Green methodology for the recovery of Cr (VI) from tannery effluent using newly synthesized quaternary ammonium salt

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Abstract
Leather tanning industries release effluents into the river through various canals. These effluents contain chromium (VI) contaminating the river and the ground water as well. To fix a solution for this issue a simple and selective solvent extraction method has been applied by using a newly synthesized quaternary ammonium salt viz 2-benzoylethylheptyldimethylammonium bromide. By varying the parameters such as quaternary ammonium salts, sulfuric acid, pH, solvents, equilibration time and aqueous organic ratio the extraction efficiency has been determined.

1. Introduction
Chromium is considered among the top 20 hazardous substances for the human health (Kalidhasan and Rajesh, 2009), which is discharged into the aquatic systems from tannery industrial sector. Several attempts have been made to avoid chromium pollution in aquatic systems. The biological effect of chromium notably depends on its oxidation state. Cr (VI) which is water-soluble has been recognized as a toxic, mutagenic and carcinogenic environmental pollutant than Cr (III) (Park Sang-Wook et al., 2002; Arun et al., 2005; Das, 2004; Bahri Basaran et al., 2008). Though various techniques such as co-precipitation, adsorption, ion-exchange are available for separation and concentration of trace constituents of Cr (VI), the solvent extraction technique is simple efficient and environmentally friendly (Avijit Bhowal and Siddhartha Datta, 2001; Thierry Vincent and Eric Guibal, 2001; Yinghui Liua et al., 2010; Battacharya et al., 2006; El-Hefny, 2009). In this study the chromium extraction was optimized spectrophotometrically by varying the solvent, pH, concentration of sulfuric acid, concentration of quaternary ammonium salts, equilibration time and the volume of the reaction mixture and effect of stripping agents with a newly synthesized quaternary ammonium salt. The optimized procedure is then applied for the elimination of Cr (VI) from the effluent sample isolated from Erode, Tamil Nadu, India.

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2. Materials and methods

2.1. Reagents required

All reagents used were of analytical grade. Potassium dichromate (K2Cr2O7) was supplied by Fluka, sulfuric acid was purchased from Merck, NaCl, NaNO3, NaOH, ascorbic acid were purchased from SRL. Dimethylaminehydrochloride (SRL, Mumbai, India), ethylacetate, toluene, isobutylmethylketone, hexane, cyclohexane, xylene, ethanol, acetone (Merck, Mumbai, India) and heptyl bromide, p-formaldehyde, acetophenone (Spectrochem Ltd, India) were used as received. Quaternary ammonium salt viz., 2-benzoylethylheptyldimethyl ammonium bromide was synthesized by the following procedure.

2.2. Synthesis of 2-benzoylethylheptyldimethyl ammonium bromide

36.5 gm of dry dimethylaminehydrochloride, powdered p-formaldehyde and acetophenone were placed in a 250 ml round bottom flask fitted with a reflux condenser. A known volume of acidified alcohol was added and was then refluxed in a water bath until the appearance of a homogeneous yellow colored solution and it was transferred to a 500 ml beaker and then acetone was added. The mixture was cooled to room temperature and kept in a refrigerator overnight. The crystals obtained were filtered and washed with acetone and dried in a hot air oven and then recrystallized with acetone–alcohol mixture, filtered and dried to get dimethylaminopropiophenonehydrochloride. A known quantity of dimethylaminopropiophenone hydrochloride was added into water in a 500 ml beaker and stirred well. With vigorous stirring, a saturated solution of sodium bicarbonate was slowly added till effervescence stopped. The amine liberated was extracted thrice with ether and the ether extract was transferred to a separating funnel, washed with distilled water and the ether layer after separation was evaporated over water bath. To the resulting tertiary amine a calculated amount of heptyl bromide was added under ice-cold condition. 2-Benzoylethylheptyldimethylammonium bromide thus obtained was purified by recrystallizing with acetone–alcohol mixture (Scheme 1).

2.3. Preparation of chromium stock solution

1000 ppm Cr (VI) has been prepared by taking 0.283 g of potassium dichromate (dried at 100 °C for one hour) with 100 ml water in a volumetric flask.

2.4. Effluent sample digestion

The samples were collected from tanning industries, river water and ground level water around the industries in Erode district. The tanning raw effluent has been digested to concentrate only Cr (VI). The river water and the ground level water do not require digestion and therefore they can be used directly for other process (Ibrahim, 2008; Deepak Pathania and Zia Mahmood Siddiqi, 2009; Meisam Noroozifar and Mozghan Khorasani Motlagh, 2003; Kalidhasan and Rajesh, 2009; Kalidhasan et al., 2009; Lo and Shiue, 1998; Sahu et al., 2008).

