

Application of Silica-Chromium Oxide Composite for the Sorption of Toxic Metals from Aqueous Stream

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Abstract

A simple solid-phase synthesis method was optimized for the synthesis of silica-chromium oxide composite particles for the efficient separation of toxic metal ions from the aqueous streams. The sorption capacity of different toxic metal ions followed the trend: $Al^{3+} > Zn^{2+} > Ga^{3+} > Fe^{3+} > Bi^{3+} > Pb^{2+} > In^{3+} > Cd^{2+} > Ag^{+} > Ba^{2+}$. The sorption followed Lagergren 1st order kinetics, while different isotherm models were employed to understand the sorption mechanism. The sorption was found to proceed via physisorption. The stability of the sorbent in presence of long time contact of aqueous stream was also evaluated and was found to be satisfactory.

Keywords — Silica-Chromium Oxide Composite, toxic metals, isotherm, 1st order kinetics

I. INTRODUCTION

Man's direct intervention in natural processes has resulted in imbalance in ecosystems [1-2]. Reckless use of natural resources for urbanization is polluting environment to such a level that now human existence is questioned. Although, industrialization after 1800s has changed the face of human lifestyle from manual to machine but on the dark side has resulted in deterioration in living quality [3-5]. Irrational growth for human comfort is continuously degrading water and air standards.

Groundwater and water in fresh water bodies make roughly 0.7 % of total water to be accessible for human consumption. All living beings require ions for a sound metabolism and water is the best source [6-7]. According to Bertrand's rule, if the concentration of an essential metal ion is not an optimum value then it is toxic. Metals like Fe, Cu, Co, Zn, Ca, Ni, Mn are micro-nutrients and are required for proper biological functioning, but at higher concentrations are known to cause health disorders [8-10]. Metals like Al, Cd, Pb, Ag, Tl, Bi, Ba, Ga, and In do not have any biological role to play other than causing disorders and ailments [11, 12]. Presence of Na, K is highly desirable, but metal ions like Hg, Pb, Co, As, Ni, Fe, Zn, Cd, Cu above their permissible limits make water unsuitable for common use [13-16]. In last few decades, a rapid decrease in water quality has been recorded due to direct disposal of industrial effluents in rivers and lakes. Heavy metal contaminants exist in waste

streams of many industries, such as tanneries, mining, metal plating, dye and paints and petro based industries. Even the soil surrounding military bases and these industries are contaminated and pose a serious threat to groundwater and surface water. The presence of toxic metals in drinking water even at very low level can be lethal to human beings. Since toxic metals are non-degradable, they can accumulate in living bodies and can amplify concentration through food chain which can cause various ailments and disorders. The presence of heavy metals in natural or industrial wastewater and their potential impact on living species has been a subject of research in environmental science for a long time [17-20].

Removal of toxic metals from industrial waste streams can be achieved by various conventional techniques like ion-exchange, chemical precipitation, electrochemical separation, membrane filtration etc [21-25]. But these techniques are either expensive or comes with secondary issues like formation of toxic sludge, high energy requirements. In recent years, efforts are being made towards finding a better method of treating industrial waste and adsorption has shown promising results. This particular method has shown high efficacy where cheaper, readily available and environmentally benign sorbents are being used. Activated carbon, biomass, farm wastes, zeolites etc. are all effective towards waste water treatment [26, 27].

Previous reported works have proven silica as a good sorbent for heavy metal removal [28]. In our previous study on the sorption of Th^{4+} onto metal oxide (Chromium oxide, Iron oxide, and Vanadium oxide) impregnated silica composite have shown high sorption performance compared to that of silica. Among the three metal oxide composites, Chromium oxide impregnated silica composite was found to be the most effective one. On the same line, sorption performance of chromium oxide impregnated silica composites can be explored for the removal of heavy metals from industrial effluents.

