

310

STUDIES ON REMOVAL OF CHLORIDE FROM SOAK LIQUOR*

G. SEKARAN, V. KRISHNAMURTHY, W. MADHAVAKRISHNA & M. SANTAPPA

Central Leather Research Institute, Madras.

Rice bran is converted into activated charcoal by treating with conc. H_2SO_4 and is used as an adsorbent for the removal of chloride present in the tannery soak liquor upto a concentration of 35,000 mgm/litre. It was found to be effective at the neutral pH. Effect of the constituents of rice bran on adsorption has also been studied. Infra-red spectra of the samples and the T. L. C. showed that the adsorption is only a physical phenomenon. The rate of adsorption of chloride over the charcoal was determined as 9.150×10^{-2} /min. The adsorption passes through triple layer formation as shown by adsorption isotherm. The charcoal removes chloride to the extent of 0.9800 meq/gm. of the charcoal. The soluble proteins present in the soak liquor are also removed with 100% efficiency. The B.O.D., C.O.D and colour of the soak liquor were seen to be reduced after passing through the charcoal.

Introduction

In tanning industry where batch processes are employed, effluents coming out of the different units will be quite different from one another.

In the case of soak liquors, the first soak liquor contains more amount of chlorides compared to the successive soak liquors. Since the chloride is harmful to the soil when it exceeds the optimum concentration and may lead to soil infertility. Continuous discharge of soak liquor on land will also result in ground water pollution. Hence, the first soak liquor alone is segregated to keep the pollution to the minimum.

There are many ways of treating the soak liquors to reduce the chlorides. They are

1. Solar evaporation
2. Electrodialysis
3. Thermal evaporation (Crystallization)
4. Ion exchange

*Paper presented at TGT 1981, CLRI.

The first three processes need electrical or thermal or solar energy which cannot be depended always. So the only method which is practicable and economical for the treatment of chloride from soak liquor is the ion exchange method.

Literature¹ shows that when rice bran is charred with concentrated H_2SO_4 it can act as a good sorbent for chlorides and also can act as an ion exchange resin for removing sodium. The charcoal after use can be easily incinerated to ash which in turn can be disposed. With this idea in view, the study was started but a charcoal comparable with the commercially available resins could not be obtained. However, the study was continued to find out the mode of adsorption on the carbonaceous material.

Materials and methods

Charcoal preparation

The charcoal was prepared by adding 50 ml of concentrated H_2SO_4 over 100 g of rice bran

slowly, and with vigorous stirring. The charred mass was allowed to stand for one hour in order the reaction is completed. Then it was suspended in enough water overnight. The charcoal was then washed with tap water until free sulphuric acid was removed from it. It was then dried over acetone. The charcoal thus prepared was graded in the range of 50/100 mesh size.

Chromatographic column preparation

Chromatographic column was set up with 275 g of the charcoal packed in a column of 32 cm length and internal diameter of 4.5 cm. The flow rate of the column was adjusted to be one drop per 6 seconds.

Standardisation of the soak liquor

The soak liquor collected from the tannery was filtered to remove the suspended solids and hairy materials. The chloride content of the soak liquor was analysed by Argentometric method² and the sodium was estimated by Zinc Uranyl Acetate precipitation method.³ The chloride concentration of the influent was adjusted to 35000 mg/litre. 50ml. aliquots of the eluates were collected and analysed for the chloride and sodium content.

Dilution studies

The dilution studies were carried out by diluting the influent in stages and then passing through the column. The amount of adsorbed chloride was calculated by finding the amount of chloride in the eluate which was subtracted from the amount of chloride in the influent.

pH studies

This study was conducted by adjusting the pH of the influent from pH 3 to 11. Then the soak liquor was passed through the column and the amount of adsorption was calculated in each case as before.

Effect of constituents

The constituents of rice bran viz., protein, carbohydrate, bran oil, phytin etc. were removed in stages after which the bran was converted into resin and packed in the column. The adsorption capacity of the resin was studied after removing each of the constituent of the bran. Bran oil was extracted with acetone,⁴ protein with sodium hydroxide,⁵ methanol was used to extract carbohydrate⁶ and dilute HNO₃ to remove the phytin.⁷ The residue after the extraction of these constituents was charred with concentrated H₂SO₄, suspended in water, washed with tap water to remove last traces of free sulphuric acid and then packed in the column.

