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RESEARCH ARTICLE

Characterization and Treatment of Effluent from Gherkin Processing Industry using activated carbon

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Abstract

Pickling is one the oldest means of food preservation. Wastes from preservation operations are characterized by high chloride, high oxygen demand and high total suspended solids. Waste treatment technology for removing suspended solids, reducing oxygen demand is available, but no economical methos is available. Water usage and waste characteristics were determined on major unit operations, including tank yard brining, desalting and processing, slicing and cutting operations. The results of the study provide a detailed characterization of the types and concentration of components of waste streams from unit operations in cucumber preservation industry.

The adsorption and treatment of organic contaminants using activated carbon is carried out. Adsorption of organics from the effluent on activated carbon was examined at room temperature. The experimental batch equilibrium data was correlated by Freundlich isotherm. The adsorption data fitted well into the Freundlich isotherm. The organic concentration expressed as Chemical Oxygen Demand (COD) and Total Suspended Solids (TSS) was reduced.

Keywords: Adsorption, Concentration, Isotherm, COD, TSS.

Introduction

Introduction about Gherkins:

Gherkin is a term generally used to refer to a savory pickled cucumber (fig 1.1). Gherkins and commercial cucumbers belong to the same species (Cucumis sativus), but are from different cultivar groups. They are usually picked when 4 to 8 cm (1 to 3 in) in length and pickled in jars or cans with vinegar or brine. India has today emerged as the origin of the finest gherkin cultivation, processing and exporters to the every-growing world requirement. Gherkin cultivation, processing and exports started in India during the early 1990s with a modest beginning in Karnataka State in South India and later extended to the neighboring states of Tamil Nadu and Andhra Pradesh. India exported 220939.2 MT of Cucumber & Gherkins, worth Rs. 1285.22 crores during the year 2017-18 with major destinations being U S A, Belgium, Spain, France and Russia[11].

Gherkins are grown in contact with small and marginal farmers. Gherkins are cultivated exclusively on "contract farming'' basis The entire activities in the cultivation practices, followed by the farmers, processing standards etc., are adhered to by the Indian gherkin manufacturers to produce very high quality gherkins for the world markets. This is the industry, which has showcased the true and successful model of contract farming, with which the industry is able to have a good quality control over the final produce as per the requirement of the international market. Gherkin industry in India is today fully oriented and its exports are mainly of two categories.

(a) Provisionally Preserved (preserved in vinegar,/acetic acid and brine): Gherkin exports are in bulk form in 220 liters, packed in food grade H.D.P.E. drums (High Density Poly Ethylene). This is later repacked by the

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Figure 1.1: Gherkins

importers into smaller, ready to eat consumer packs to suit their consumer's requirement. The brain is discarded as effluent.

(a) Preserved in Vinegar: These are ready to eat gherkins which are in smaller packs of jars and cans.

1.2 Introduction about Waste water.

Industrial wastewater is often contaminated with various compounds such as: suspended solids, dissolved organic compounds, chloride contents etc, and it is imperative that it should be treated to an environmental acceptable limit. The current problems in wastewater treatment stream primarily from the increasing pollution of waters by organic compounds that are difficult to decompose biologically, because these substances resist the self-purification capabilities of the rivers as well as decomposition in conventional wastewater treatment plant. Among the physical chemical processes that have proved useful for this is adsorption on activated carbon because dissolved and difficult-to decompose organic substances can be selectively removed by activated carbon.

Literature Survey

From the literature survey it if found that, the country has exported 220939.2 MT of Gherkins to the world for the worth of Rs. 1285.22 crore during the year 2017-18. Major Export Destinations are U S A, Belgium, Spain, France and Russia during the period (2017-18)[11]. Sources of wastewaters from cucumber preservation industry are readily apparent as one follows the progress of cucumbers from field to finished product. The three major divisions in production of waste water are (1) brining, (2) processing or freshening and (3) finishing.

The major source of waste water is from tank yard which is discarded as effluent. The presence of organic content increases the COD, TSS and BOD concentration which are difficult to treat.

Figure 1.2: Sample for Characterization

COD and TSS

Yacouba Sanou[1] et al (2016), studied the removal of COD in wastewater by activated charcoal from rice husk. They found that removal of COD depends on the adsorbent quantity and there was a effective removal of COD.

Mrunmai Joshi[2] et al (2014), Carried out the experiment for removal of acetic acid from wastewater by low cost material. From the experimental results and discussions it is found that for treatment of chloride content large quantity of activated carbon dosage was required and using coconut husk as adsorbent for treatment is economical for removal of organic contents.