II. EXPERIMENTAL

Reagents and Instruments

Extra pure sodium silicate solution containing 25 % SiO_2 (density 1.37 g mL^{-1} , pH 12.1) was procured from LobaChemie, Mumbai, India. Chromium nitrate was procured from Triveni Aromatics and Perfumery

Private Limited, Gujrat, India. The synthesis and characterization of the chromium oxide impregnated silica has been reported in our previous work. Standard solution for all the elements were prepared from the CentiPUR @ ICP Multi Standard solutions (E-Merck, Darmstadt, Germany). Suprapur @ HNO₃ (E-Merck, Darmstadt, Germany) and deionized water were used throughout the experiment. Merck solutions are basically mixture of defined concentration of metal ion solution in nitrate form. The analyses were performed using Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) procured from Spectro ARCOS, Germany.

The synthesis and the characterization of Silica-Chromium Oxide Composite particles for the sorption and its characterization was reported earlier. **Fig. 1** is summarizing the synthesis step in a simplified form. Transparent solution of Cr(NO₃)₃·9H₂O was prepared by dissolving 5 g of nitrate solution in distilled water. 3 g of this 1.195 mmol g⁻¹ solution was used to obtain slurry by mixing 6 g of sodium silicate containing 25 wt% of SiO₂. This slurry was stirred well to get the gel and it was dried subsequently. It was washed with distilled water. Finally, it was dried to have 2g product.

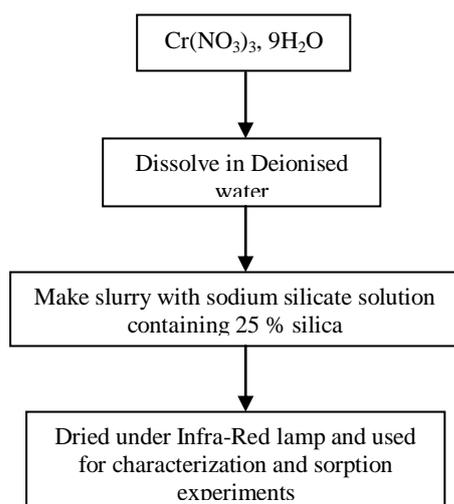


Fig. 1: The simplified synthetic scheme for Silica-Chromium Oxide Composite

X-ray diffraction plot, showed peaks due to Cr₂O₃ indicating a high degree of purity with hexagonal structure, which is similar to that observed in our previous investigation [28] and hence did not show in the present case. SEM image showed highly rough surface of the particles. More the roughness of the surface, more will be the effective area for interaction with the metal ions present in the aqueous system. The contact angle is the measure of hydrophilicity of the materials. It gives an idea about the interaction of the materials with the water. If the material is hydrophobic in nature, it may not be suitable for the aqueous ion to interact with it. Therefore, the contact angle of the sorbent was measured. The contact angle

for the sorbent was found to be 72°. This indicates the sorbent is hydrophilic in nature. The Cr=O bonds are polar and the π electron cloud is denser over oxygen atom. Consequently, it leads to dipole moment within the molecule and makes it hydrophilic in nature. The zeta potential was found to be negative at higher acidity. With increase in acidity, the zeta potential was found to go towards the positive value. Beyond 0.3 M HNO₃, the zeta potential was found to show reverse trend. Therefore, it is expected that, the interaction of sorbent particle with the positively charged metal ion should be minimum in the acidity range 0.01 M to 1 M.

A known amount (~50 mg) of homogenized Cr₂O₃-silica was taken in an equilibration tube with 10 mL of aqueous solution in required acidity having 100 μg mL⁻¹ of metal ion concentration. It was equilibrated in a shaker at the speed of 100 rpm for defined amount of equilibration time. Then the system was centrifuged and allowed to settle for 10 min. Then suitable amount of aliquot was taken out and was fed in to plasma for the analysis. The K_d values were determined as follows: [29]

$$K_d = \frac{(C_0 - C) V}{C m} \quad (1)$$

Where, C₀ is the initial concentration of metal ion (mg L⁻¹), C is the concentration after the equilibration (mg L⁻¹), V is the volume of the aqueous solution (mL), and m is the mass of the Cr₂O₃-silica (mg). All the experiments were carried out in triplicate and the results were found satisfactory.