Grading of the charcoal

The charcoal obtained from rice bran was powdered in a glass pestle and mortar and then passed through the sieve. The particles with 50-100 mesh were collected and packed in the column.

Infra-red spectra of the samples

The sample was dried completely under vacuum at 110°C and then the I.R. Spectra of the sample at different condition was taken in a Perkin Elmer model 120 spectrophotometer. The spectra of the samples were taken by pelletizing with KBr.

Specific conductivity of the samples

The Specific Conductivity of the sample was found out using dip type conductometer by suspending at 5 g sample in 50 ml of water. Another sample of the charcoal was dried at 110°C under vacuum and the electrical conductivity of the sample was measured by placing the sample in the sealed polythene tube and the conductivity was noted at the end of the sample with the Autobalance Universal Bridge B642 (Fig 1).

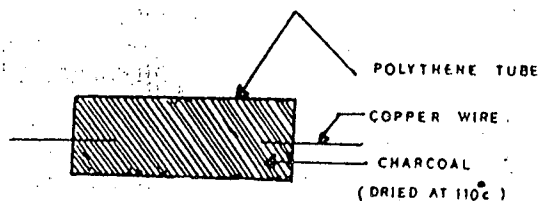


Fig. 1

Thin layer chromatography

The sample after the adsorption with chloride was suspended in water and the sample was spotted on the T.L.C. plate. Solvents used were: acetone-n-butanol-conc. NH_4OH , water (65 : 20 : 10 : 5) and the spraying agent used was 1% solution of ammoniacal silver nitrate and 0.1% ethanolic fluorescein. Then the R_f value was found out.

Percentage transmission of the eluate

The percentage transmission of the U V light for the samples of influent and the eluate was measured with the spectrometer, Spectron-120 at 523 mm.

BOD and COD analysis

The BOD and COD of the influent and eluate samples were found out by the standard methods of analysis⁴.

Nitrogen content

The total nitrogen content of the influent and the eluate of the column was found out. The protein present in the influent along with the dissolved nitrogen was separated by clarifying the influent, dialysed against distilled water, precipitated with 0.1 N trichloroacetic acid at pH 4.3. The nitrogen present in the precipitated protein was estimated by Kjeldahl method.⁵ The protein in the eluate of the column was also estimated in the same manner.

Rate of adsorption

The rate of adsorption of chloride on the charcoal was found out by using the simpler model as shown in Fig. 2. The calculated amount of charcoal was taken in the paper bag which was previously saturated with water. It was then supported on steel wire. Then the container was filled with the soak liquor upto the level of the resin in the bag. The rate of adsorption was studied by analysing the content of chloride at 10 minutes intervals.

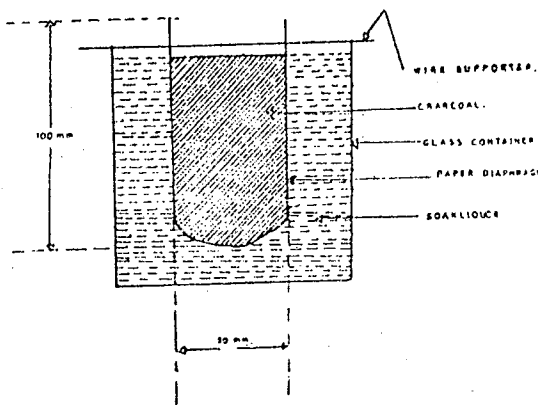


Fig. 2

Regeneration of the column

The column was regenerated by washing with distilled water until the elutant gave negative test for chloride with silver nitrate.

Results and discussion

From the fig. 3, it may be seen that as the dilution increases the amount of chloride ion adsorption is decreasing, which may be due to the carbon substrate being covered with the water molecules. Adsorption can be possible by replacing the water molecules from the carbon substrate by the chloride ion. Energy that is needed for the replacement of the water molecules adsorbed on the substrate is more when the chloride ion is heavily hydrated leading to an increase in volume of the ion. Hence at higher dilution, adsorption

decreases which is shown in the Fig. At higher concentration, the possibilities for the chloride ions to be held at the surface are more to cause a measurable adsorption. So the resin will be effective if it is employed in the higher concentration of chloride.

