters are analyzed for process optimization.

Removal of Main Pollutants: The analytical results of important pollution parameters such as BOD, COD, Turbidity, TDS and TSS of the feed wastewater (FWW) and treated wastewater (TWW) are presented in the Figure 3. The results indicated that, the main pollution parameter such as COD and BOD is reduced to 95.57 and 93.50 % respectively. Similarly, TDS, TSS and turbidity are well reduced to 79.95, 94.61 and 95.92 % respectively. It is noted that, the pH of the feed wastewater (FWW) was 4.4 and it is elevated to 7.2 in treated wastewater (TWW). Similarly, the level of dissolved oxygen in treated wastewater is significantly increased to 6.8. Hami et al., [20] investigated effective use of powdered activated carbon (PAC) on the performance of a pilot-scale laboratory dissolved air flotation (DAF) unit. It is observed that, the removal efficiencies for BOD in wastewater is increased from 70 – 94% while those for COD increased from 64 – 92.5%, respectively.

Removal of Salts of Common Metal Ions: The presence of common metals like, calcium, magnesium, sodium and potassium in the form of it chloride and sulphates are also influence the quality of distillery industry wastewater. Because, during the processing of molasses and allied fermentation operation for the production of sprit these chemicals are used. The analytical results of presence of these metal ions in feed wastewater and treated wastewater is presented in the Figure 4. It is observed that, the concentration of chloride is higher than sulphate. However, in treated wastewater, all the metal ions and chloride and sulphates are well reduced. It indicates, the biosorption process is operating effectively for the removal of such ions in wastewater.

Removal of Heavy Metals: The feed wastewater contains significant amount of toxic heavy metals. The percent reduction of heavy metals is Cu (91.17%), Cd (96.66%), Cr (93.14%) and Pb (92.30%) respectively (Fig. 5). It is noted that, the concentration of heavy metals in treated wastewater is very low. The results supports that, complete removal of heavy metals are also possible by altering the biosorption conditions.

Decolourization of Distillery Wastewater: The decolourization process is carried out by using distillery feed wastewater (FWW). It is evident from the experimental results that the contact time required to attain the equilibrium depends on the concentration of coloring species present in the wastewater. In the present study, the removal of color of the wastewater was gradually increased by increasing contact time. It attains a maximum removal of 99.5 % at 150 min (Fig. 6).

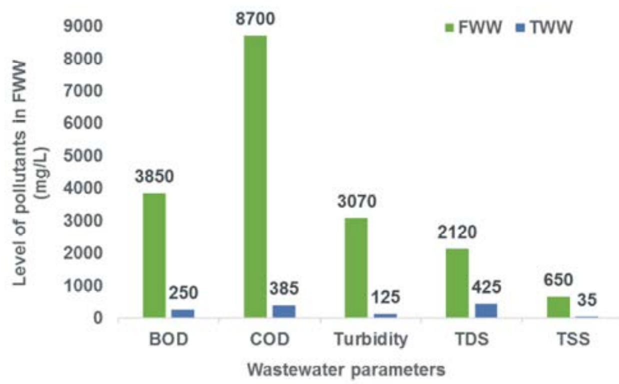

Fig. 3: Characteristics of feed and treated wastewater

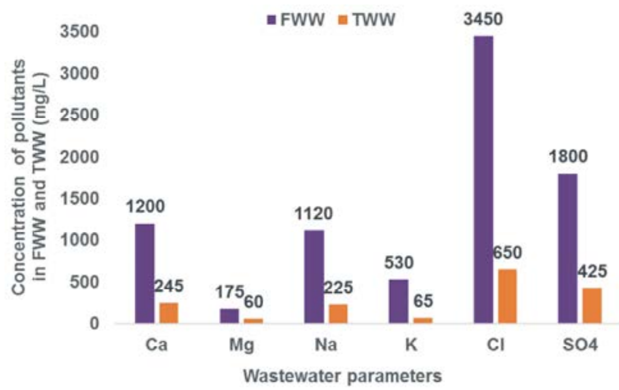

Fig. 4: Level of common metals, chloride and sulphate in feed and treated wastewater

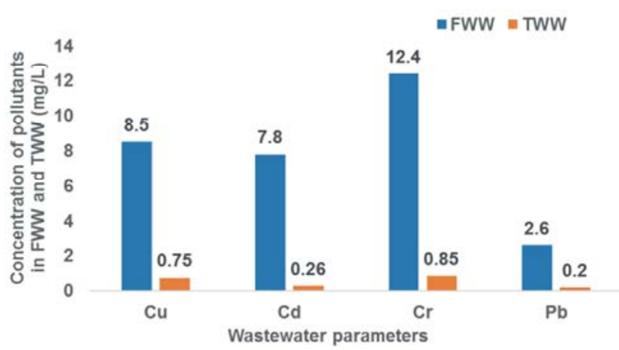

Fig. 5: Level of heavy metals in feed and treated wastewater

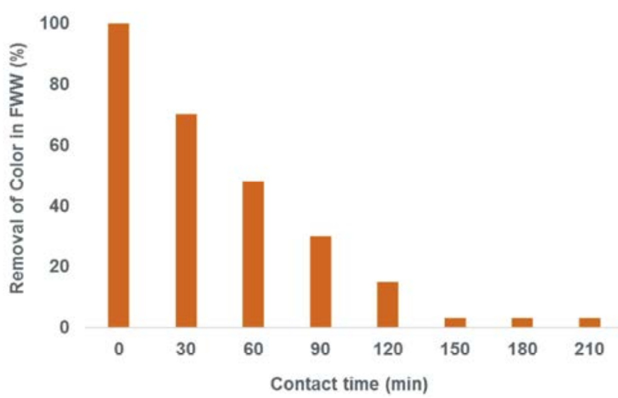

Fig. 6: Removal of color from distillery wastewater

Table 3: Growth characteristics of selected farming crops

S.No	Parameters	*Setaria glauca*	*Coriandrum sativum* L.	*Amaranthus caudatus*
1.	Field size	12 × 12 Sq. ft	12 × 12 Sq. ft	12 × 12 Sq. ft
2.	Growth period	120 days	120 days	120 days
3.	Total biomass	3.0 Kg	3.0 - 4.0 Kg	3.2 - 4.3 Kg

Growth Characteristics of Farming Crops: The growth characteristics of selected farming crops such as *Setaria glauca, Coriandrum sativum* L. and *Amaranthus caudatus* using treated wastewater is evaluated and is presented in Table 3. Comparatively, the productive yield is very good. Hence, the treated wastewater can be effectively used for the production of variety of agricultural practices.

CONCLUSION

From the present study it has become evident that feed wastewater shows better biosorption results. The main pollution parameters in distillery wastewater is COD and BOD, its level is well reduced in treated wastewater. Significantly, the concentration of common metal ions and heavy metals are also reduced in the treated wastewater. The results supports that, the biocarbon technology is an eco-friendly technique and can be used for treatment of any type of industrial wastewater. Moreover, it also noticed that, the pilot scale experimental studies on the farming of leafy vegetable and fodder grass are showing promising results. Hence, the treated wastewater can be effectively used as irrigation water for seed germination and propagation of agricultural crops for sustainable development.

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