LITERATURE SURVEY ON METHOD USED FOR DETECTION OF CHROMATES IN WATER

M.Sc. dissertation report by:

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LITERATURE SURVEY ON
METHOD USED FOR DETECTION
OF CHROMATES IN WATER

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CERTIFICATE

This is to certify that the dissertation entitled "**literature survey on methods used for detection of chromates in water"** is Bonafide work carried out by Miss. Shivani Shivram Chari (analytical chemistry) under my supervision in partial fulfilment of the requirement for the award of the degree of Master of Science in Chemistry at the School of Chemical Sciences, Goa University

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ABSTRACT

One of the important resources that plays an important role for the survival of human beings as well as for plants and animals is water, but the recent surveys have pointed out the contamination of various water bodies due to different pollutants. The pollutants existing in different forms such as chemical, biological, industrial and sewage has entered the water bodies. The introduction of these pollutants in water bodies introduces different ions such as organic, inorganic and heavy metals. The heavy metals include arsenic, cadmium, chromium, copper, nickel, lead and mercury. Chromium acts as on of the most toxic among all. The most common oxidation state of chromium are +3 and +6. The Cr (VI) is relatively more toxic than Cr (III) that degrades the quality of water. To improve the quality of water Cr (VI) needs to be detected and removed from the water bodies. Different methods for the detection of chromate in water have been given such as colorimetric, spectrophotometric, ion chromatograph, flame atomic absorption spectrometry, normal and surface enhanced spectrometry, quenched phosphorescence, and electrochemical sensors. These methods detect the presence of chromate based on complex formation and absorption and emission spectra. once the chromate has been detected it is very important to remove theses Cr (VI) from the water bodies by different removal methods like cross flow micellar enhanced ultrafiltration, chitosan-zirconia microballs, sorption, zeolites and nanomaterials.

INTRODUCTION

The survival of any form of life is dependent on three basic requirement air, water and soil. Water being one of the important sources for survival. The surveys conducted all over world and India pointed out that the quality of water is deteriorating[1] due to discharge of variety of water pollutants that causes water pollution. The water pollution is caused due to various sources which include point[2] and non-point[2] sources. The contaminated water discharged from sewage, industries, land runoff, agricultural lands, chemical fertilizers, insecticide and pesticides[1] etc. degrades the water quality as it contains large amount of pollutants [2] like organic and inorganic pollutants, acids, alkalis, anions, detergents, heavy metals. Water pollution is observed when the amount of pollutants discharged in the water is no longer contained by natural ecosystem[3]. The contamination occurs due to pollutants[2] which may be biodegradable or non-biodegradable. Water pollution is divided into different categories. The two basic categories include dissolved and undissolved substances.[3] The dissolved category includes organic and inorganic components whereas undissolved includes precipitated components, suspended solids, colloidal materials, floating materials ,oils, grease, foam, clay and heavy metal etc[3]. Among all these pollutants “heavy metal” contamination due to metals like arsenic, cadmium, chromium, copper, nickel, lead and mercury along with their cationic and anionic form is found. Chromium is considered as an important trace element as it plays an important role in biological system and an important component for humans. Among all other metals chromium has one of the top places as one of the toxic contaminants. The common ores include Ferric chromite (FeCr2O4) is the principal Cr ore, found mostly (with 96% of the world's reserves) in South Africa. Minor common sources include chrome ochre (Cr2O3), and crocoite (PbCrO4) are also present[3].

The wide distribution of chromium in the surrounding has been a reason for major contamination of water. The effluents from industries being one of the major source of it as chromium is widely used in industrial applications like metallurgical industries(ore refining, and steel and alloy production), chemical industries (pigment manufacturing, plating/metal finishing, corrosion inhibition, leather tanning and wood preservation),and combustion of coal and oil.[4]

chromium shows a range of oxidation states from -2 to +6 and exhibits both cationic and anionic forms. The commercially stable Cr forms are Cr(0), Cr(III), Cr(VI).[5] Cr (0) is found in metallic form, as a component of metallic base.[5] The most commonly known oxidation states are +3 and +6. The hexavalent chromium Cr[Cr(VI)] forms chromates and dichromate's, which are more toxic and mutagenic, which show solubility over a wide pH range ; the trivalent Cr[Cr(III)] is comparatively less toxic and non-mobile because it precipitates as oxides and hydroxides above pH 5.[4]

Cr(VI) is known as a potent oxidant at an acidic pH[5] when organic molecules having oxidisable group can carry out its reduction ability forming Cr(III). At near neutral and alkaline pH Cr (VI) attains a stability. Cr (VI) in aqueous solution exists as an oxo species such as dichromate ($Cr_2O_7^{-2}$), chromates (CrO_4^{-2}) and acid chromates ($HCrO_4^-$). Cr (VI) consumption can cause large number of health problems such as stomach problems, kidney and liver damage, convulsion, allergic reactions such as redness and swelling of skin, cardiovascular, nervous, bone diseases, carcinogenesis, mutagenesis, teratogenesis, nutrient deficiency, enzyme malfunctioning, renal tubular dysfunction accompanied by osteocalcin and other complications.[6]

Cr (VI) is not only harmful for humans but also for plants. It causes phytotoxicity in plants leading to problems like seed germination, imbalance caused due to nutrient deficiency, pigment degradation, and decrease in enzyme concentration causing stress to the plant.

As the problems arising due to the presence of chromate in varying concentration, pH and caused large amount of contamination in various water bodies such as rivers, ponds and lakes. The contaminated water has caused serious problem to health of human's plants and animals, different measures need to be taken in order to reduce these contaminants. One of the measures being detection of chromate followed by removal of it.

LITERATURE SURVEY ON METHODS USED FOR DETECTION OF CHROMATES IN WATER

COLORIMETRY METHOD

CHROMATE DETERMINATION BY COLORIMETRIC METHOD USING 1,5-DIPHENYL CARBAZIDE.