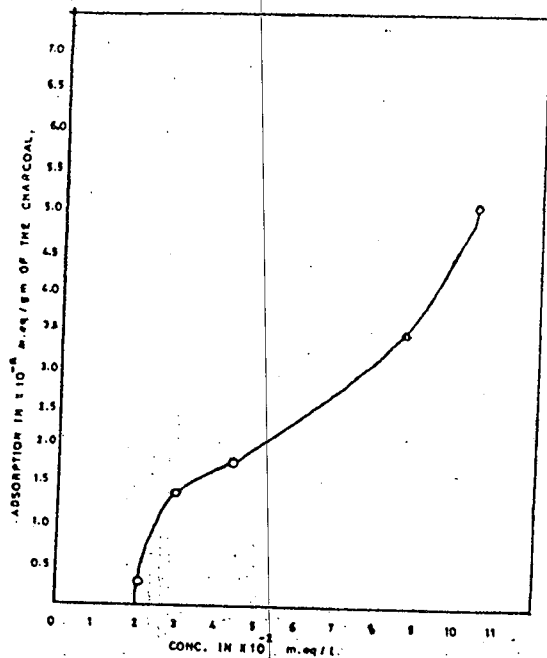


Fig. 3 ; Adsorption versus concentration

Fig. 4 shows that the adsorption increases with pH upto neutral pH. Above pH 7 the adsorption decreases. This kind of variation of adsorption with pH reflects the structural property of the charcoal. The charcoal is assumed to become positively charged during the preparation of the resin. The positively charged resin attracts negatively charged hydroxyl ions.¹² This forms a layer over the substrate. At lower pH, concentration of (OH) is lesser than the concentration of (H) ions⁷. Hence, some of the preferentially adsorbed hydroxyl ions balance the positive charge of the substrate. The rest of the charge on the substrate is unbalanced which remains on the surface while the (H+) ions form a

second layer which is static as a result of electrostatic repulsion between the surface charge and layer which inhibits the chloride ion to reach the surface.

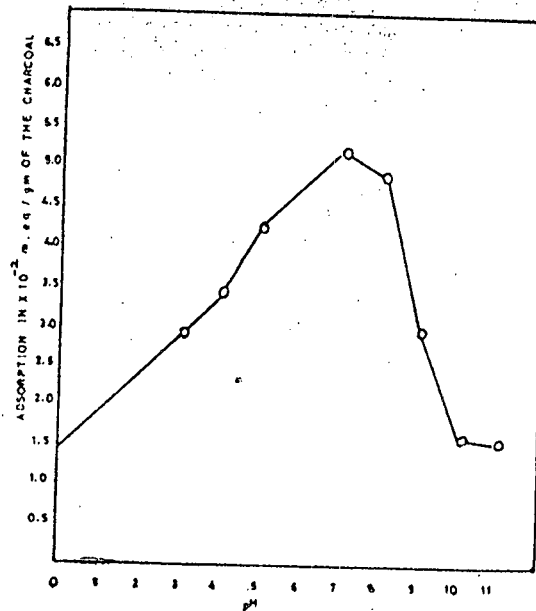


Fig. 4 : Adsorption versus pH

As the pH is increased to neutral, (H+) ions balance with (OH-) ions resulting in the increase of chloride adsorption. When the pH is increased still further the reverse phenomena takes place and hydroxyl ions form a static layer near the surface which prevents the chloride ion to reach the surface.

The fact that the surface of the substrate is positively charged can be explained by the electrical and specific conductivities of the samples at different conditions as shown in table 1.

The conductivity of the sample can either be electronic or ionic. The conductivity observed in the case of sample 1 of table 1 may be due to some of the occluded sulphuric acid but in sample number 2 which has been dried at 110°C the conductivity observed in

the dry state must be purely an electronic conduction. The conduction may be similar to that of the movement of vacancies in defective crystal.

