

**Sudan University of Science
and Technology , Faculty of science**



Department of chemistry

Preconcentration of trace heavy metals

Cr³⁺ and Cu²⁺ using natural clay

A thesis submitted in partial fulfillment of the requirement

of B.SC.(honor) degree in chemistry

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الآية

قال تعالى :

وَجَعَلْنَا مِنَ الْمَاءِ كُلَّ شَيْءٍ حَيٍّ

صدق الله العظيم
سورة الانبياء الآية (30)

Dedication

To

My

Family

Acknowledgement

I would like to express my deep thanks to Dr:Mutasimmaknoon ,department of chemistry ,sudan university of science and technology for his supervision ,guidance ,constructive criticism and changing my ideas through this research project .

My thanks are also to the family of Sudan University of science and technology.

Last, my deepest gratitude goes to my family and my friends for helping me in the difficult time of the research.

Abstract

This review gives some outlines of fundamental principles of adsorption and adsorption process.

Clay has a potential to adsorb heavy metal ions. A number of theoretical models and equations are available for the purpose and the best fit of the experimental data to any of these models is interpreted as giving the appropriate kinetics for the adsorption process.

In this research we tried to use the natural clay as an adsorbent to be applied for preconcentration of some heavy metals namely chromium and copper.

Most heavy metals are found in trace concentration in environment and very difficult to be detected by atomic absorption or other simple techniques ,so they need to be concentrated .

The results show chromium can be preconcentrated using this clay with high efficiency up to 96.1% while copper is 49% only

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Chapter one

Introduction

1.Introduction:-

The need for preconcentration of trace elements or ions in aqueous solution results from the fact that instrumental analytical methods often don't have the necessary selectivity, sensitivity, or freedom from matrix interferences.

Preconcentration occurs by reducing the volume by many methods e.g. evaporation, adsorption of heavy metals on active surfaces.

In a preconcentration procedure to adsorb Cu, Cr on the surface of clay. Many studies have been presented in the preconcentration of metals by dissolving the metal adsorbed with acid "nitric acid" and determining the metal concentration by atomic absorption spectrometry. These studies have examined the preconcentration of single elements such as Cu, Cr, and Cd.

Chapter two

Literature review

2.1 Chemistry of Chromium

2.1.1 The Metals:

At ordinary temperatures, Cr metal is resistant to chemical attack "Although it dissolves in dilute HCl and H₂SO₄".

Nitric acid renders Cr passive, and Cr is resistant to Alkalis.

At high temperature the metal is reactive. It combines with O₂ halogens and most other non-metals.

Borides, carbides and nitrides exist in various phases "e.g. CrN, Cr₂N, Cr₃N, Cr₃N₃" and are inert materials "e.g. CrN used in wear-resistant coating".

The black sulfides Cr₂S₃ is formed by direct combination⁽¹⁾ of the elements on heating.

The main oxidation states of chromium are +6, +3 and +2, a few compounds of Cr (V) and (IV) are known but are unstable with respect to disproportionation.

Chromium (0) is stabilized by π-acceptor ligands.

2.1.2 Chromium III:

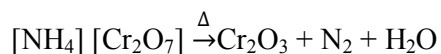
The "+3" oxidation state is the most stable for chromium in its compounds and octahedral coordination dominates for Cr "III" centers. Cr "III" complexes are generally kinetically inert.

Anhydrous CrCl₂ "red-violet solid m.p 1425K" is made from the metal and Cl₂ – and is converted to green CrF₃. Which is structural with VF₃ and CrCl₃ adopts a BiI₃ structure.

The dark green tri bromide and tri iodide can be prepared from Cr and the respective halogen and are iso structural with CrCl₃.

Chromium (III) fluoride is sparingly soluble and may be precipitated as the hexahydrate.

Chromium (III) oxide is made by combination of elements at high temperature by reduction of CrO₃. It has the corundum structure and is a semi-conducting and antiferromagnetic and is an important green pigment; the hydrate is used in paints. Cr III oxide prepared by the reactions:



When ignited it⁽²⁾ becomes inert towards both acid and bases, chromium (III) fluoride and chloride, made from Cr₂O₃ and hydrogen fluoride and from the metal and chlorine respectively, both contain octahedral coordinated Cr (III) in the same structures as the tri fluorides and tri chlorides of scandium, Ti, V, Chromium tri fluorides is only sparingly Soluble and may be precipitator as a hexahydrate, though at equilibrium very Soluble in mater, dissolve only very slowly.