Chromate being unstable when exposed to different environmental conditions it is very important that the method to detect it must be of simple, portable, cost effective and sensitive. Microfluid detection system is one of the most simple and portable system which can be used on site that reduces the sample requirement and to reduce waste generation. The DCP method was optimised for incorporation into micro scale detection systems.[7] The sample preparation was carried out using Cr(VI) solution with sulphuric acid and 1,5-diphenylcarbazide. In acidic medium the Cr (VI) and 1,5- diphenylcarbazide formed a purple coloured complex due to the redox reaction, where Cr (VI) reduces to Cr (III) and DCP oxidises to 1,5-diphenylcarbazone (DCPA). The formed purple coloured complex of Cr (III) and DCPA. The structure of Cr(VI)-DCP complex is given below[8]. The complex has a lambda max of 540 nm.[7]

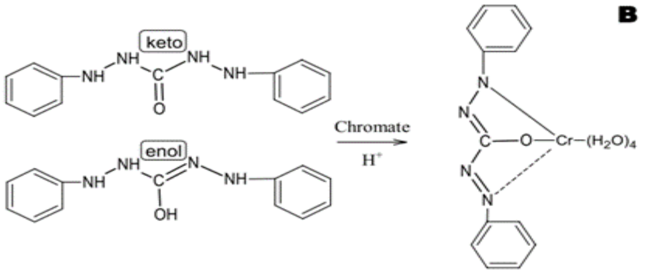

Figure 1. Complex of nickel with dimethylglyoxime (A) and of chromium with diphenylcarbazide (B).

The optimisation of various parameters such as path length, pH, sample reagent ratio, reagent stability, effect of acid concentration, colour stability, gave better results compared to regular parameters.

The DCP method shows a absorption at 543nm in a UV-VIS spectrophotometer in plot of absorbance versus wavelength which helps to detect chromate as a complex with DCP

The plot of concentration vs absorbance depicts a linear graph indicating that the Beer lamberts law has been obeyed.

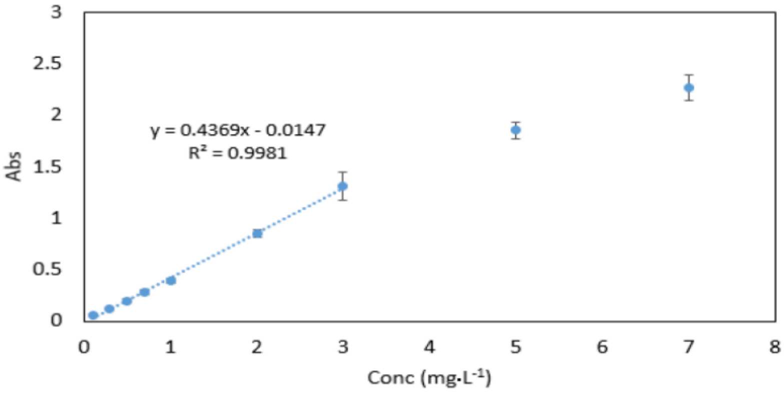

Figure 10. Calibration curve for Cr VI ranging between 0.03–7 mg·L^{-1}. All measurements were carried out in triplicate (*n* = 3).

SPECTROPHOTOMETRIC METHODS

SPECTROPHOTOMETRIC DETERMINATION OF CHROMATE USING COMPLEX FORMATION WITH EDTA USING H-POINT METHOD.

In this complex formation method of chromate with EDTA it is observed that this method deals with detecting the dissolved form of Cr^{+6} in contaminated water in presence of other ions.[9] The H-Method plays an important role as to avoid interference caused due to presence of other ions such as Fe^{+2}, Fe^{+3} and Cr^{+3}.The H point method is applicable for two cases that spectral interferences is constant in selected spectral range or equal in two different wavelengths.[9] as shown in fig. 1 and 2[9]

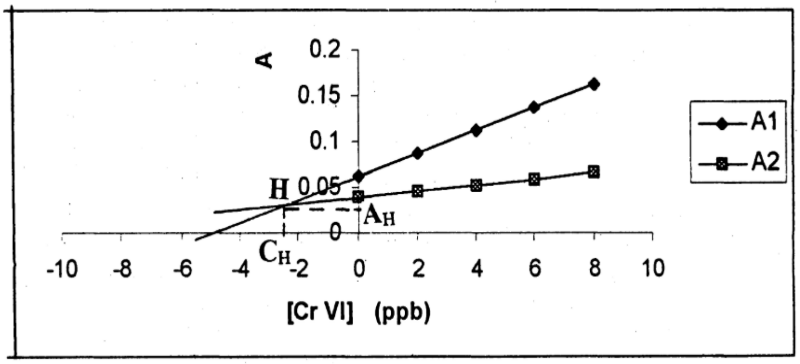

Fig. 2. The H-point calibration curves

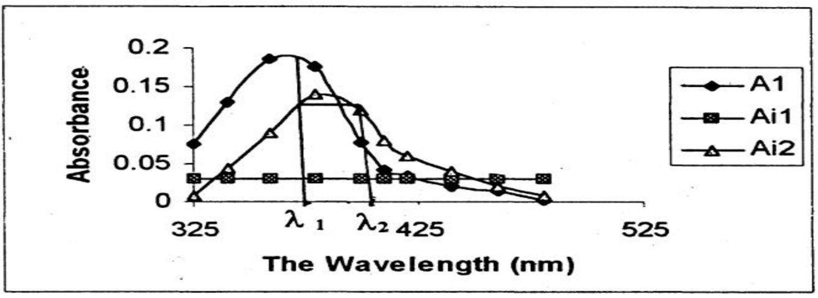

Fig. 1. The spectral curves of: (a) A_1: analyte (b) A_{i1}: constant interference (c) A_{i2}: interfering element

The experiment is performed in such a way that the sample must be stored at low temperature (4ºC) and Cr^{+6} should not be initially acidified to avoid reduction. The sample is transferred to a colorimetric tube followed by dropwise addition of 5% HCl or 5% NaOH pH=7 or ± 0.3. further a solution of NaF/sample is added and upon dissolving NaF, EDTA is added to this solution. This content is further diluted using distilled water and stirred until a homogeneous solution is obtained.