TABLE 1

Relationship between specific conductivity and the nature samples

| Name of the Sample | Cell constant | Conductance OHM ⁻¹ | Sp. Conductivity OHM ⁻¹ /Cm. |
|--|---------------|-------------------------------|---|
| Charcoal (obtained without removing any of the constituents of the rice bran) & suspended in water | 1.58 | 2.10×10^{-4} | 0.318×10^{-4} |
| Charcoal (obtained without removing the constituents) Dry state. | — | 1.6×10^{-3} | |

The adsorption of the chloride over the charcoal surface is only physical and not chemical. The I.R. Spectra of the rice bran samples treated differently viz. i burnt in the absence of oxygen, ii chemically treated without removing the constituents, iii after the removal of the constituents, iv same as sample 2 but after adsorption with chloride washed with water, and dried in vacuum at 110°C, v sample washed with acetone and dried, vi sample without washing and dried at 110°C show that there is no specific region for C-Cl vibration which indicates that the bond formed between the substrate and the chloride is not a chemical but only a physical phenomenon.

This was again confirmed by using the sample previously adsorbed with chloride along with sodium chloride in thin layer chromatographic plate. This R_f values in both the cases were found to be the same. This shows that the adsorption is not chemical

but only physical. Hence, the interaction between carbon substrate and the chloride ion in solution may be strongly due to Vander Waals forces.

The removal of other constituents like protein, carbohydrate, oil from the rice bran has improved the adsorption capacity of the charcoal as shown by the results given in Table 2. This may also be attributed to an increase of the active sites or energetically favoured positions.

TABLE 2

Effect of the constituents on adsorption

| Nature of the sample | Concentration of the solution | Adsorption percentage |
|--|-------------------------------|-----------------------|
| Charcoal prepared without the removal of the constituents. | 0.1401 m.moles/litre | 57.01 |
| Charcoal after the extraction of protein | 0.1401 m.moles/litre | 69.96 % |
| Charcoal after the extraction of carbohydrate | 0.1401 m.moles/litre | 88.76 % |
| After the extraction of phytin | 0.1401 m.moles/litre | 79.40 |
| After the extraction of bran oil | 0.1401 m.moles/litre | 80.08 |
| After the extraction of bran oil and carbohydrate | 0.1401 m.moles/litre | 95.01 % |
| After the extraction of protein and bran oil | 0.1401 m.moles/litre | 92.38 |

The size of the particles plays a dominant role in adsorbing the ion as shown in Table 3. From the results given in Table 3, it may be seen that as the size of the particle reduces the adsorption increases. It is also clear that the amount of adsorption is proportional to the area of the active surface of the resin.

TABLE 3

Relationship between particle size and adsorption

| Nature of the sample | Adsorption of the chloride |
|--|--------------------------------|
| Coarse charcoal as obtained of the resin. by the charring of the bran | 3.491×10^{-2} m.eq/g. |
| Particles of 50-100 mesh of the resin. size after charring of bran | 4.946×10^{-2} m.eq/g. |

The mode of interaction of the chloride on the carbon surface is triple layer formation which can be seen from Figure 5. The adsorption of chlorides in m.eq/g. of the charcoal is plotted against the number of fractions. The curve shows three peculiar regions depending upon the different phenomena occurring in the adsorption process. In the first region the slope of the curve is descending gradually compared to other regions where the slope is high enough showing that the decrease in adsorption is advancing rapidly. Again, it takes the gradual decrease in the adsorption (Region 2) and again steep decrease in adsorption and finally the gradual decrease in the adsorption occurring in the region three (3). The gradual decrease in adsorption may be attributed to the formation of the layer structure whereas steep decrease in regions 1' and 2' are due to the free chloride ions in the diffused region. Initially, the available sites are occupied by the hydrated chloride ions to the maximum extent after which the hydrated chloride ions get absorbed by a special kind of rearrangement in the first layer leading to lesser force of interaction with carbon substrate and in fact some of the free chloride ions will be escaping without adsorption. Again, the second layer forms over the first layer as that of hexagonal close packed arrangements. The final third layer is formed as the hydrated chloride ions are placed over the second layer

but in all these types of formation each ion is in contact with the carbon substrate.