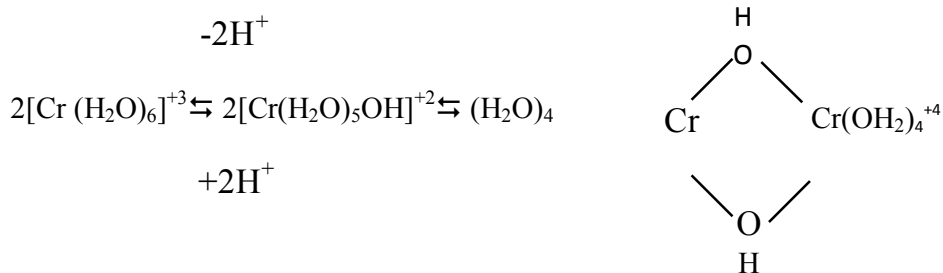
Large number of mononuclear octahedral Cr "III" complexes are known⁽¹⁾ with magnetic moments close to the spin-only value at 3.87 **μB**.

The electronic spectra at octahedral d³ complexes contain three absorptions due to d-d transitions.

Complex halides include [CrF₆]⁻³ and [CrCl₆]⁻³ and [CrCl₉]⁻³ have magnetic data are consistent with presence of three unpaired of electrons per Cr (III) Centre .i.e. no Cr-Cr Interaction.

Chromium (III) This is the most stable oxidation state of "Cr" and since, Cr (III) complexes are kinetically inter to substitution immense numbers of there are known. The hydrated [Cr(H₂O)₆]⁺³, which is pale violet in color, is obtained when dichromate is reduced by sculpture dioxide or by ethanol and sculptures acid below to C, a bore this temperature, the green sulphato complex [CrCd₂OI₅SO₄]⁺ is produced. The commonest salt containing thehexa aqua is chrome atom, KCr(SO₄)₂.12H₂O ordinary chromium (III) chloride is dark green trans [Cr (H₂O)₄Cl₂] Cl2H₂O from solutions of Cr(III) salts, alkali precipitates hydrous Cr₂O₃.

Which dissolves in excess forming [Cr(OH)₆]⁻³ ion, the aqua ions is quite⁽²⁾ acidic, and hydroxo bridged polymers are present in solution containing it e.g.



The presence of ammonia ammine complexes is slowly formal.

The dissolution process – may, however, be accelerated by addition at a trace of Chromium (II) chloride; the rapid redox reaction between Cr (III) in the lattice and Cr (II) in then followed by rapid substitution of chloride by water at the solid surface.

Complex halides of chromium (III) include salts containing $[\text{CrF}_6]^{-3}$, $[\text{CrCl}_6]^{-3}$ and $[\text{CrCl}_9]^{-3}$ ions. The last ion has a structure which consists of two CrCl_6 octahedral sharing a face.

There is no interaction between the Cr^{+3} ions. Each of which has a magnetic moment corresponding to the presence at the usual three unpaired electrons (in the analogous molybdenum and tungsten species, metal bond are formed).

The electronic spectra at Cr(III) complexes contain in three band due to d-d transitions; The reasons for this number of bands are exactly analogous to these given in the discussion of the spectra at V (III) complexes except that here we are dealing with two holes instead of two electrons, and the lowest energy state, corresponding to one electron in each of the t_2 orbitals, is the singly degenerate state 4A_2 , the transitions being to the three other possible quarter states (1).

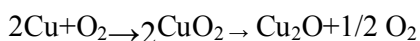
2.2 The Chemistry of Copper

2.2.1 The Metal:

Copper is the least reactive of the first row metals, it's not attack by non-oxidizing acid in the absence of air but It reacts with hot concentrated sulfuric acid and with HNO₃ at all concentration (1).

In the presence of air, Cu reacts with many dilute acids, and also dissolve in a aqueous [Cu(NH₃)₄]⁺² in unstable by relatively small margin with respect to Cu II and the metal.

Cu combines with O₂:-



Heating Cu with F₂, Cl₂ or Br₂ produces the corresponding di halide.