2.5. Chromium extraction

1 ml of chromium was mixed with the reagents such as sulfuric acid, quaternary ammonium salts, distilled water and Isobutylmethylketone in a reaction tube to get bilayer. The reaction tube was tightly sealed with its lid and subjected to shaking until the color changed. A known quantity of the aqueous layer was withdrawn by using a glass syringe and examined for Cr (VI) determination. The percentage of extraction was arrived by using the formula

\[ D = \left( \frac{E}{100 - E} \right) \times \frac{V_{Aq}}{V_{Org}} \]

where \( D \) is the distribution ratio which implies the concentration of the organic phase and the aqueous phase, \( E \) denotes the percentage of extraction, \( V_{Aq} \) and \( V_{Org} \) refers to the volume of the aqueous and volume of the organic phase respectively (Fig. 7).

2.6. Mass spectrometer

Mass spectral studies were done on a FINNIGAN MAT 8230MS instrument and the molecular ion and the base peaks were observed and the fragmentation pattern was also analyzed with the mass spectral range up to 1200 amu.

2.7. UV–Visible spectrophotometer

Beckman DU640 UV/Vis spectrophotometer was used to record the absorbance. 1 cm matched quartz cells were used for absorbance measurements.

2.8. pH Measurements

The Eutech pH-millivolt Simulator was used for pH measurements.
2.9. FT-IR

The Fourier transform infrared (FT-IR) spectrum of the quaternary ammonium salts and the stripped, non-stripped solvents were recorded on a FT-IR spectrometer (Perkin Elmer RX I) in the spectral region from 4000–500 cm\(^{-1}\).

2.10. \(^1\)H and \(^{13}\)C nuclear magnetic resonance spectrometer

The \(^1\)H and \(^{13}\)C Nuclear magnetic resonance (NMR) spectra were recorded with a Varian HA JEOL 400 MHz spectrometer by using D\(_2\)O as a solvent and tetramethylsilane as the internal reference.

2.11. CHN analysis

Thermo Finnigan EA 1112 Series Flash Elemental Analyzer, this analyzer measures the amount of C, H, N, O, and S in samples by the rapid combustion of small amounts (1–2 mg) of the sample in pure oxygen (Dumas method or “flash combustion”).

2.12. Quantitative determination of quaternary ammonium salts

5 ml of 1% sample has been taken with a little amount of sodium hydroxide and 5 ml of chloroform. 0.5% solution of bromophenol blue in ethanol/H\(_2\)O was also added in drops and the mixture has been shaken for a few minutes. The formed two layers were to be separated from one another. The chloroform became blue, which indicated the existence of quaternary ammonium salt. The above experiment has been examined for the three synthesized quaternary ammonium salts. In Fig. 6 the bromophenol blue remains unreacted with the chloroform due to the absence of quaternary ammonium salt. This procedure has been verified successfully with the synthesized quaternary ammonium salt, which turns the chloroform to blue color.

3. Results and discussion

3.1. Mass spectrum of 2-benzoylethylheptyldimethylammonium bromide

The molecular weight of the newly synthesized quaternary ammonium salt has been confirmed by the appearance of the molecular ion peak at 356 (Fig. 1).

![Figure 1](image1.png)

**Figure 1** Mass spectra of 2-benzoylethylheptyldimethylammonium bromide.

![Figure 2](image2.png)

**Figure 2** FT-IR 2-benzoylethylheptyldimethylammonium bromide.
3.2. FT-IR of 2-benzoylethylheptyldimethylammonium bromide

FT-IR spectra confirm the C–N stretching vibration by the peaks from 1225 cm\(^{-1}\). Peaks at 1376 cm\(^{-1}\) and 1445 cm\(^{-1}\) show the inplane and out of plane bending of the CH\(_2\) group. C=O stretching is confirmed by the peak at 1675 cm\(^{-1}\). Symmetric and asymmetric stretchings of the CH\(_2\) group are shown by the peaks at 2840–2950 cm\(^{-1}\), respectively. Aromatic C–H stretching vibration is confirmed by the peak at 3070 cm\(^{-1}\) (Fig. 2).

3.3. Proton NMR of 2-benzoylethylheptyldimethylammonium bromide

Proton NMR spectrum confirms the aromatic ring protons by the multiplets between 7 and 8 ppm. Other alkyl protons produce peaks between 1 and 4 ppm. The signal due to aromatic ring, n-methyl protons and alkyl methyl protons confirms the structure of the compound (Fig. 3).

3.4. \(^{13}\)C-NMR of 2-benzoylethylheptyldimethylammonium bromide

The carbonyl carbon gives its characteristic signal close to 200 ppm. The aromatic ring carbons produce signals between 125 and 145 ppm. Below 80 ppm, other aliphatic carbons produce signals (Fig. 4).

