

Research Article

Aniline/Cupric Ion Complex on Silica Surface: Synthesis, Characterization and Analytical Application

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Abstract

Aniline / cupric ion solid phase complex has been synthesized through three steps process: (i) functionalize the silica gel by silane coupling agent, (ii) immobilization of the functionalized silica gel (FSG) with aniline, (iii) coordination of the immobilized product with cupric ion. The synthesized organic-inorganic hybrid material is characterized by chemical, FTIR and TGA techniques. The anion selectivity, ion exchange capacity and

metal ion binding capacity of the product has been evaluated with a view to explore the analytical applicability. The role of cupric ion has been studied in improving analytical aspect of well known aniline / silica composite. The formation of aniline / cupric ion complex both in presence and absence of silica have been evaluated in terms of cyclic voltammetry.

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Introduction

In the past few years, silica gel (SG) is immobilized with aniline moieties to use it as solid adsorbent or stationary phase in different type of chromatographic techniques for the removal and recovery of heavy metal ions from aqueous solution [1-8]. An improved technique for the immobilization of aniline on to silica surface has reported recently by S. P. Bayen and P. Chowdhury [6]. Literature survey reveals that the major problems associated with the removal of metal ions by the aniline / silica systems are mainly due to low selectivity, poor anion exchange capacity, narrow pH range and slow kinetics.

There are numerous publications [9-13] related to complexes between aniline and first row of transition metals. Labanowska et al. [14] investigated the electron paramagnetic resonance of ammonia and aniline copper (II) complexes, $\text{CuCl}_2(\text{aniline})_2$, which remains as distorted octahedron in solution. But in the solid phase, the complex has infinite chains with two halides bridges between adjacent copper atoms. Two neutral polar ligand (aniline) remains in axial position above and below each copper atom [15]. Heller and Yariv [16] found that aniline forms complexes with transition metal ions in the clay minerals interlayer by the coordination of free electron like montmorillonite (belong to the group of layer silicates) pair of the amino group to the metal ions. Cocq et al. [17] investigated the reaction of aniline with copper (II) compounds in relation to the formation of copper-polyaniline composites. As per literature searched so far there are no reports regarding aniline /cupric ion solid phase complex.

In the present study, we have immobilized silica gel with aniline through functionalization the former by (3-chloropropyl) trimethoxysilane (3-CPTS) through new green and facile technique and then coordinated it with cupric ion ($\text{FSG@ANI} \rightarrow \text{Cu}^{2+}$) for the study of analytical aspect.

Nomenclature

FSG: Functionalized silica gel

FSG@ANI: Aniline immobilization onto functionalized silica gel

FSG@ANI→CuCl₂: Aniline /cupric ion solid phase complex

Experimental

Materials and Reagents

Aniline (Merck, Mumbai, India) was purified by distillation over zinc dust. Anhydrous Copper chloride (Glaxo, Mumbai, India), 3-CTPS (97%) (Sigma, St. Louis, MO, USA), Toluene (Merck, Mumbai, India), Diethylether (Merck, Mumbai, India), Silica gel (60-120 mesh, Merck, Mumbai, India) were used as received. Potassium dichromate (Pfizer Ltd., Mumbai, India) was used for the preparation of stock solution of Cr (VI) (200 mg L⁻¹). All the working solutions were prepared by proper dilution of the stock solution with double distilled water. 1,5 diphenyl carbazide used for spectrophotometric estimation of Cr(VI), was of analytical grade (Merck, Mumbai, India). Methylene blue stain (Merck, Mumbai, India) was used to determine the specific surface area of FSG@ANI and FSG@ANI→CuCl₂ ion solid phase complex.

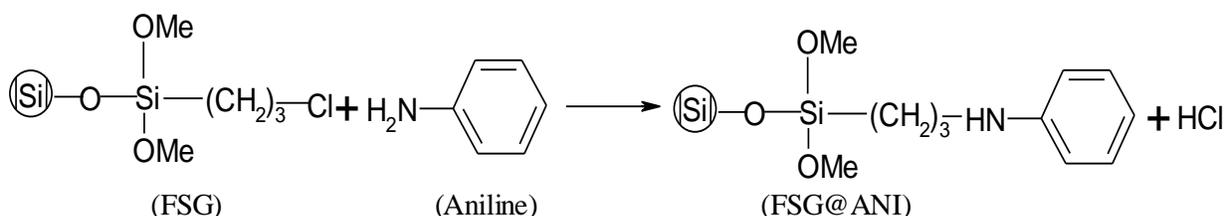
Instruments

UV-VIS-NIR spectrophotometer (Shimadzu Model UV-PC) was used for the analysis of chromate ion from aqueous solution. The Fourier Transform Infrared (FTIR) was recorded using KBr pellets by Shimadzu-8400S spectrometer. Thermo-Gravimetric Analysis (TGA) was done using a Pyris Diamond TG/DTA (Perkin Elmer) thermal analyzer in nitrogen atmosphere at a heating rate of 20°C min⁻¹. Cyclic voltammogram (CV) was taken by Versa StatTM II (Princeton Applied Research). The magnetic susceptibility measurement was carried out using the Sherwood Scientific Balance, Cambridge, UK. An ELICO made pH meter (Model LI120) was used for the pH measurement.