III. RESULTS AND DISCUSSION

Fig. 2 is presenting the K_d values for Al³⁺, Ag⁺, Ba²⁺, Bi³⁺, Cd²⁺, Co²⁺, Cu²⁺, Fe³⁺, Ga³⁺, In³⁺, Mn²⁺, Ni²⁺, Pb²⁺, Tl³⁺ and Zn²⁺ at pH 3 (0.001 M HNO₃) using chromium oxide impregnated silica and only silica particles. Though, the silica as a sorbent showed high extraction efficiency for these metal ions, yet not much selectivity was observed. The impregnation of chromium oxide layer on the silica surface was found to improve the extraction efficiency almost an order of magnitude than the base silica. Moreover, a selectivity in sorption efficiency was also noticed. This improvement in performance certainly is desirable for bulk operation. With the increase in HNO₃ concentration, the K_d values for all the metal ions were found to decrease abruptly up to pH 1. After 0.1 M HNO₃ concentration, a gradual increase in the K_d value was observed for almost every metal ion. The trend in K_d values as a function of aqueous feed acidity was found to be based on the surface charge on the sorbent. At higher and lower acidity, the negatively charged sorbent interacts favorably to enhance the K_d values for the positively charged metal ion, while in the acidity range 0.01 M to 1M, the reduction in negative charge on the surface results the reduction in the K_d values. The size for Al³⁺, Ga³⁺, Fe³⁺ and Zn²⁺ are 53 pm, 62 pm, 60 pm and 74 pm,

respectively. Due to the smaller size, their chemical potentials, which is governed by mainly charge to size ratio are also found to be large. More the chemical potential, more will be the interaction with the sorbent materials and hence they can have higher affinity towards sorbent. Moreover, higher chemical potential also leads to higher hydration number of these metal ions. Consequently, the interaction between the metal ions and the sorbent can lead to release of the water molecules due to formation of inner sphere complex. More release in water molecules to the system enhances the overall entropy of the system and ultimately contributes to Gibb's free energy to be more negative and hence more spontaneous.

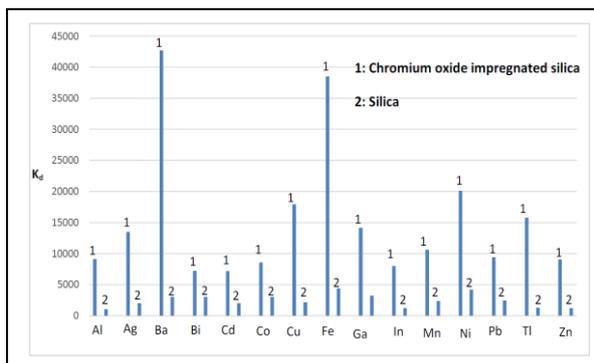


Fig. 2: The extent of sorption of different metal ions at pH 3 using chromium oxide impregnated silica and base silica

Sorption kinetic study

Different mechanisms like mass transfer, chemical reactions, and particle diffusion control sorption kinetics. The fractional attainment of the equilibrium (F) can be expressed as [30]

$$F = \frac{C_t}{C_{te}} \quad (2)$$

where C_t is the M^{n+} concentration onto Cr_2O_3 -silica at time 't', C_{te} is the M^{n+} concentration to Cr_2O_3 -silica at equilibrium. The plots of (1-F) as a function of equilibration time for different metalions have been shown in Fig. 3. For metal ions other than Cd^{2+} , Mn^{2+} , Zn^{2+} , and Ni^{2+} , sorption equilibrium was achieved in 2 hour of contact time. In order to understand the kinetic characteristics of metal ion sorption onto Cr_2O_3 -silica composite, the experimental data was fitted to Lagergren's first order kinetic model. Parameters involved in kinetic model have been tabulated in Table I. Lagergren suggested a rate equation for the sorption of sorbate from a liquid solution onto solid sorbent and can be expressed mathematically as [31]