A Pye Unicam SP6-550 UV/vis spectrophotometer[9] is used for recording the absorbance at λ=370 and λ=410nm. Since EDTA forms stable complexes with most of the metal ions at pH =7 spectral interferences showed presence of Cr^{+3}, Fe^{+2}, Fe^{+3}, Co^{+2}, Ni^{+2} and Cu^{+2} complexes with EDTA at various characteristic wavelength. The molar absorptivity data at different wavelength of different interfering ions and Cr^{+6} showed a strong absorption peak at 370 for Cr (VI) and iron. Cr (III) showed absorbance peak at 370[9] for other elements was very low ; for Co^{+2}, Ni^{2+} and Cu^{+2}, as the absorbance has high difference which determines the absence of other interfering ions. The interference of $Fe^{+2,+3}$ and Cr^{+3} can be eliminated by using NaF.[9] The interference at 370 to 410 is constant due to $Fe^{+2,+3}$ and Cr^{+3} thus H Point method applied to avoid this and detects Cr^{+6}-EDTA complex.

The pH=7 has been chosen to ensure high stability of Cr^{+6}-EDTA complex. The calibration curve for absorbance at 370nm. Helps to interpret that there is a good relation between concentration of chromium and absorbance value for Cr^{+6}-EDTA complex.[9] The method suggests that the combination of spectrometric method with H-point is helpful for determination of Cr(VI) in water.

EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM AS TETRABUTYLAMMONIUM-CHROMATE

The method is based on extraction-spectrophotometric procedure for determination of Cr^{+6} and Cr^{+3} in natural water. Tetra butylammonium bromide forms a very stable ion pair in acidic medium. The separation of ion pair can be carried out using solvent extraction method using methyl isobutyl ketone MIBK[10] as a extracting solvent, as (MIBK). As MIBK showed highest absorbance as compared to the reagent blank. The separation and extraction of $CrO_4^{2-}(TBA^{+})_2$ can be studied using the given figure[10]

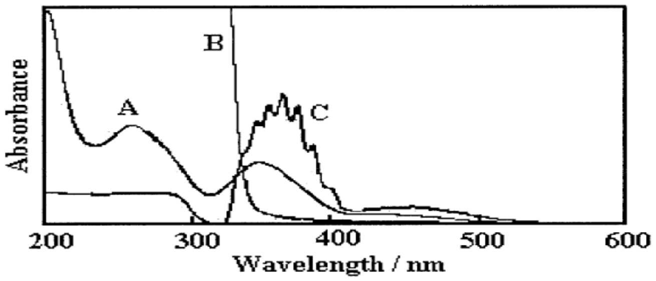

Fig. 1 UV-vis spectra of A) aqueous solution of Cr^{VI}, B) TBAB in MIBK and C) extracted $CrO_4^{2-}(TBA^+)_2$ ion-pair into MIBK, [TBAB]/M in MIBK = 0.02, $[Cr^{VI}] = 0.6\ \mu g\ L^{-1}$.

The separated $CrO_4^{2-}(TBA^{+})_2$ with MIBK was again back extracted from acidic Diphenyl carbazide (DPC), due to which the acidic Cr^{+6} produced a soluble violet colour complex with DPC. This complex was then determined by spectrophotometry at 548 nm.[10] The standard solutions were then compared with the analysed sample. In case of Cr (III) the before formation of

complex the Cr (III) oxidised to Cr (VI). So, prior to ion pair extraction it should be oxidised with Ce (IV). For a fixed amount of chromium, the effect of variation of TBAB concentration on absorbance indicated that the optimum concentration was 0.02M TBAB. A calibration curve plotted for optimised conditions like fixed volume, shaking time and concentration of TBAB and standard concentration of Cr (VI), the curve obtained was linear, thus the method can be applied for determination of chromate.

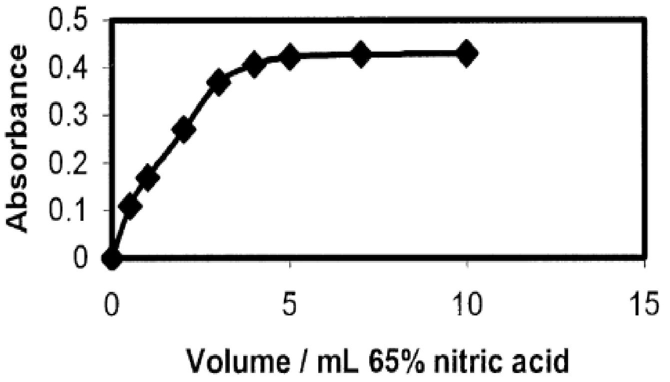

Fig. 2 Acidity dependence of the ion-pair extraction of $[Cr^{VI}] = 0.06\ \mu g\ L^{-1}$ by [TBAB]/M in MIBK = 0.02; and shaking time/min = 5.

DETERMINATION OF NANOMOLAR CHROMATE IN DRINKING WATER WITH SOLID PHASE EXTRACTION AND A PORTABLE SPECTROPHOTOMETER

Solid phase extraction method is a pre concentration sorbent extraction method. Adsorbents like silica gel, alumina and Ambersorb resin are used for forming Cr-DCP complex[11]. The complex is preconcentrated on commercial SPE(Sep-Pak C18)[11] and eluted which is then quantified on visible spectrophotometry. The absorbance was recorded at 542 and absorbance at 700nm was used for baseline drift correction[11]. The analysis in the field were carried out using a custom LED based portable spectrophotometer[11]

The sample was initially passed through a Sep Pak which was useful for removal of interference using a cation exchanger. this analytical procedure offers the benefits of improved sensitivity, reduced sample consumption, shorter analysis time, greater operational convenience, and lower cost.[11] The chromate sample preparation was done of known concentration with acid solution (H_2SO_4) and DPC and was loaded on a C18 column. The eluted Cr-DPC with methanol was used for measuring absorbance.