Copper (S) can be stabilized by the formation at an insoluble compound (e.g. CuCl)

Copper II:

Cupric is the old name for copper (II). Throughout (1)copper(II) chemistry. in black copper (II) oxide each copper atom has four oxygen in atoms in planar coordination and each oxygen atom four copper atoms in tetrahedral coordination, in this compound there are no other atoms in what might be considered a bonding distance from the copper atom. The atom insoluble blue hydroxide Cu(OH)₂ is readily dehydrated to the oxide, It's soluble not only in acids but also in concentrated aqueous alkalis, in which ill-defined hydrate Cu⁺² ion in solution is [Cu(H₂O)₆]⁺² with a distorted octahedral structure; This ion has been round in (NH₄)₂ [Cu(H₂O)](SO₄)₂ and [Cu(H₂O)₆](ClO₄)₂, though in each case there are three sets of Cu – OH₂ distances (cf. manganese tri /fluoride).

In the familiar blue sulphate CuSO₄ 5H₂O, planar [Cu₉(H₂O)₄]⁺² ions are present, the coordination at the copper is completed by two more distant oxygen atoms of sulphate ions, and the remaining water molecule is liked hydrogen bonding to both cation and anion. Dehydration yield the almost colorless anhydrous salt in which the coordination of the cation remains distorted octahedral, though in this case all the oxygen atom belong to anions.

Two other interesting copper (II) salts of OXO acids are the nitrate and the acetate. Anhydrous copper (II) nitrate cannot be obtained by dehydration of the interaction of the metal and dinitrogen tetroxide (as described in section 8-6) and decomposition of the compound

No[Cu(NO₃)₃] first produced. Copper (II) nitrate has a complicated layer structure in which nitrate ion bridge planar four – coordinated copper ions. With the usual two weak bonds to more distant oxygen atom, it volatilizes in vacuum at 150°c to give moleculeCu(NO₃)₂, in which two nitrate group both act as bidentate ligands copper (II) monohydrate in dimeric with a structure similar to that of chromium (II) acetate, but with a larger metal – metal separation of 2.64 Å, a magnetic moment of 1.4 MB per Cu⁺² ion suggested that the unpaired electrons and that little metal – metal interaction occurs.

When the Cu⁺² ion interacts with ammonia in aqueous solution no more than four NH₃ molecules replace coordination water, but [Cu(NH₃)₆]⁺² salts containing the distorted octahedral cation can be isolated from liquid ammonia [Cu(en)₃]⁺³ is formal is very concentrated aqueous ethylene diamine.

Large number of Cu complexes involving multidentate oxygen and nitrogen – containing ligands are known, their structures show that the discussion in this section has by no means covered all the stereochemical configuration found for copper (II) the deep blue aqueous solution of [Cu(NH₃)₄](OH)₂ has the remarkable property of dissolving cellulose and if the solution is squirted into acid one variety of artificial silk is produced, the solution is also used for coating canvas with a water tight coating of cell also When a copper (II) salt is treated with excess of potassium cyanide at ordinary temperature, cyanogen is evolved and complex cyanide of copper (I) is formed, a reaction similar to that which occurs with potassium iodide in aqueous methanol of low temperatures, however violet [Cu(CN)₄]⁻² can be characterized, its electronic spectrum is compatible with the expected planar structure

2.3 Adsorption:

Adsorption is a separation process in which certain components of the fluid phase are transferred to the surface of the solid adsorbents. When a solid surface is exposed to a fluid phase, the molecules from the bulk of the fluid phase have tendency to accumulate or concentrate at the surface of a solid.

The phenomenon of the enrichment of chemical substances at the ⁽³⁾ surface of a solid is called 'adsorption'. All adsorption performance processes are depends on solid-liquid equilibria and on mass transfer rates⁸. If the mass transfer is in opposite direction then it is called as 'Desorption

Most adsorbents are highly porous materials, and adsorption takes place primarily on the walls of the pores or at the specific sites inside the particles. separation occurs because differences in molecular weight, shape, or polarity cause some molecules to be held more strongly on the surface than others or because the pores are too small to admit the larger molecules. The overall rate of adsorption is controlled by the rate of diffusion of solute within the capillary pores of the adsorbent and varies with square root of the contact time with the adsorbent.

2.3.1 TYPES OF ADSORPTION :

At molecular level, adsorption is due to attractive interactions between a surface and the species being adsorbed

- Physical adsorption: It is a result of intermolecular forces of attraction between molecules of adsorbent and the adsorbate. In this case the molecular attractive forces that retain the adsorbent on the surface are purely physical are called Vander Walls forces. This is a readily reversible phenomenon. The energy of interaction between the adsorbate and adsorbent has the same order of magnitudes as, but is usually greater than the energy of condensation of the adsorptive.