$$\log(q_e - q) = \log q_e - \frac{k_{ads}t}{2.303} \quad (3)$$

where, q is the M^{n+} concentration onto Cr_2O_3 -silica composite at time 't', q_e is the M^{n+} concentration onto Cr_2O_3 -silica composite at equilibrium condition, and k_{ads} is the first order rate constant (min^{-1}). Plots of

$\log(q_e - q)$ versus 't' give a straight line. From the slope and intercept, k_{ads} and q_e values can be calculated. The K_{ads} values were in 0.018-0.072 min^{-1} range for all the metal ions and followed the trend: $Mn^{2+} < Ni^{2+} < Tl^{3+} < Bi^{3+} \sim Ba^{2+} < Zn^{2+} < Cd^{2+} \sim Ag^+ < In^{3+} < Pb^{2+} < Al^{3+} < Co^{2+} < Ga^{3+} < Fe^{3+} < Cu^{2+}$. The q_e values were in the order: $Ga^{3+} < Fe^{3+} < Pb^+ < Bi^{3+} < Mn^{2+} < Ni^{2+} < In^{3+} < Ba^{2+} < Tl^{2+} < Ag^+ < Zn^{2+} < Cd^{2+} < Cu^{2+} < Al^{3+} < Co^{2+}$.

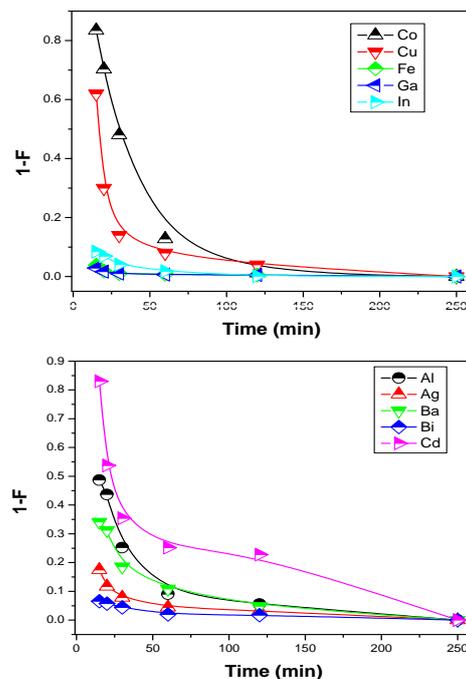


Fig. 3: Extraction kinetics of metal ions

Sorption Isotherm

To understand the process involved in the sorption of metal ions onto Cr_2O_3 -silica composite, experimental data were fitted to isotherm models. Parameters involved in isotherm models were calculated to know about the surface properties and affinity at fixed temperature and pH. In present investigation, Langmuir, Freundlich, Dubinin–Radushkevich (D–R) and Temkin isotherm models have been studied and parameters along with linear regression values for all four isotherm models have been summarized in Table II. Different isotherm model is based on different assumptions and hence associated with different sorption mechanism. The data pertaining to the sorption in the present investigation were tried to fit in different linear equation from different models. The fitting parameter, i.e. the regression coefficient indicates the extent of fitting. If the experimental data showed good fitting for a particular isotherm model, it is concluded the sorption proceeds predominately based on the mechanism associated with that model. The assumptions considered to obtain the linear equation holds good for the present process. Similar

approaches were seen in literature in order to understand the sorption mechanism [32-34]