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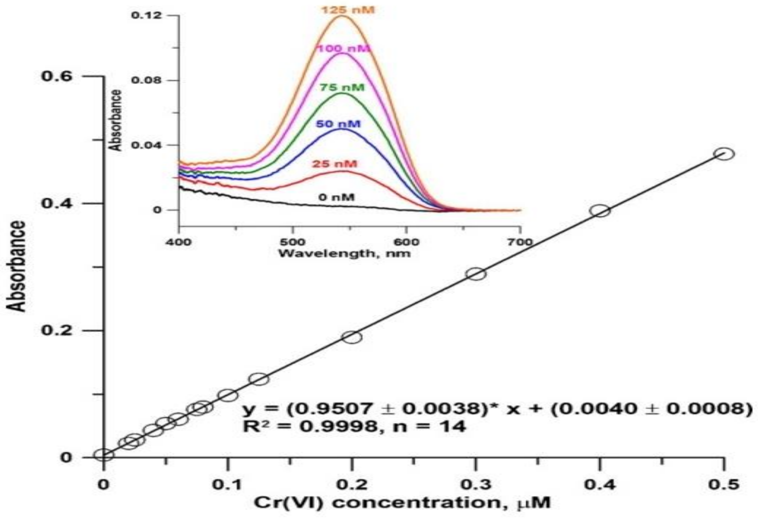


Fig. 5. Calibration curve obtained using the optimized parameters. The inset figure shows the Cr–DPC absorbance spectra of low-chromate samples in methanol eluent.

A calibration cure over range of Cr(VI) gave a linear absorbance as shown in figure .[11] By decreasing the volume of sample the range of linear absorbance can be broadened. The figure shows that the absorbance spectra for low chromate concentration[11]. With verification of beer lambers law and use of solid phase extraction cartridge the method can be applicable for determination of chromate in various sample.

SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM (VI) USING 2-HYDROXY, 3-METHOXY BENZALDEHYDE THIOSEMICARBAZONE (HMBATSC)

In a simple spectrophotometric determination of trace amount of Cr^{+6} by complexing with 2-Hydroxy, 3-Methoxy Benzaldehyde Thiosemicarbazone (HMBATSC)[12] which at pH=6 forms a stable yellowish green complex. Different sets of solution containing cr^{+6} along with buffer of pH=6 and HMBATSC

were prepared and absorbance was measured at 385nm with pH=6 in concentration range of 0.26 to 2.6μg mL^{-1} [12]. The standard chromium (VI) solution was prepared with the HMBATSC solution which was dissolved in DMF solution[12].the set of different solutions were prepared with buffer solution(pH=6) and HMBATSC. These solutions were used for recording the absorbance spectra at 380-500nm for a yellow green coloured [Cr(VI)-HMBATSC][12] complex. The blank solution used was HMBATSC.

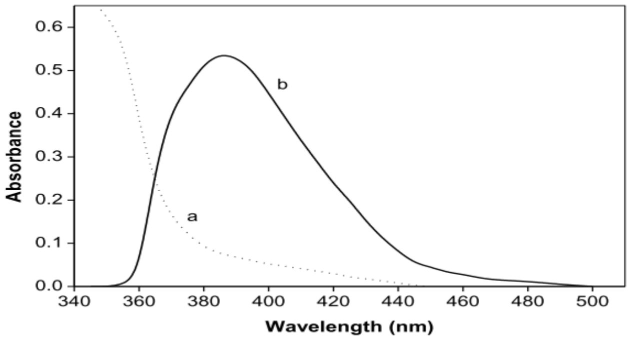
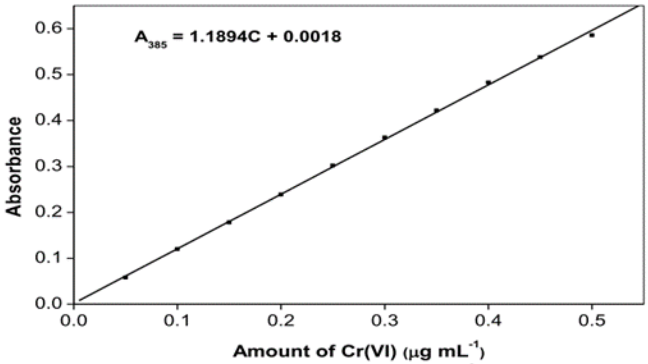


Figure 2: Absorption spectra of
(a) HMBATSC Vs Buffer Blank
(b) [Cr(VI) – HMBATSC] Vs Reagent blank

The spectrum indicated that the maximum absorption was at 385nm. The set of solutions containing different concentration solution for 385 nm gave a straight-line spectrum. A straight line obtained indicates that it obeys beer lamber's law.

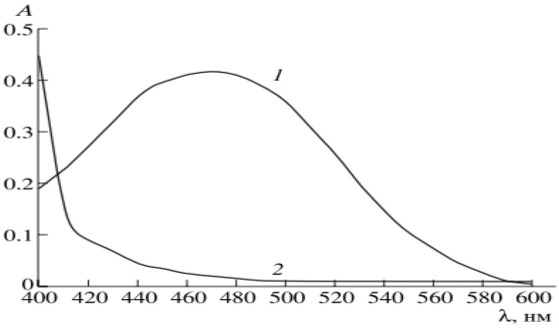


Calibration plot for Cr(VI) [HMBATSC]=1×10^{-3}; Wavelength= 385nm, pH = 6.0

The sensitivity of the proposed method has been derived from its molar absorptivity value ($\epsilon=1.20\times10^{3}$ lit. mol $^{-1}$cm^{-1}), detection limit (0.014μg mL^{-1}) and determination limit (0.041μg mL^{-1}), correlation coefficient (0.9999) and relative standard deviation (0.32%) confirm the best suitability of the proposed method for the determination of Cr (VI). Job's continuous variation method determined the stoichiometry of [Cr (VI)-HMBATSC] complex with mole ratio as 1:1 (M: L).

SPECTROPHOTOMETRIC DETERMINATION OF TRACE AMOUNTS OF CHROMIUM WITH CITRAZINIC ACID

The spectrophotometric determination of chromate using citrazinic acid is based on diazotization and coupling reaction[13] includes indirect method for chromate determination Cr^{+6} . A series of chromium samples were prepared with addition of acetate buffer of pH=4.0 and hydroxylamine hydrochloride solution. On addition of p-aminoacetophenone the solution was kept for some time. The coloured azo dye[13] solution on dilution was used for measuring the absorbance at 470 nm.



Absorption spectra of an azo dye. A. Sample Cr(VI) [1 ppm] vs reagent blank. B. Reagent blank vs water.