Therefore, no activation energy is needed.

- Chemical adsorption: It is a result of chemical interaction between the solid and the adsorbed

substance. It is also called activated adsorption. It is irreversible. It is particularly important in catalysis. Therefore, the energy of chemisorption's considered like chemical reaction.

It may be exothermic or endothermic processes ranging from very small to very large magnitudes. The elementary step in chemisorption often involves large activation energy (Activated adsorption).

2.3.2 APPLICATION OF ADSORPTION:

Adsorption can be applied to both gaseous and liquid separations.

- Gaseous separations:

1. Removal of toxic gases and removal of objectionable⁽³⁾ odors from industrial gases for air pollution control and deodorization of air.
2. Recovery of valuable solvents vapors from dilute mixtures of air or other gases.
3. Fractionation of mixtures of hydrocarbon gases.

- Liquid separations:

1. Removal of moisture dissolved in gasoline.
2. Decolourization of petroleum products and aqueous sugar solutions.
3. Removal objectionable taste and odor from water.
4. Fractionating mixtures of aromatic and paraffin hydrocarbons.

- In the electrochemistry, molecules adsorbed to the surface of an electrode donate or accept electrons from the electrode

- Adsorption plays an important role in processes such as heterogeneous catalysis.

- Purification by adsorption is perhaps the oldest known application. Wine clarification is still accomplished by the use of adsorbents. Exhausts of industrial plants can be stripped off undesired components. .

2.3.3 Adsorption Kinetic:

A kinetics study was carried out to determine the equilibrium time required for the uptake of metals from a liquid solution. Both adsorption reaction model and adsorption diffusion model which are mathematical models can apply for kinetic adsorption

can A pseudo first order kinetics is present to describe the rate of adsorption process in liquid-solid phase. It be described as the following equation (3)

$$dq_t/dt = K_1 \times (q_e - q_t), \quad \dots (1)$$

Where K_1 (min^{-1}) is the pseudo first order adsorption rate coefficient. q_t and q_e is the mass of adsorbed of solute per unit mass of adsorbent at time, t and at equilibrium respectively. Integrated form of the eq. (1) for the boundary conditions of $t=0, q_t = 0$, and $t = t, q_t = q_t$.

$$\ln(q_e - q_t) = \ln q_e - K_1 t. \quad \dots (2)$$

The value of K_1 is obtained from the slope of the linear plot of $\ln(q_e - q_t)$ vs t .

Initial sorption rate for pseudo first order kinetic is expressed as

$$V_0 = K_1 \times q_e$$

A pseudo second order kinetics has been extensively used to obtain more reliable kinetic constants for heterogeneous adsorption of heavy metals.

$$dq/dt = K_2 \times (q_e - q)^2 \quad \dots (3)$$

Integrating equation (3) for the boundary conditions $t=0$ to t and $q=0$ to q gives:

$$1/(q_e - q) = 1/q_e + K_2 t \quad \dots (4)$$

When it linearized, it gives:

$$t/q = 1/K_2 q_e + t/q_e \quad \dots (5)$$

Initial sorption rate for pseudo second order kinetic is expressed as

$$V_0 = K_2 q_e \quad \dots (6)$$

V_0 ($\text{mg g}^{-1} \text{min}^{-1}$) is the initial sorption rate. V_0 and q_e values of the kinetic tests can be determined experimentally by plotting t versus t/q .

The pseudo second order kinetic rate constant (K_2) is expressed as a function of temperature.

When the flow of the reactants through the liquid film surrounding the adsorbent particles is the slowest process determining kinetics of the rate process, the liquid film diffusion model given by the simple relation

$$\ln(1-F) = -K_f t \quad \dots (7)$$

Where F is the fractional attainment of equilibrium (q/q_e) and K_f (min^{-1}) is the film diffusion rate coefficient. A linear plot of $-\ln(1-F)$ vs t with zero intercept suggest that the kinetics of the adsorption process is controlled by diffusion through the liquid film.

In many cases, intra-particle diffusion may control the rate⁽³⁾ of uptake of an adsorbate, which is represented by the following familiar expression

$$q_t / q_e = 1 - \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-n^2 \pi^2 D_c t / r^2) \quad \dots (8)$$

The ratio, q_t / q_e giving the fractional approach to equilibrium, D_c is intra-crystalline diffusivity, r is the particle radius, t is the reaction time and the summation is carried out from $n=1$ to ∞ .