Table I: Parameters for Lagergren plots

Metal ion	K_{ads} (min ⁻¹)	q_e	χ^2
Cd ²⁺	0.033	331.08	0.91811
Bi ³⁺	0.026	95.37	0.99997
Ba ²⁺	0.026	134.08	0.92123
Ag ⁺	0.033	227.98	0.94261
Al ³⁺	0.038	811.86	0.98761
Zn ²⁺	0.029	230.45	0.95789
Tl ²⁺	0.025	201.27	0.90803
Pb ²⁺	0.036	86.51	0.91721
Ni ²⁺	0.019	125.38	0.83436
Mn ²⁺	0.018	114.06	0.66137
In ³⁺	0.034	128.54	0.96652
Ga ³⁺	0.055	54.94	0.98418
Fe ³⁺	0.062	73.72	0.96691
Cu ²⁺	0.072	717.55	0.97411
Co ²⁺	0.042	975.82	0.99754

Langmuir isotherm model

This isotherm models the monolayer sorption occurring on a structurally homogeneous sorbent where all the sorption sites are energetically identical. It can be expressed as [35, 36]

$$\frac{C_e}{q_e} = \frac{1}{q_0 b} + \frac{C_e}{q_0} \tag{4}$$

where, C_e (mg L⁻¹) is the equilibrium concentration of Mⁿ⁺ ion, q_e (mg g⁻¹) is the amount of Mⁿ⁺ sorbed on to Cr₂O₃-silica composite at equilibrium, q_0 (mg g⁻¹) is the sorption capacity of Cr₂O₃-silica composite for Mⁿ⁺ ion, and b (L mg⁻¹) is the Langmuir isotherm constant.

Freundlich isotherm model

The multilayer sorption process onto heterogeneous surface with uniform energy can be best explain by this model and can be expressed mathematically as [37, 38]

$$q_e = K_f C_e^{\frac{1}{n}} \tag{5}$$

$$\log q_e = \log K_f + 1/n \log C_e \tag{6}$$

where, q_e (mg g⁻¹) is the amount of Mⁿ⁺ ions sorbed per gram of the Cr₂O₃-silica composite at equilibrium condition, K_f (mg^{1-(1/n)} L^{1/n} g⁻¹) is the Freundlich isotherm constant, C_e (mg^{1/n} L^{-1/n})is the equilibrium concentration of Mⁿ⁺, and n is the sorption intensity. K_f is an indication of the relative sorption capacity of the Cr₂O₃-silica composite and $1/n$ is the indication of the intensity of sorption process.

Table II (a): The analytical results for Langmuir isotherm model

Metal ion	q_0 (mg g ⁻¹)	b (L mg ⁻¹)	χ^2
Ag ⁺	71.43	0.129	0.96255
Al ³⁺	566.49	0.534	0.98331
Ba ²⁺	59.02	0.156	0.79308
In ³⁺	111.52	0.186	0.96488
Mn ²⁺	38.54	0.137	0.95565
Cu ²⁺	16.20	0.123	0.95688
Fe ³⁺	380.54	0.411	0.93989
Ga ³⁺	404.96	0.520	0.90687
Ni ²⁺	5.08	0.112	0.93934
Pb ²⁺	255.23	0.302	0.93901
Bi ³⁺	371.79	0.289	0.99768
Cd ²⁺	98.63	0.186	0.96765
Co ²⁺	4.79	0.113	0.94351

Table II (b): The analytical results for D-R isotherm model

Metal ion	X_m (mg g ⁻¹)	E (kJ mol ⁻¹)	χ^2
Al ³⁺	618.26	1.32	0.98914
Ag ⁺	78.08	5.11	0.95897
Ba ²⁺	41.11	2.35	0.57026
Co ²⁺	4.47	0.92	0.95417
Cu ²⁺	13.01	1.30	0.94807
Fe ³⁺	320.01	3.44	0.96311
Ga ³⁺	378.45	3.63	0.92070
In ³⁺	116.41	2.30	0.98455
Mn ²⁺	27.08	1.84	0.96044
Ni ²⁺	8.74	0.97	0.97648
Pb ²⁺	265.28	2.95	0.94193
Cd ²⁺	114.52	2.95	0.98621
Zn ²⁺	583.03	0.88	0.94562