R.Elliss Yogesh[3] et al (2016) studied the COD Removal Efficiency of Activated Carbon Adsorbent for Tannery Wastewater Treatment, from the results it was concluded that as per various studies the adsorbents are good for reduction of COD. Increase in the dosage of activated carbon decreases the concentration of COD.

Fares R[4] et al(2018), studied Biological Treatment of Wastewater by Addition of Activated Carbon Powder (CAP) from the result it was concluded that the activated carbon powder CAP used in this study showed its adsorption capacity of oils, solvents and hydrocarbons which subsequently decreases the levels of the COD effluents.

Adsorption Studies

Abd ElAziz A.Nayl[5] et al (2017) studied Adsorption studies on the removal of COD and BOD from treated sewage using activated carbon prepared from date palm waste. The experimental results obtained showed that the activated carbon prepared form date palm shell waste by chemical activation method is a good adsorbent for the removal of COD and BOD.

R. Mailler[6] et al (2016) carried out the experiment on Removal of emerging micro pollutants from wastewater by activated carbon adsorption: Experimental study of different activated carbons and factors influencing the adsorption of micro pollutants in waste water. The experimental results obtained showed that The activated carbon dose and the contact time have a great influence on adsorption, both the quantity and composition of organic matter impact the adsorption.

Ademiluyi F T[7] et al (2009), studied the adsorption and treatment of organic contaminants using activated carbon from waste Nigerian bamboo. From the experiment they found that activated carbon can effectively removed organic contents and COD was reduced.

Adsorption Isotherm

Adsorption is generally described through isotherms, and defined as the amount of adsorbate on the adsorbent as a

function of pressure (for gases) or concentration (for liquids) at a constant temperature. Freundlich isotherm: It is an adsorption isotherm which relates concentration of solute on the surface of the adsorbent to the concentration of the solute in the liquid with which it is in contact. This model assumes that adsorption takes place on heterogeneous surface.

The linear form can be written as:

$\log q_e = \log k_f + (1/n) * \log C_e$

Where, k_f and n (dimensionless constants) are the Freundlich adsorption isotherm constants.

Materials and Methodology

Materials

The materials used for the experiment were: activated carbon, wastewater from a Gherkin processing industry, distilled water, hydrochloric acid, 0.1N $K_2Cr_2O_7$, 0.1N FAS, $0.1NH_2So_4$, $AgSo_4$, $MgSo_4$, Ferroin indicator. Equipment's used in the experiments were: Electronic weighing balance, Laboratory electric muffle furnace and heater.

Experimental Procedure

Determination of COD.

To determine the COD, 10 ml of 0.1N standard potassium dichromate solution was added to 10 ml of wastewater sample (1ml of sample in 9ml of distilled water) in a 250 ml round-bottom flask. 1g of silver sulphate and 30 ml of concentrated sulphuric acid were added in small portions with thorough swirling, until the silver sulphate was completely dissolved. A few glass beads were added to serve as anti-bumping aid. The mixture was heated gently for 2 hours at 80°C, after which the content of the flask was now cooled. 40ml of distilled water added, and the cooling was completed under running tap water. 2 drops of indicator solution were added and the resulting mixture titrated with standardized ferrous ammonium sulphate solution till the end point i.e., reddish brown colour A blank value was determined in the same way with 10 ml of distilled water. The COD values of the respective samples were calculated using equation (1).

COD = (a-b)*N*8*1000 / V, mg/lt (1)

In equation (1), a and b are the respective volumes of ferrous ammonium sulphate used for the blank and sample (ml), V is the volume of sample (ml), and N is the normality of ferrous ammonium sulphate.

Figure 3.1: Samples for COD Determination

Table 3.1: Tabular Column for Determination of COD (For Back Titration).

Trials	*1*	*2*	*3*
Initial Burette Reading	0	20	0
Final Burette Reading	20	43.7	20.5
Volum of FAS Consumed (ml)	20	23.7	20.5
Average	21.4		

Table: 3.2: Tabular Column for Determination of COD (For Blank Titration).

Trial	*1*
Initial burette reading	0
Final burette reading	38
Volume of FAS consumed (ml)	38

COD = (a-b)*N*8*1000 / V,
= (38-21.4)*0.1*8*1000 / 10,
=1328 mg/lt

Determination of TSS

Determination of Filterable Solids.

50 ml (0.05 liter) of water sample was filtered through a previously weighed filter paper. Filter paper was kept in an oven at 110°C for 1 hour and weighed. The difference in final weight (W_2) and initial weight (W_1) gives the weight of filterable solids.