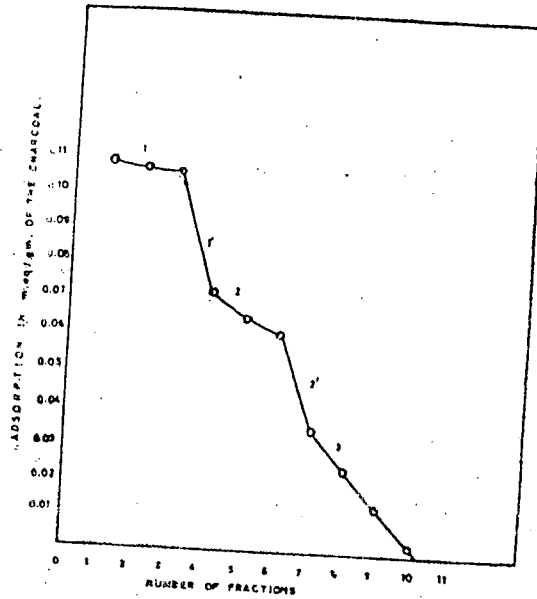


Fig 5: Adsorption versus number of fractions

In order to support this view, the same type of pattern with the inverted shape of curve (Fig. 6) for desorption of the chloride ion from the carbon substrate was obtained, which clearly indicates that the adsorption process follows the triple layer formation. The rate study was also conducted (Table 4). The rate of adsorption of chloride from the soak liquor follows first order at the initial stages and after some time it follows the second order and finally follows the first order. The first order clearly indicates that the adsorption depends only on the concentration of the sodium chloride in the soak liquor. i.e. Rate \propto (NaCl). But after sometime, when it takes the second order equation, the rate is proportional to the product of the substrate concentration (which in turn is proportional to the available free sites) and also on the concentration of the sodium chloride. Hence, it shows this anomaly. After the chloride ion makes room for the

adsorption, the rate depends only on the concentration of chloride.

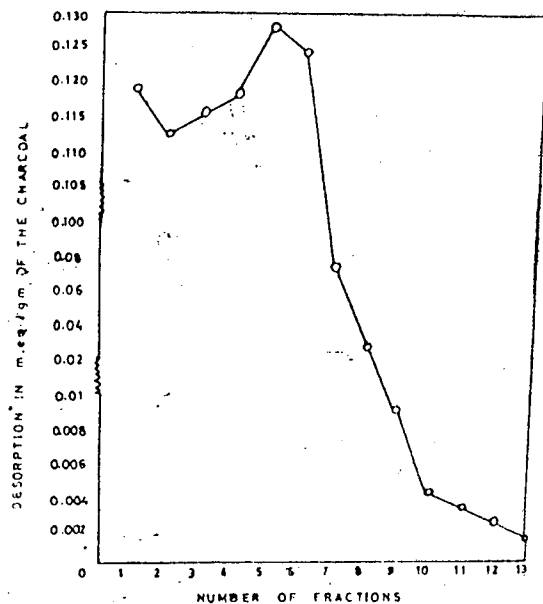


Fig. 6 : Desorption versus number of fractions

TABLE 4

Concentration Rate of adsorption of chloride in the soak liquor is 0.9665 g./eq./lt.

| Time min. | Rate of adsorption $\times 10^3$ mt^{-1} | Rate of adsorption $\times 10^3$ litre g-eq ¹ mt^{-1} | Average |
|-----------|--|--|---------|
| 0 | | | |
| 10 | 9.28 | | |
| 20 | | 1.591 | |
| 30 | | 1.367 | 1.301 |
| 40 | | 1.247 | |
| 50 | 9.152 | | |
| 60 | 9.250 | | |
| 70 | 9.028 | | 9.150 |
| 80 | 8.82 | | |
| 90 | 9.371 | | |
| 20 hours | | | |

Rate $\propto (N_0)$ (NaCl) where N_0 is the Number of available sites.

This study also confirms the triple formation. The colour of the soak liquor and its BOD and COD have also been found to be reduced when the liquor was made to pass through the column. Hence, the column acts as a fixed bed filter to remove organics and also proteins as may be seen from the results presented in Table 5.