Dubinin–Radushkevich (D–R) isotherm model

It is an analogue of Langmuir model but it does not consider the homogeneity of surface or a constant sorption potential. Mean free energy of the sorption process can be estimated by this model. It is expressed as [39-40]

$$\ln q_e = \ln X_m - \beta \varepsilon^2 \tag{7}$$

where, q_e is the amount of Mⁿ⁺ ions sorbed onto Cr₂O₃-silica composite at equilibrium, X_m is the maximum sorption capacity, and β is the activity constant. The Polyani potential, ε can be evaluated by

$$\varepsilon = RT \ln(1 + 1/C_e) \tag{8}$$

where, R is the universal gas constant (8.314 J mol⁻¹ K⁻¹), T (K) is the absolute temperature, and C_e is the equilibrium concentration of Mⁿ⁺ ions. The energy (E)

can be determined from β , slope of the $\ln q_e$ vs. ε^2 plot, expressed as,

$$E = 1/(-2\beta)^{1/2} \quad (9)$$

The mean free energy of sorption is an outcome of sorbate-sorbent interaction. E values lesser than 8 kJ mol⁻¹ results from physical interaction in the sorption process.

Table II (c): The analytical results for Tempkin isotherm model

metal ion	b (kJ mol ⁻¹)	A_T (L mg ⁻¹)	χ^2
Ag ⁺	-7.63	0.79	0.95871
Ba ²⁺	-2.61	0.66	0.86377
Bi ³⁺	-8.33	0.87	0.58898
Cu ²⁺	-2.17	0.65	0.95090
Cd ²⁺	-6.85	0.71	0.92482
Co ²⁺	-1.77	0.65	0.90925
Fe ³⁺	-4.00	0.72	0.97247
Ga ³⁺	-4.39	0.72	0.9014
In ³⁺	-2.35	0.66	0.89536
Mn ²⁺	-3.74	0.67	0.9478
Ni ²⁺	-2.09	0.65	0.90395
Pb ²⁺	-3.22	0.69	0.90234
Zn ²⁺	-1.72	0.65	0.91258

Table II (d): The analytical results for Freundlich isotherm model

Metal ion	n	K_f (mg g ⁻¹)	χ^2
Al ³⁺	0.077	689.81	0.93603
Ag ⁺	1.585	75.41	0.70223
Ba ²⁺	0.180	43.31	0.76364
Cd ²⁺	0.675	13.54	0.92097
Co ²⁺	0.064	4.02	0.95287
Cu ²⁺	0.129	13.98	0.94722
Fe ³⁺	1.277	289.05	0.92055
Ga ³⁺	1.403	357.92	0.95728
In ³⁺	0.439	114.14	0.98403
Mn ²⁺	0.285	40.39	0.96721
Ni ²⁺	0.070	6.71	0.97600
Pb ²⁺	0.841	275.48	0.91736
Zn ²⁺	0.058	481.04	0.97668

Temkin Isotherm model

This model can be applied for estimation of sorption heat. It considers the effect of some indirect sorbate-sorbent interactions on sorption isotherms and because of these interactions, heat of sorption decreases linearly rather than logarithm with increasing coverage. It can be expressed as [41-43]

$$q_\varepsilon = \frac{RT}{b} \ln(A_T C_\varepsilon) \quad (10)$$

$$q_\varepsilon = \frac{RT}{b} \ln A_T + \frac{RT}{b} \ln C_\varepsilon \quad (11)$$