The equation 8 can be rewritten in the form of

$$1 - q_t / q_e = 6/\pi^2 \exp(-\pi^2 D_c / r^2 t) \dots (9)$$

$$\ln(1 - q_t / q_e) = (-\pi^2 D_c / r^2) t + \ln(6/\pi^2) \dots (10)$$

Therefore, the plot of $\ln(1 - q_t / q_e)$ versus t should be linear with a slope of $(-\pi^2 D_c / r^2)$, which is known

as the diffusion time constant. The slope can be expressed as

$$K' = \pi^2 D_c / r^2$$

Where K' is the overall rate constant, inversely proportional to the square of the particle radius. Simpler expression to obtain the diffusion rate coefficient, K_i ,

$$q_t = K_i t^{0.5} \dots (11)$$

The significant feature of this expression is that the linear plots of q_t vs $t^{0.5}$ should pass through the origin.

2.3.4 Adsorption Isotherm:

:Equilibrium adsorption processes are described by isotherms governing the distribution of a given sorbate between liquid phase and the sorbent. Usually the amount adsorbed is only

a fraction of a monolayer. There are so many isotherms to describe the sorption are Langmuir, Freundlich, Redlich Peterson, Dubinin-Kaganer-Radushkevich (DKR), Tempkin and Sips isotherms^{15,16}.

- Langmuir isotherm assumes monolayer sorption onto a surface containing a finite number of identical sorption sites. If a site is occupied, no further sorption can take place at that site.

$$q_e = q_m K_L C_e / (1 + K_L C_e) \dots (12)$$

Where q_m is the amount of sorbate needed to form a complete⁽³⁾ monolayer per mass of sorbent in mg/g and K_L is the Langmuir equilibrium constant in l/mg which is related to the heat of adsorption by the equation. $K_L = K_o \exp q/RT \dots (13)$

The linear form of the Langmuir isotherm used was

$$C_e/q_e = C_e/q_m + 1/q_m \dots (14)$$

- Freundlich isotherm supposes that the ratio between the amount of adsorbed sorbate and the concentration of sorbate in the liquid phase is not a constant at different concentrations. It is used to describe adsorption in aqueous systems. The Freundlich isotherm is shown as the following equation 15

$$q_e = K_F C_e^{1/n} \quad \dots (15)$$

Where K_F is the adsorption equilibrium constant. The linear form of equation can be written as equation 16

$$\log q_e = \log K_F + 1/n \log C_e \quad \dots (16)$$

$1/n$ is the adsorption intensity. A plot of $\log q_e$ against $\log C_e$ gives straight line, the slope and intercept of which corresponds to $1/n$ and $\log K_F$.

- The Redlich-Peterson isotherm contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms. It can be described as following equation 17

$$q_e = A C_e / (1 + B C_e^g) \quad \dots (17)$$

The linear form of the above equation is as following equation 18

$$\ln(A C_e / q_e) = g \ln(C_e) + \ln(B) \quad \dots (18)$$

- The DKR isotherm is reported to be more general than the Langmuir and Freundlich isotherms. It helps to determine the apparent energy of adsorption. The characteristic porosity of adsorbent toward the adsorbate and does not assume a homogeneous surface or constant sorption potential.

The Dubinin-Kaganer-Radushkevich (DKR) has the linear form as following equation 19

$$\ln q_e = \ln X_m - \beta \epsilon^2 \quad \dots (19)$$

Where X_m is the maximum sorption capacity, β is the activity coefficient related to mean sorption energy, and ϵ is the Polanyi potential, which is equal to

$$\epsilon = RT \ln(1 + 1/C_e) \quad \dots (20)$$

Where R is the gas constant. The slope of the plot of $\ln q_e$ versus ϵ^2 gives β and intercept yields the sorption capacity, X_m . The values of β and X_m as a function of temperature.

- Tempkin isotherm assumes that the heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbent-adsorbate interaction and the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy.

Tempkin model is expressed as

$$q_e = (RT/bT) \ln(A C_e) \quad \dots (21)$$

Where $RT/bT = B$, which is the Tempkin constant related to heat of sorption whereas A is the equilibrium binding constant corresponding to the maximum binding energy, R is the universal gas

constant and T is the absolute solution temperature. A plot of $q_{eq}/\ln C_e$ gives a linear graph with B as a slope and $B(\ln AT)$ as the intercept.