Filterable solids = W_1-W_2 mg/lt Where:

W_1 = mass of filter paper + dried residue (mg)

W_2= mass of filter paper (tare weight) (mg)

W_2 (mass of filter paper) = 989 mg

W_1 (mass of filter paper + dried residue) = 1239 mg

[Conversion factor to convert gram to milligram is multiplied by 10^3]

- *Calculations:*

Filterable solids = 1239-989
= 250 mg/lt

Determination of Dissolved Solids.

Clean and dried evaporating dish was taken. Weight is noted W_3. 10 ml (0.01 liter) of sample (filtered) was taken on it and evaporated at 105°C. It is dried, cooled and weight

Figure 3.2: Determination Filterable Solids

is noted W_4

Dissolved solids = (W_4-W_3) / V, mg/lt Where:

W_4 = mass of evaporating dish + dried residue (mg)

W_3= mass of Evaporating dish (tare weight) (mg)

V = volume of sample filtered (lt)

- *Observation:*

W_4 (mass of evaporating dish + dried residue) = 34.692*10^3 mg

W_3 (mass of Evaporating dish) = 34.690*10_3 mg

V (volume of sample filtered) = 0.01 lt

[Conversion factor to convert gram to milligram is multiplied by 10^3 and ml to liter is divided by 10^3].

- *Calculations:*

Dissolved solids = (W4-W3) / V

= (34.692*103 - 34.690*103) / 0.01 = 160 mg/lt

Determination of Total Solids.

Clean and dried evaporating dish was taken. Weight is noted W_5. 10 ml (0.01 liter) of sample (unfiltered) was taken on it and evaporated at 110°C. It is dried, cooled and weight is noted W_6.

Total solids = (W_6-W_5) / V, mg/lt

Where:

W_6 = mass of evaporating dish + dried residue (mg)

W_5= mass of Evaporating dish (tare weight) (mg)

V = volume of sample filtered (lt)

- *Observation:*

W_6 (mass of evaporating dish + dried residue) = 35.028*10^3 mg

W_5 (mass of Evaporating dish)= 35.487*10^3 mg

V (volume of sample filtered) = 0.01 lt

[Conversion factor to convert gram to milligram is multiplied by 10^3 and ml to liter is divided by 10^3]

- *Calculations:*

Total solids = (W_4-W_3) / V

= (35.487*103 - 35.028*103) / 0.01 = 458 mg/lt

Total Suspended Solids.

The difference in the weight of total solids and dissolved solids gives the value of total suspended solids.

Total suspended solids = Total solids – Dissolved solids, mg/lt

- *Observation:*

Total solids = 458 mg/lt Dissolved solids = 160 mg/lt

- *Calculation:*

Total suspended solids = Total solids – Dissolved solids

= 458 – 160 = 298 mg/lt

Adsorption

Adsorption is the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent.

Table: 3.3: Concentration of Solids.

Parameters	*Concentration, mg/lt*
Filterable solids	250
Dissolved solids	160
Total solids	458
Total suspended solids	298

Batch Adsorption

For a batch adsorption, a known volume of sample is taken in a beaker which contains 2, 3 and 4g of activated carbon. The contents are stirred for about an hour the mixture is allowed for settling of to obtain clear solution. Concentration of adsorbate in solution after adsorption is calculated using.

$q_e = (C_i - C_e)v/m$, g

Where, qe= concentration of adsorbate in solution after adsorption m= mass of adsorbent, g

C_e= decrease in concentration, mg/lt

C_i= Initial concentration, mg/lt

V= volume of the solution, ml

Equilibrium concentration (C*) = Decrease in concentration / mass of adsorbate, mg/lt

Freundlich isotherm: It is an adsorption isotherm which relates concentration of solute on the surface of the adsorbent to the concentration of the solute in the liquid with which it is in contact. This model assumes that adsorption takes place on heterogeneous surface.

The linear form can be written as:

$\log q_e = \log k_f + (1/n)*\log C_e$

Where, k_f and n (dimensionless constants) are the Freundlich adsorption isotherm constants. Graph of $\log q_e$ v/s $\log C_e$ gives the value k_f and n.

The graphical representation shows the evolution of the COD as a function of the mass adsorbate used. There is a decrease in the concentration of the rapid COD during the test hours due to the adsorption phenomenon and a stabilization of the COD after two hours following the saturation of the active carbon pollutants. The presence of powdered activated carbon improves the purification efficiency thanks to the adsorption phenomenon, which increases with increasing concentration of activated carbon

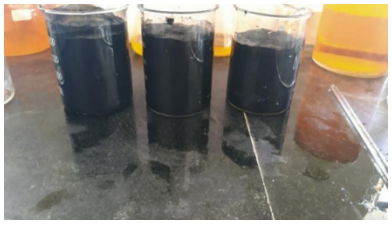

Figure 3.3: Adsorption Trials.