The reaction involves oxidation of hydroxylamine to nitrite using a pH range around 3.5-4.5. the pH of the solution was maintained using acetate buffer which further diazotizes p-aminoacetophenone and the citrazinic acid in alkaline pH couples with the earlier formed diazonium salt, to form an azo dye[13].The parameters were set to record the absorbance for azo dye at 470nm. The absorbance spectra is given below, nitrite by Cr^{+6} was done by diazo-coupling reaction with standard nitrite solution ,the generated nitrite was determined by diazo-coupling reaction[13].

This method gave a linear calibration graph was obtained for a trace level of chromium (VI). The precision for the method was developed by using 10 different samples. This method also shows high colour stability compared to other standard methods. The linear graph obtained for chromium (VI)

MULTI-WAVELENGTH SPECTROPHOTOMETRIC DETERMINATION OF Cr (VI) IN WATER WITH ABTS

Chromate determination using 2,2’-azino-bis(3-ethylbenzothiazoline-6-sulfonate) (ABTS)[14] by spectrophotometric method, shows single electron transfer reaction of a stable and colourless ABTS with free radical or other oxidants to produce a green coloured $\mathrm{ABTS}^{\bullet+}$ a radical ion[14]. The other application of this reaction includes radical detection and as kinetic probe formation and determination of Fe (VI), recent studies showed that selective oxidation of ABTS by Cr (VI) under acidic medium gives rise to $\mathrm{ABTS}^{\bullet+}$ thus UV spectrophotometer could be used to detect this radical ion. The absorbance spectrum with variety of doses of solution as seen in the figure, indicates no absorbance at 350-800 nm. The spectrum shows intense and broad peak with maxima peaks at 415, 649, 732nm are due to $\mathrm{ABTS}^{\bullet+}$ that were similar to standard method.

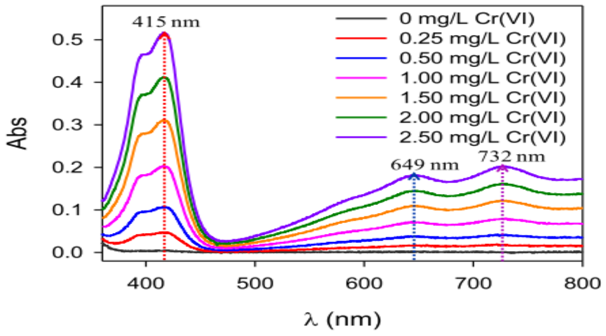


Fig. 2. Absorption spectra of $\mathrm{ABTS}^{\bullet+}$ after reaction of ABTS with Cr(VI) of different concentrations. Reaction conditions: $[\mathrm{ABTS}]_0 = 19.24\ \mu\mathrm{M}$, $[\mathrm{H}^+] = 3.0$ M. (If not stated otherwise, Cr(VI) concentration was that of the standard solution while the concentrations of H^+ and ABTS referred to the corresponding concentrations in the 10 mL colorimetric tube).

As the concentration of the Cr (VI) was increased there was increase in the absorbance of the given three wavelengths, but the Cr (VI) concentration didn’t show any effect on opposition of the peaks. Hence the further analysis was carried out at these wavelengths.

This method being highly flexible and sensitive can be used for Cr(VI) determination at three different wavelength as mentioned above. This method has a anti interference ability in the Cr(VI)-S(IV) and Cr(VI)-Co(II) system for Cr(VI) determination[14]. Also it is not applicable in basic medium as well as for chromate determination in presence of other co-existing oxidants with Cr(VI) determination indicating obeying of Beer lambert’s law, thus this method can be used for chromate detection.

SPECTROPHOTOMETRIC HPLC AND EDTA CHELATION FOR SIMULTANEOUS DETERMINATION OF Cr (III) AND Cr (VI)

A simultaneous study carried out in HPLC for determination of Cr (III) and Cr (VI), that shows a formation of chelate of Cr (III) with EDTA. A reversed phase column with varied time factors showed a resolved separation of peaks, showed mutual separation which was detected by absorbance on revered phase column. The chelating compound used for forming a complex with Cr(III) was EDTA.[15] EDTA in alkaline condition is found to form complex with most of the metals so as to confirm the chelate formation of Cr(III) investigations were done to focus on EDTA as well as metal-EDTA.[15] along with chromate and dichromate.

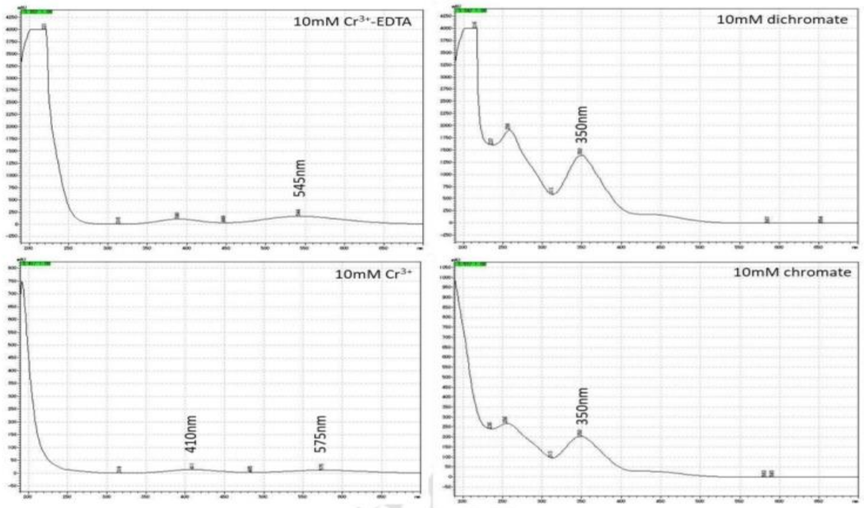


Fig. 1. Absorption spectra of Cr(III), Cr(III)–EDTA, chromate, and dichromate.

The figure shows similarity between chromate and dichromate, where dichromate having higher absorption. The lower absorbance for Cr (III) was indicated the need for derivatization. At 350 nm Cr (VI) showed detection of two types of compounds. The weak peaks indicated that retention was weak.

ION CHROMATOGRAPHY

DETERMINATION OF CHROMATE USING ION CHROMATOGRAPHY

In the recent studied the use of different hyphenated technique with traditional method have the advantage of low detection limit and quantification limits. On the other hand, these techniques are expensive and cannot be used for everyday routine analysis.