2.3.5 Adsorbate:

A substance that has been or is to be adsorbed on a surface .

2.3,6 Adsorbent:

A material on which adsorption can occur

2.3.7 clay:

Chemical Properties of Clay:

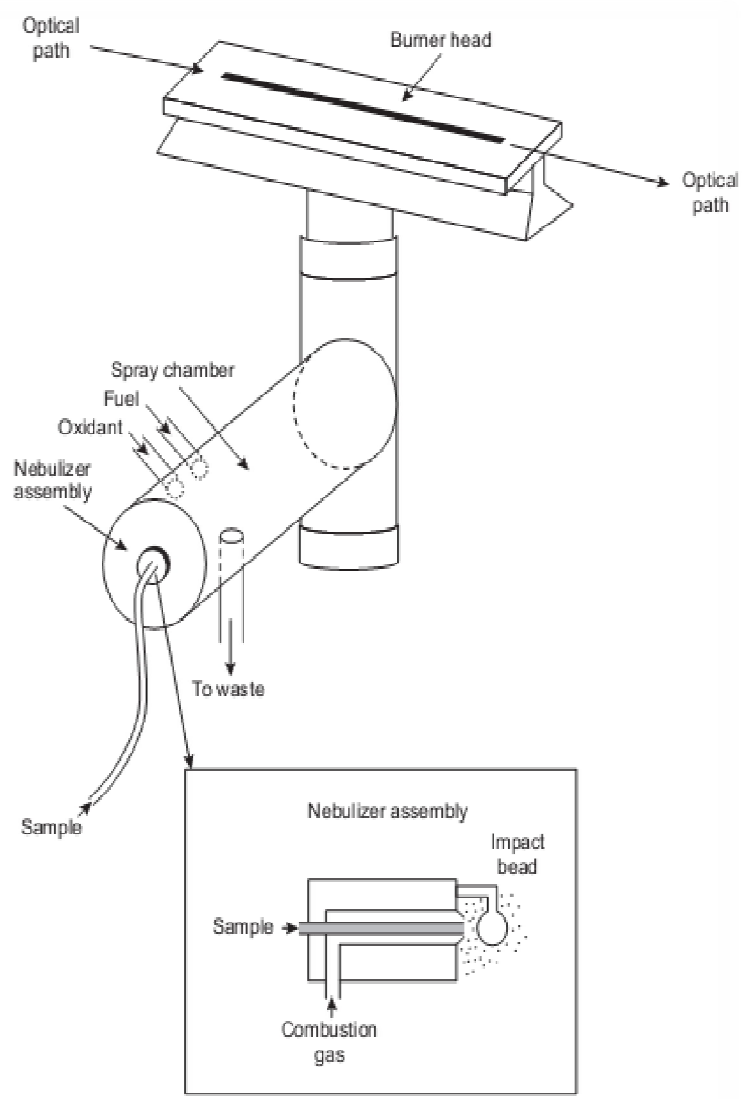
Chemically the clay is a highly polar, reactive system. Although it's polar nature stems in considerable measure from its large surface per unit of weight polarity.

The clay fraction of the soil and in particular the kind and amount of the respective clay minerals present, determines in large measure the chemical and physical properties (5)

Atomic Absorption Spectroscopy (AAS):

Atomic absorption is the process that occurs when a ground-state atom absorbs energy in the form of electromagnetic radiation at a specific wavelength and is elevated to an excited state. The atomic absorption spectrum of an element consists of a series of resonance lines, all originating with the ground electronic state and terminating in various excited states. Usually the transition between the ground state and the first excited state is the line with the strongest absorptivity, and it is the line usually used. Transitions between the ground state and excited states occur only when the incident radiation from a source is exactly equal to the frequency of a specific transition. Part of the energy of the incident radiation P_0 is absorbed. The transmitted radiation P is given by $P = P_0 e^{-(Kvb)}$ where k_v is the absorption coefficient of the analyse element and b is the horizontal path length of the radiation through the flame. Atomic absorption is determined by the difference in radiant power of the resonance line in the presence and absence of analyse atoms in the flame. The width of the line emitted by the light source must be smaller than the width of the absorption line of the analyse in the flame. The amount of energy absorbed from a beam of radiation at the wavelength of a resonance line will increase as the number of atoms of the selected element in the light path increases.⁽⁴⁾