where, A_T (L g⁻¹) is the Temkin isotherm equilibrium binding constant, b (kJ mol⁻¹) is the Temkin isotherm constant which is the variation of adsorption energy, R is the universal gas constant (8.314 J mol⁻¹ K⁻¹) and T (K) is the absolute temperature. The linear regression analysis revealed that the nature of interaction of metal ions with the sorbent particles are different. Ag⁺, Ba²⁺, Cu²⁺, Bi³⁺ were found to follow Langmuir isotherm, while Al³⁺, In³⁺, Fe³⁺, Ni²⁺, Pb²⁺, Cd²⁺ and Co²⁺ followed D-R isotherm model. On the other hand, Mn²⁺, Ga³⁺ and Zn²⁺ were found to follow Freundlich isotherm. The lower sorption energy evaluated by D-R isotherm revealed the physi-sorption nature of the process. The sorption efficiency for the metal ions were found to follow the trend: Al³⁺ > Zn²⁺ > Ga³⁺ > Fe³⁺ > Bi³⁺ > Pb²⁺ > In³⁺ > Cd²⁺ > Ag⁺ > Ba²⁺. There is almost negligible sorption was observed for the metal ion Cu²⁺, Ni²⁺ and Co²⁺. The 1/n values from Freundlich isotherm were found to be more than 1 for most of the metal ions, revealing the predominance of physi-sorption with cooperative mechanism.

Stability of the sorbent

The stability of the sorbent was evaluated by equilibrating the sorbent (10 g) with aqueous medium (100 mL, 3 M HNO₃) and monitoring the concentration of Cr and Si at different time interval using inductively coupled plasma atomic emission spectrometry.

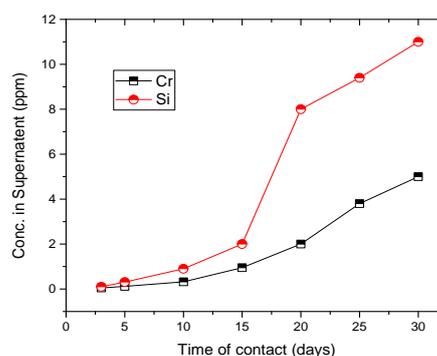


Fig. 4: The stability of the sorbent in presence of aqueous media

The study revealed that after 5 days of continuous equilibration, only 0.12 ppm of Cr and 0.31 ppm of Si were found to present in the raffinate. After a continuous equilibration upto 30 days, 5 ppm of Cr and 11 ppm of Si were found to be present in the supernatant. This investigation revealed that, the sorbent is quite stable in processing aqueous stream. **Fig. 4** is showing the ICP-AES results for the stability test of the sorbent

IV CONCLUSION

Simple method has been utilized for the synthesis of Silica-chromium oxide composite particle. The sorbent was found to be highly useful in separation of different toxic metal ions from the aqueous stream. The sorption capacity was found to follow the order $Al^{3+} > Zn^{2+} > Ga^{3+} > Fe^{3+} > Bi^{3+} > Pb^{2+} > In^{3+} > Cd^{2+} > Ag^{+} > Ba^{2+}$. Lagergren first order kinetics model was applied for the analysis of the sorption kinetics. The rate constant for the sorption was found to follow the order: $Mn^{2+} < Ni^{2+} < Ti^{3+} < Bi^{3+} \sim Ba^{2+} < Zn^{2+} < Cd^{2+} \sim Ag^{+} < In^{3+} < Pb^{2+} < Al^{3+} < Co^{2+} < Ga^{3+} < Fe^{3+} < Cu^{2+}$. Ag^{+} , Ba^{2+} , Cu^{2+} , Bi^{3+} were found to follow Langmuir isotherm, whereas Al^{3+} , In^{3+} , Fe^{3+} , Ni^{2+} , Pb^{2+} , Cd^{2+} and Co^{2+} were found to follow D-R isotherm model. Mn^{2+} , Ga^{3+} and Zn^{2+} followed Freundlich isotherm. Physi-sorption was found to be responsible for the high uptake of these metal ions. The sorbent was also found to be stable for longer time of equilibration.

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