3.5. Elemental analysis of 2-benzoylethylheptyldimethylammonium bromide

Synthesized phase transfer catalyst has been subjected to elemental analysis, the results show that for carbon 58.17, nitro-
gen 3.55, hydrogen 7.81 and for bromine 20.17 and oxygen 3.97.

3.6. FT-IR of solvent stripping

The chromium present in the organic phase has been giving signal at 894 cm\(^{-1}\), this has been already reported and confirmed that due to the presence of H\(_\text{CrO}_4\) the peak appears. Moreover the stripping solvent also contains the quaternary ammonium salt peaks, which confirms the transfer of quaternary ammonium salt from aqueous to organic (Fig. 5).

![Figure 7 Chromium extraction.](image1)

![Figure 8 Absorbance of the aqueous layer.](image2)

![Figure 9 Absorbance of the organic layer.](image3)

![Figure 10 Effect of solvents.](image4)

![Figure 11 Effect of pH.](image5)
3.7. UV–Visible spectrophotometer

Chromium has been determined in the case of aqueous solutions by making complex with 1,5diphenyl carbazide and examined under UV–Visible spectrophotometer, it is showing signal on 540 nm and the organic phase has been given a single peak around 364 nm while performing with blank solution. These two values are there to determine the amount of chromium present and also they confirm the quantity of chromium transferred (Figs. 8 and 9).

3.8. Effect of solvents

Efficiency of chromium extraction increases with an increase in polarity (Fig. 10).

3.9. Effect of pH

The effect of pH on the extraction of chromium has been studied by varying the pH from 2 to 8. At lower pH, the attraction of quaternary ammonium salt over chromium was very high and at pH 6 the extraction percentage reduced drastically. This may be due to a decrease in HCrO₄ and Cr₂O₇ respectively. After pH 6 the chromium will leave CrO₂⁻⁻ and this species does not form complex with quaternary ammonium salts. This can be attributed that at higher pH reduction potential of Cr (VI) decreases and therefore less reactive (Fig. 11).

3.10. Effect of sulfuric acid

The percentage of extraction has been arrived using different volumes of 1 M sulfuric acid. Fig. 2 clearly pictures this variation as previously mentioned the higher acidity induces a higher percentage of extraction due to the presence of HCrO₄⁻. Addition of sulfuric acid from 1 to 5 ml gradually increases...
the extraction. This variation has been performed under static conditions (Fig. 12).

3.11. Effect of quaternary ammonium salt

Fixing the other parameters constant, the effect of quaternary ammonium salt (i.e.) 2-benzoylethylheptyldimethylammonium bromide, on the extraction of chromium was studied by varying the concentration. Increase in the extraction was noticed with the increase in quaternary ammonium salt. In the absence of quaternary ammonium salt no extraction took place and from this it is evident that quaternary ammonium salt played a vital role in the extraction process (Fig. 13).

3.12. Variation in equilibration time

The effect of equilibrium time on the chromium extraction was evaluated by varying the time from 1 to 5 min, keeping other parameters constant. The percentage of extraction increased in few seconds and then attained a maximum percentage of extraction in 2 min and became steady thereafter (Fig. 14).

3.13. Variation in aqueous/organic ratio

A slight increase in the aqueous phase does not have any characteristic effect on the extraction but with a large increase results in a decrease in the percentage of extraction, this may be due to the increase of the aqueous phase which may reduce the pH and turns the Cr (VI) to become disinclined in the case of oxidation potential which results in the decrease in percentage of extraction (Fig. 15).


Stripping was done by adding the stripping agent into the organic portion and shaken for few minutes. The chromium
present in the organic solvent will turn into salt of stripping agent which was isolated. Stripping reduces the Cr (VI) to Cr (III) with the help of NaOH and ascorbic acid (Fig. 16).

3.15. Effluent treatment

The collected different tanning effluent samples were digested with the aforementioned procedure and then treated for the extraction procedure. The samples were getting the best percentage of extraction and the level of purity of the effluent water was commendable. The river water and the ground water samples were treated for extraction without any further digestion. This solvent extraction method is really a convenient and cost effective method compared to other available methods and therefore it can be used to treat the effluents from tannery industries to minimize the pollution of river and ground water (Scheme 2).

4. Conclusion

Green methodology is the one of the finest techniques which induces the environment safety. The present work dealt with the extraction of the chromium (VI) from the tanning industrial effluent water by the solvent extraction method. The samples were thoroughly analyzed by the UV–Visible spectrophotometric method, from which the quantity of Cr (VI) was analyzed. It has been eliminated from effluent by using newly synthesized quaternary ammonium salts. The results of all the experiments clearly explain the efficiency of this process and it can be effectively availed for the eradication of toxic chromium from the tannery effluents in a large scale manner.

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