TABLE 5

Estimation of BOD and percentage transmission

| Sample | B.O.D. mg/l litre | % Transmission |
|--|-------------------|----------------|
| Influent (soak liquor before passing through the column) | 72.8 | 13.00 |
| First fraction | 342.2 | 98.00 |
| Second fraction | 30.0 | 98.25 |
| Third fraction | 21.4 | 98.25 |
| Fourth fraction | 12.8 | 99.25 |
| Fifth fraction | 8.5 | 100.00 |
| Sixth fraction | 4.2 | 101.50 |

Nitrogen present in the soak liquor before and after passing through the column and the nitrogen content of curing salt was analysed (Table 6). The results show that column is able to adsorb only the protein while it is incapable of adsorbing the elemental nitrogen present in the curing salt.

TABLE 6

Estimation of nitrogen

| Nature of the sample | Amount of nitrogen per g. of sample |
|--|-------------------------------------|
| Soak liquor (containing soluble protein, elemental nitrogen) | 8.057×10^{-4} g. |
| Curing salt | 3.883×10^{-4} g. |
| Effluent (liquor after passing through the column) | 5.731×10^{-4} g. |
| Protein present in the soak liquor | 1.953×10^{-4} g. |
| Protein present in the effluent | — |

Conclusion

The charcoal prepared from rice bran is capable of removing chloride from the soak liquor to the extent of 0.9800 m.eg/g of resin. Proteins and colour are also found to be removed effectively, while the elemental nitrogen is not adsorbed.

It was found that sodium also is trapped but the nature of adsorption could not be established as yet.

Since regeneration of the column is also important, attempts are being made to regenerate the column.

REFERENCES

1. Kunikullaya, U. V. & Kini, M N., *Proceedings of the Tanners' Gas-Together*, CLRI, 2-19 (1979).
2. Arthur I. Vogel, *Volumetric (Titrimetric) Analysis, Quantitative Inorganic analysis*, The English Language Book Society and Longmans, pp. 260-61 (1968).
3. Arthur I. Vogel, *Gravimetric Analysis, Quantitative Inorganic Analysis*, The English Language Book Society and Longmans, pp. 558-59 (1968).
4. Vaccarino, C (1st Chim. Ind. Univ. Messina Messina (Italy), *Riv. Italy Sostanz Grasse*, 54 (4), 183-7 (Ital), (1977) Through C. A. 87, 166235 (1977).
5. Conner M. A., Samders, R. M., Kohler, G., *Ceval Chemists*, 53 (4), 488-96 (1976) (Eng.), Through C. A. 85, 122026 (1976).
6. Znore, Hiroshi, Noguchi, Jacsu O, Hokkai artises Nogyo, Shikinjo, Hokku 89, (6-14) (1977). *Hokkaiduritsu Vogyo Shikenjo Hokoku*, 189, 6-14 (1972). Through C. A. 78, 2928 (1973).
7. Saidakh medrol, U. A., Rizaer, N. V., Tadziev, A. K., Alier M. N., Mirza Karimov, R. M., Arslanov, M. A., USSR, 427, 716 (Cl A61K), *Otkrytiye. Teobert prom Obrqzisy. Toyaraye Znalet*, 51, (18) 114 (.974), Through C. A., 82, 34443 b (1975).
8. *Biochemical, oxygen demand, Standard methods for the examination of water and waste water*. American Public Health Association, Washington, U.S.A., 14th edition, pp. 543-549 (1976).
9. Arthur I. Vogel, *Volumetric, (Titrimetric) analysis, Quantitative Inorganic Analysis*, The English Language Book Society and Longmans, pp. 256-57 (1968).
10. Paul & Delahay, *Structure of double layer with Specific adsorption, "Double Layer and Electrode Kinetics"*, Inter Science Publishers, New York, pp. 52-73 (1965).
11. James, S. Mahson & Harry B. Mark Jr., *Nature of Electrical Double Layer 'Activated Carbon (Surface chemistry and adsorption from solution)'* Marcel Dekker Ind. New York, pp. 121-22 (1971).
12. Alexander King, *J. Chem. Soc. London* 20, 893 (1935).