Table 3.4: Adsorption data

M,g	*C_e, mg/lt*	*q_e*10^3, mg/lt*	*$logq_e$*	*Ce* *10^{-4}, mg/lt*	*$logC_e^*$*
2	412	5.8	0.76	20.0	1.30
3	322	6.87	0.85	10.0	1
4	218	7.75	0.92	5.4	0.73

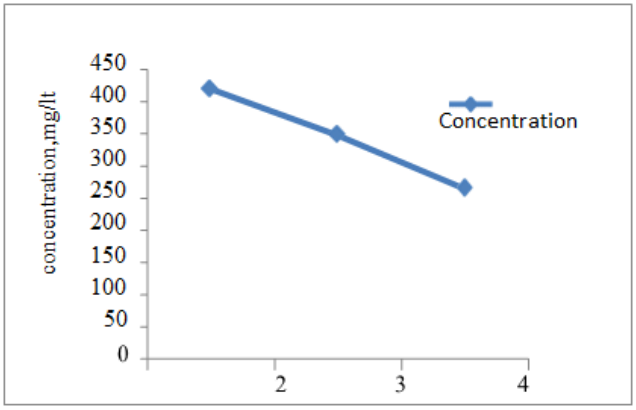

Figure 3.4: Graph of Concentration v/s Mass of Adsorbent

From graph 3.5 , Freundlich adsorption isotherm was studied and by plotting the graph of $logq_e$ v/s $logC_e^*$. where we can understand that the adsorbate concentration decreases with adsorption process. At equilibrium it is noted that decrease in concentration is proportional to mass of adsorbate.

Result Discussions

*T1 = Trial 1 (2g of adsorbent)
T2 = Trial 2 (3g of adsorbent)
T3 =Trial 3 (4g of adsorbent)

Total Dissolved Solids (TDS) : The results obtained are showed that there was a decrease in the amount of TDSafter treatment. It is reduced from 298 to 104 mg/lt

- Chemical Oxygen Demand (COD): From the experimental result there was a decrease in the value of COD with respect to COD in waste water before and after treatment, it was observed that the value of COD is reduced from 528 mg/lt to 218 mg/lt
- From figure 3.5 , for Freundlich isotherm intercept is 0.683, k_f is 0.8 and the value of R^2 is 0.994

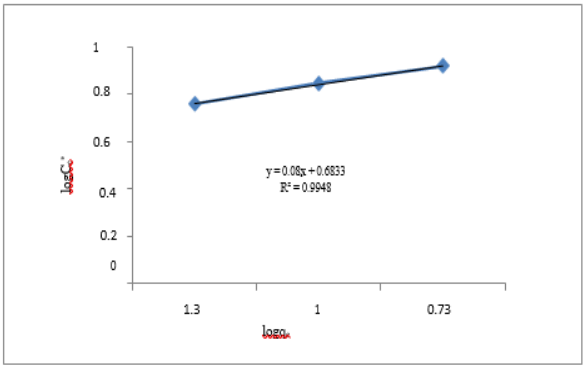

Figure 3.5: Graph for Freundlich Isotherm

Table 4.1: Concentrations Before and After Adsorption

Parameters	*Concentrations Before Adsorption, mg/lt*	*Concentrations After Adsorption, mg/lt*		
		T 1	*T2*	*T3*
COD	1328	412	323	218
TSS	298	215	176	104

Conclusion

Total Dissolved solid (TDS): The results obtained showed that there was a decrease in the amount of total dissolved solid after treatment. It was reduced from 298 to 104 mg/lt.

- Chemical Oxygen Demand (COD): From the experimental result in, with respect to COD in waste water before and after treatment, it can be observed that the COD was reduced from 528mg/l to 218 mg/l.
- From figure 3.5, For Freundlich isotherm intercept is 0.683, kf is 0.8 and the value of R2 is 0.994.
- This research work has revealed some facts about the usefulness of activated carbon.
- It was observed for the adsorption that the organic concentration expressed as COD and TSS was reduced.
- Efficiency rates of adsorption 21.9%, 38.8% and 58.7% were achieved.
- Concentration of COD and TSS decreases with increase in the amount of activated carbon. According to MOFE and CPCB the permissible limits for disposal of effluent were 250mg/lt of COD and 100 mg/lt TSS (±5mg/lt). From Table 4.5, Concentration COD and TSS were in permissible limits.

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