The different types of samples can be analysed using classical methods as well as instrumental methods. In case of ion chromatography for determination of cations and anions the conductivity detector system is applied. Ion chromatography has advantage of short analysis time, sensitivity on low level, high selectivity, and simultaneous detemination.[16] ion chromatography is usually used to water analysis for determination of common cations and anions like F-,CL^-,NO_3^-,PO_4^{-2},SO_4^{-2}, Na^+, k^+,NH_4^+ and Mg^{+2}. This method is employed for detection of non-typical ions which are not considered for regular analysis like chromate. The simultaneous determination of chromate along with other anions by using isocratic ion chromatography.[16]

A number of columns were selected based on their popularity, and from their low er to higher capacity. And the best results were shown in dionex IonPac AS14 column. Thus, this column was used for separation.

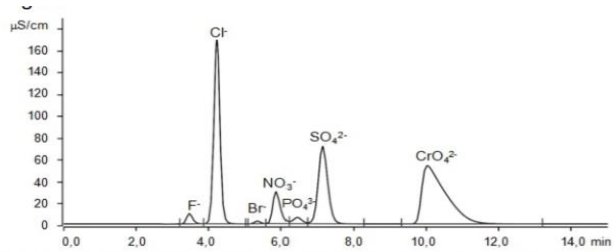


Figure 1. Chromatogram of anions for Dionex IonPac AS14 column.

The separation quality for ion separation are dependent on factors like stationary phase flow rate and the eluent type.[16] this method points out the lacking of other analytical columns for separation which are carried out based on changing few parameters on regular bases. This isocratic ion chromatography employs anion exchange column, carbonate/bicarbonate eluent and supressed conductivity detection[16] which can be used for common as well as less used anions in waste consisting of complex matrix and can be applicable for chromate detection.

FLAME ATOMIC ABSORPTION

FLAME ATOMIC ABSORPTION SPECTROMETRIC DETERMINATION OF CHROMIUM(VI) BY ON-LINE PRECONCENTRATION SYSTEM USING A PTFE PACKED COLUMN

Atomic absorption spectroscopy method for detection of chromate is performed by separating the individual element or atom, which follows the use of light for measuring the gas phase atom concentration[17] the energy absorbed by ground state atom with required wavelength. The comparison with the standard helps to identify the amount of light existing in any unknown compound.

The Flame atomic absorption spectroscopy is a widely used method for detecting different elements. This method requires sample pre-treatment which includes isolation of the analyte from other interfering ions by using different techniques such as flow injection technique. This technique incorporates a column reactors packed with polar or non-polar sorbents.[18] Solid phase extraction can also be used for this technique. The chromium sample is initially sorbed on FI materials directly or by initially chelating them with diphenylcarbazide. This method was based on determination of ultra-trace amount of Cr (VI). Which includes use of APDC-isobutyl methyl ketone (IBMK) on the column for FAAS detector.[18] As the sample was loaded the Cr(VI)-PDC retained on the column which was eluted using IBMK. The eluted complex then on passing through FAAS nebulizer. The column was arranged for IBMK flows in reverse manner to the sample and reagent. The peak height was proportional to the Cr(VI) concentration[18] thus this was used for all analysis. IBMK produces higher and more sharp peaks due to more enhancement of flame atomization[18] and is considered a better eluent. Some advantages of IBMK includes its immiscible nature with water and other less polar solvents, that enables it to produce better elution and low concentration dispersion of analyte. The FI-FAAS method had advantage of low costs, and the detection limits and precision is similar to other methods but this method is based on much simple apparatus. The use of PTFE as a sorbent material improves the features to a better determination and analysist.

Other methods such as Electrothermal atomic absorption spectrometry (ETAAS) improves sensitivity by 2-3 folds and eliminates the matrix before atomization which helps to increase the time of residence of analyte on the atomiser giving better results. The Graphite furnace atomic absorption (GFAAS) is a improved form, which used an electrically heated graphite tube instead of flame. This tube when heated removes matrix component. This method shows improved sensitivity and detection limit as all the analyte has been atomized, in this case, for determination of Cr (III) and Cr (VI) elements present in different water samples a zirconium dioxide made of nano meter size was developed which was analysed using Electrothermal atomic absorption spectrometry, solid phase extraction and direct ultrasonic slurry sampling was used.

RAMAN SPECTROSCOPY AND SURFACE ENHANCED RAMAN SPECTROSCOPY

CHROMATE DETERMINATION BY NORMAL RAMAN SPECTROSCOPY AND BY SURFACE ENHANCED RAMAN SPECTROSCOPY

Raman spectroscopy due to its vibrational frequency of symmetric stretch in Cr^{+6} ions its is applicable for Cr^{+6} detection. The observations were mad that water does not interfere in analysis. The Cr^{+6} and Cr^{+3} is Raman active having a limit of detection is 146ppm and 239ppm respectively[19]. Raman spectroscopy coupled with fibre optic Raman spectroscopy could be used for trace amount of sample.

The Surface Enhanced Raman Scattering (SERS) allows rapid, sensitive and in situ Cr^{+6} detection. SERS involves analyte adsorbed on roughened metal surface (gold or silver) shows enhanced magnitude over their normal values.[19] Raman active mode is shown by both chromate and dichromate as they are polyatomic in nature. The important feature for SERS is the choice of fabrication of reproducible metallic nanoparticles[19] which acts as active surface adsorbent. SERS shows degradation of SERS signal in presence of low concentration of chromate and dichromate. The use of gold SERS were able to even better results. The metal surface of pure gold was not able to adsorb the analyte. the effect of polymer such as polyaniline/poly composite and poly (diallyl dimethyl ammonium chloride) (PDDA) on hexavalent chromium adsorption from aqueous solution was studied. Optically stable PDDA-Au nanoparticles was highly SERS active. Normal Raman spectra for Cr^{+6} figure, shows intense Raman peak for $Cr_2O_7^{2-}$ in aqueous solution at around 902cm^{-1} which was used for detecting and for identifying Cr (VI) in sample. Cr^{+6} being Raman active were detectable at low initial concentration. As the concentrations of solutions were increased around 902 $cm-^{1}$ Raman band was also increasing.