The relationship between the amount of light absorbed and the concentration of the analyse present in standards can be determined. Unknown concentrations in samples are determined by comparing the amount of radiation they absorb to the radiation absorbed by standards. Instrument readouts can be calibrated to display sample concentrations directly. Atomic absorption spectrophotometers are designed using either the single-beam or double-beam optics described earlier for molecular absorption spectrophotometers.⁽⁴⁾



flameatomizer

Chapter three

Materials and Methods

3.1 Materials:-

Natural clay:

This clay was collected from jabal Um Ali in NahrElnil state

3.2 Chemicals:-

1-copper sulphate pentahydrate

($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, M.W 249.68, LOBA cheminc, Mumbai India)

2-chromium chloride hexahydrate

($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, M.W 266.45, Certified Company, India)

3-Nitric acid 1M

3.3 Glass ware:-

Volumetric flask, beakers, pipette, funnels, conical flask,

3.4 Instruments:-

1-Atomic absorption spectrometer

2-Magnetic stirrer

3.5 Methods:

3.5.1 Preparation of clay as adsorbent

The clay was grinded using mortar and sieved with 500 and 600 micron mesh .This clay was stored in glass bottles for further use.

3.5.2 Preparation of standard solution of Cu^{2+} :

10ppm of Cu^{2+} was prepared by dissolving 0.0098g of copper sulphate pentahydrate in water and the volume was completed to 250 ml in volumetric flask (sample 1).

3.5.3 Preparation of standard solution of Cr^{3+} :

10ppm of Cr^{3+} was prepared by dissolving 0.0128g of chromium chloride hexahydrate in water and the volume was completed to 250 ml in volumetric flask (sample 1).

3.5.4 Adsorption of Cu^{2+} by the natural clay:

100 ml of standard solution of Cu^{2+} (10ppm) were added to 5.00g of clay .The mixture was stirred with magnetic stirrer for 20 minutes. The clay was filtered and the filtrate was transferred to plastic container and recorded sample (2). The residue of the clay on the filter paper was kept for desorption step.

3.5.5 Desorption of Cu^{2+} the clay:

The clay on the filter paper was washed with 20ml nitric acid 1M and the volume was completed to 25ml and transferred to a clean plastic container and recorded sample(3)

The concentration of three samples determined using atomic absorption spectrometer.

3.5.6 Adsorption of Cr^{3+} :

100 ml of standard solution of Cr^{3+} (10ppm) were added to 5.00g of clay .The mixture was stirred with magnetic stirrer for 20 minutes. The clay was filtered and the filtrate was transferred to plastic container and recorded sample (2). The residue of the clay on the filter paper was kept for desorption step.

3.5.7 Desorption of Cr^{3+} by the natural clay:

The clay on the filter paper was washed with 20ml nitric acid 1M and the volume was completed to 25ml and transferred to a clean plastic container and recorded sample(3)

The concentration of three samples determined using atomic absorption spectrometer.

Chapter four

Result and discussion

Table (4.1):**3.2.1 Preconcentration of Cu²⁺:-**

Initial concentration (ppm)	Concentration after adsorption (ppm)	Chromium adsorbed	Amount of chromium adsorbed	% removal
8.663	4.417	4.246	4.246 *100/1000 =0.4246mg	0.4246/0.8663*100 =49%

Table (4.2)**3.2.2 Preconcentration of Cr³⁺ :-.**

Initial concentration (ppm)	Concentration after adsorption (ppm)	Chromium adsorbed	Amount of chromium adsorbed	% removal
3.0824	.1188	2.9636	2.9636 *100/1000 =0.29636 mg	0.29636/0.30824*100 =96.1%

Discussion:

From the result chromium has high affinity towards this clay. It can be adsorbed and removed from the solution depending on time of contact between the metal ion and active surface of clay.

Results show chromium is adsorbed more on this clay compared to copper which gives less percentage.

The results show that desorption of the adsorbed heavy metal ions is also possible by using nitric acid.

The adsorbed chromium and copper can be desorbed completely and the results gave 102% and 71% desorption respectively.

Chapter five

Conclusion

Conclusion:

Trace heavy metals can be determined by preconcentrated the solution using natural clay

The parameters, such as adsorbent size, adsorbent dosage, contact time, agitation speed and pH are influenced on adsorption.

Generally, percent adsorption increases with increasing adsorbent dose, contact time and agitation speed. However, favorable conditions may be varied for different materials.

This clay can used to remove heavy metals from waste water.

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