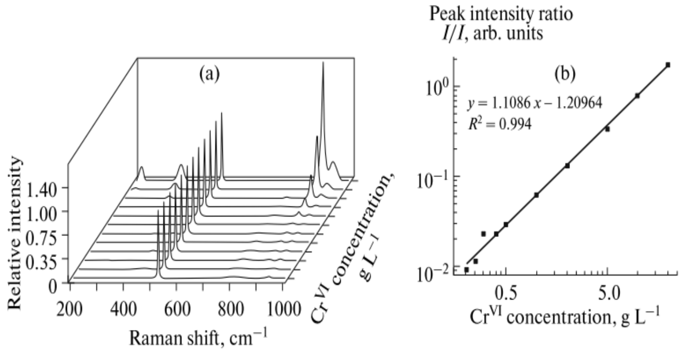


Fig. 5. (a) NRS analysis of $Cr_2O_7^{2-}$ at concentrations of 0.05, 0.1, 0.2, 0.25, 0.3, 0.4, 0.5, 1, 2, 5, 10, 20 g/L at pH 5.60. (b) Log-log plot with linear regression of peak intensity ratio I_{902}/I_{520} as a function of Cr^{VI} concentration from 0.2 to 20.0 g/L.

There were no Raman spectra for dichromate solution at low concentration thus for detecting chromate at low concentrations signals must be enhanced. The use of PDDA-Au NPs showed that the electrostatic attraction between Cr(VI) anions enables close contact and the concentration of Cr(VI) on Au nanoparticles[19]. The surface modification of AU nanoparticles enables high sensitivity. The positively charged PDDA were able to carry out sorption and led to even distribution of Cr (VI) on Au nanoparticles, this indicates that the surface modification played a important role for even distribution of analyte. this indicates that surface PDDA Au particles were advantageous for detecting Cr (VI) having higher sensitivity and reproducibility.

PHOSPHORESCENCE METHOD

TIME RESOLVED QUENCHED PHOSPHORESCENCE DETECTION OF CHROMATE USING PAIRED ION REVERS PHASE HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

The method describes the selective determination of chromate on separation with paired ion reversed phase HPLC system using quenched phosphorescence. The quenched room temperature phosphorescence in liquid was developed based on the measurement of phosphorescence of biacetyl (2,3-butanedione) in deoxygenated mobile phase[20]. Analytes on interaction with biacetyl in their excited triplet state led to decrease of phosphorescence signal. The absence of quencher signal *lo* observed that corresponded to triple lifetime τ_0 of biacetyl whereas in presence of quencher τ_0 is decreased to τ, and lo to *l*. The Perkin-Elmer LS-2 luminescence detector with time quencher ability helped to exclude scattering and background fluorescence and it worked on pulse source time resolved phosphorescence mode. The excitation of biacetyl a broad band filter with transmission at 400 nm was applied[20], and the emission wavelength was observed to be 400 nm. The biomolecular quenching constant for chromate are one order of magnitude larger than for Cr (III), that is based on electron transfer. This case is only possible if the if chromate if chromate consists of excited electronic state with lower energy than triplet state of biacetyl.[20]

For studying the method on real samples and surface water samples, the solutions were spiked with chromate on a deoxygenation column. The further improvement to avoid peak tailing was done by adding the 3% acetonitrile before injection, caused due to interaction of chromate in silanol group of the column. The low recoveries obtained were due to reducing component reacting with chromate. On the other hand, blank and spiked surface water sample gave a higher recovery. The dependence of from spiked amount of chromate caused difficulty for calculating limit of detection for real sample. Since the chromate peak was found to be clearly separating from the matrix interference in all types of water sample (20 ppb) depicted a realistic value as compared to a standard value. This indicated that in originally chromate containing sample the concentration remained constant on attaining equilibrium.[20]

The comparison of this method with other described HPLC method Lod's are found to be similar, except for colorimetric method, so this method can be applied.

ELECTROCHEMICAL SENSORS

ELECTROCHEMICAL SENSORS FOR DETECTION OF Cr (VI) IN WATER

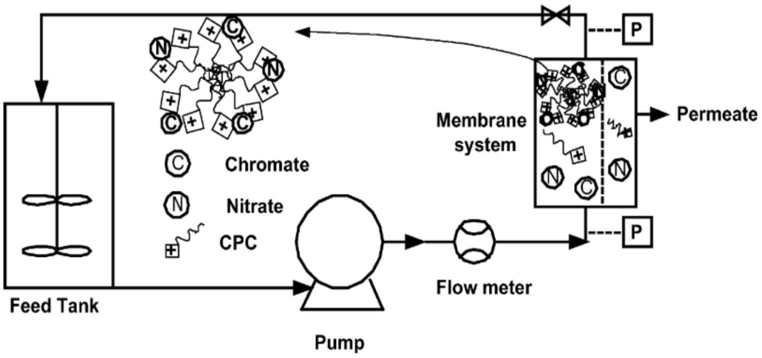
The traditional being expensive are very inefficient. This can be overcome by use of electrochemical sensor. In these sensors a charge transfer phenomenon takes place from electrode to another phase.[17] Chemical changes occurs during these processes, around the electrodes where charge is conducted around the bulk of sample. These electrode reactions and charge transport is chemically controlled. Chemical sensor and biosensors have advantage of minimising sample pre-treatment, low cost, better sensitivity, selectivity and time consumption. Self-contained devices like chemical sensors provides all type of real time information while testing. Sensor's two important functions are recognition and transduction. During analysis the analyte interacts with receptor and with different concentrations there is variation in physical and chemical properties of sensing element, which is detected by the transduce that further translates it. For chromate detection biosensor is used which combines biological components with physiochemical detector and helps in detection.

METHOD FOR REMOVAL OF CHROMATE

The contamination of water due to introduction of heavy metals has led to a number of health problems as well as environmental problems. The presence of these heavy metals such chromate needs to be eliminated using different removal methods. The methods for removal of chromate are as follows

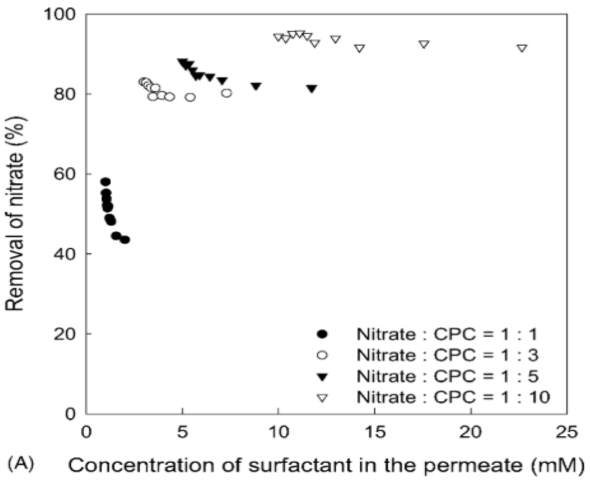
CROSS-FLOW MICELLAR-ENHANCED ULTRAFILTRATION FOR REMOVAL OF NITRATE AND CHROMATE: COMPETITIVE BINDING

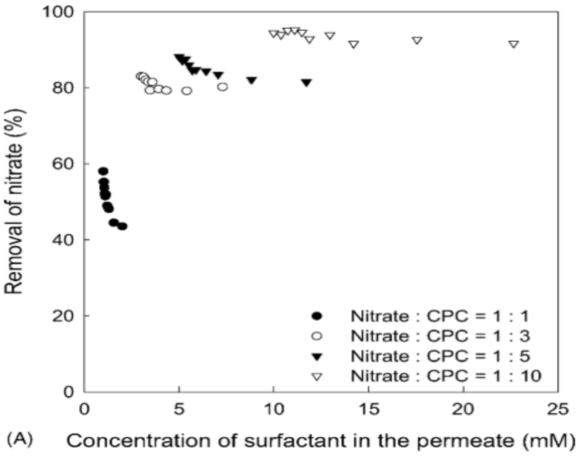
A Cross-flow micellar-enhanced ultrafiltration method is a type of separation technique which involves addition of surfactant to a polluted water bodies[21]. These leads to formation of micelles that contains a large number of molecules. For the removal of anionic pollutants like chromate and nitrate a cationic surfactant is used as these cationic micelles contains a high positive electrical potential on its surface where that contains charged hydrophilic group, where the cationic pollutants attach. On treatment using cross flow ultrafiltration unit with membrane of fine pore size(molecular weight cut-off of 8000) that helps to block the passage of micelles as shown below.[21]



Studies reported that the compounds having a higher valence inhibited the removal of compound having low valence[21] e.g. the compound ferricyanide having -3 valence caused the inhibition on removal of chromate with -2 valence.

Cetylpyridinium chloride also called as (CPD) was used as cationic surfactant. The preparation of feed was done by mixing CPC, nitrate and chromate in stoichiometric ratio as nitrate and chromate was employed in a co-existed manner. On feeding the tank with feed solution the permeate was sampled. The UV-VIS spectrophotometer was used for analysis of concentration at 258, 232,372 nm respectively and removal of these element was calculated. The removal of the nitrate and chromate are given in the figure





In a co-existd condition, chromate binds to CPC micelles preferentially to nitrate, as chromate has -2 valence is observed to bound to CPC micelles prior to -1 valence of nitrate. With increase in molar ratios of chromate and CPC the removal of chromate increased. At a higher molar concentration of 1:1:10 the removal of nitrate and chromate was 91% and greater than 97%. As this method includes usage of surfactant it is also important that surfactant is removed as it is also a pollutant.

CHITOSAN-ZIRCONIA MICROBALLS FOR PROFICIENT REMOVAL OF CHROMATE AND PHOSPHATE IONS FROM WATER BODIES

As seen in above case which involves surfactant which is also a contaminant, a method involving natural polymer (polysaccharide) has been developed such as chitin and chitosan found in the shells and skeleton of arthropods. Chitosan having a polycationic nature in acidic medium leads to adsorption of metal anions ,like chromate[22]. Zirconia-chitosan beads (Zr-CTB) were synthesized for detoxification of Chromate. These micro balls showed maximum removal capacities at pH=5. The experimental data fitted well with Langmuir adsorption isotherm model and followed pseudo-second-order kinetics and thermodynamics parameters confirmed that the process of adsorption was spontaneous[22].

SORPTION OF CHROMATE WITH OTHER INORGANIC ANIONS USING ORGANO-ZEOLITE

Sorption method showed significance removal of chromate by stable modified hexadecyltrimethyl ammonium (HDTMA)[23]. Since the large HDTMA was unable to enter the zeolite internal portion[23] sorption of amine on its external site was carried out. The efficiency of NaP1 zeolites was also evaluated for removal of heavy metals (Cr(III), Ni(II), Zn(II), Cu(II), and Cd(II)) from wastewater[24]

REMOVAL OF POLLUTANTS USING NANOMATERIALS

Different types of nanomaterials have been introduced for removal of heavy materials such as nanosorbants that include CNT's, zeolites and dendrimers. Metal based nanoparticle like TiO_2 provide better removal of heavy metals. A nanocomposite of TiO_2 anchored on graphene sheet helps to reduce Cr (VI) to Cr (III).[24] Palladium nanoparticles were also used for Cr treatment.

CONCLUSION

The discharge of effluents into various waterbodies has led to contamination of water to a large extent. The heavy metal contamination due to chromate has adverse health effect on human beings as well as plants. Cr (VI) is found to be more toxic than Cr (III). Therefore, there is a need of different methods for detection of these chromate anions. To reduce the adverse effect of Cr (VI) caused due to water contamination methods are developed which will help to detect the presence of these ions in water. Different methods include colorimetric method, spectrophotometric methods atomic absorption spectroscopy, ion chromatography, Raman spectroscopy etc. some methods show poor results due to interfering ions whereas some methos carryout detection by complex formation like in case of spectrophotometry where the plots of absorbance vs wavelength show detection of chromate in these methods. The optimisation of some parameters helps o obtained better results. The process of detection doesn’t put an end to these problems because there is need for the removal of these ions present in the water bodies. Along with detection method the method development also shows methods for removal of these chromate ions by using cross flow micellar ultra-filtration in which ions binds to surfactant like substances, as these surfactants acts like water pollutants Chitosan-Zirconia micro balls can be used as these are organic substances obtains from shells and exoskeletons of arthropods. Sorption and nanoparticles can also be used.

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“Thank You”

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