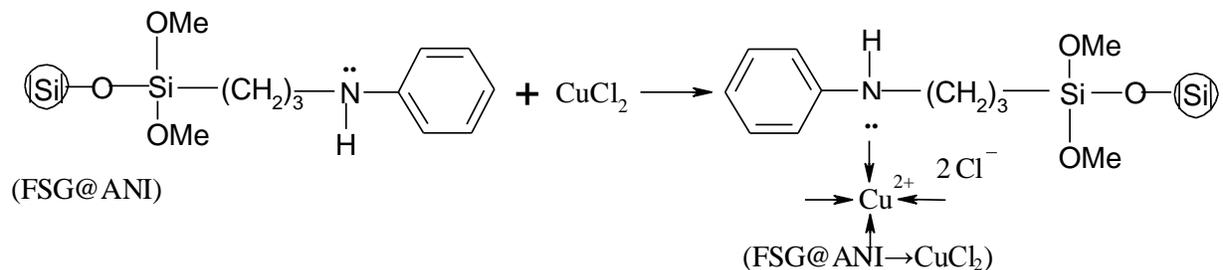
Synthesis of aniline / cupric ion solid phase complex

Synthesis of aniline/cupric ion solid phase complex material was carried out in three steps; viz. functionalizing of SG (FSG), immobilization of the functionalized SG with aniline (FSG@ANI), (**Scheme 1**) and then coordinated with CuCl₂ (**Scheme 2**). The first two steps (functionalizing of SG and immobilization of the functionalized SG with aniline) that the detail procedure is given in our previous work (S. P. Bayen and P. Chowdhury [6]).

In the last step, took anhydrous CuCl₂ (0.144 g, i.e., 1 m mol) and FSG@ANI (0.196 mL of aniline, i.e., 2 m mol which was previously immobilized onto FSG) in the ethanol solution and stirred continuously for about 2 h at room temperature. Then obtained black color material was filtered, washed with ethanol and dried at under vacuum condition for 4 h. Finally, we got the aniline/cupric ion complex (FSG@ANI→CuCl₂) (**Scheme 2**). The CuCl₂·2 (aniline) complexes were prepared other researchers in solution [9-14].



Scheme 1 Immobilization of aniline onto functionalized silica gel



Scheme 2 Synthesis of aniline / cupric ion solid phase complex

Cyclic voltammetry

The working electrode was prepared by pasting a mixture of functionalized silica gel containing aniline/cupric ion solid phase complex (FSG@ANI→CuCl₂) with conducting additive carbon black, graphite powder (10:1:1) in nafion binder on carbon felt and cyclic voltammogram was taken in 0.5 M KCl solution using Pt counter and Saturated Calomel Electrode (SCE) as reference electrode respectively at the scan rate of 5 mV s⁻¹ from potential range +0.7 Volt to -0.7 Volt.

Determination of ion exchange capacity

Ion exchange capacity was determined by Volhard's method [18]. The measured amount synthesized material (FSG@ANI→CuCl₂) was taken into 10 mL 1.5 (N) HNO₃ and stirred well. Excess amount of 0.1 (N) AgNO₃ (10 mL) was added to it. The residual silver nitrate was determined by a standard 0.1 (N) ammonium thiocyanate using ferric alum indicator. From the consumed silver nitrate solution, the exchangeable chloride ion was calculated using the relationship:

$$1.0 \text{ mL } 1 \text{ (N) AgNO}_3 \equiv 0.0355 \text{ g exchanged Cl} \quad (1)$$

Selectivity test

Chromate ion selectivity of the material with respect to high concentration of sulfate (competitive anion) was performed at pH 1-5 at 27±1°C. The FSG@ANI→CuCl₂ material was suspended (0.2 g) in the solution containing chromate and high concentration of competitive anion (400 fold molar excess of sulfate compared to chromate). The mixture was then shaken well for 1 hour to reach the equilibrium. The selectivity (S) is defined as:

$$S = q/q_0 \quad (2)$$

Where q = chromate binding capacity (mg g⁻¹) in presence of competitive anion; q_0 = chromate binding capacity (mg g⁻¹) in absence of competitive anion. The chromate binding capacity (mg g⁻¹) was measured as reported earlier by S. P. Bayen and P. Chowdhury [6].

Study of Cr (VI) binding capacity

Cr (VI) binding ability of the synthesized novel material was studied by batch method. To determine the amount of Cr (VI) bound, 0.15 g sorbent (FSG@ANI→CuCl₂) was taken in a conical flask. Then 20 mL sorbate solution containing chromate ion at different pH was mixed and stirred. The initial concentration of Cr (VI) was kept to 5-100 mg L⁻¹. After suitable time interval, the adsorbent was filtered and the residual solution was analyzed for Cr (VI) ions spectroscopically. Amount of chromate extracted was calculated using the relationship:

$$q_t = (W_f - W_i)/M \quad (3)$$

Here q_t is the amount of Cr (VI) adsorbed per unit mass of adsorbent (mg g^{-1}). W_i and W_f are the initial and residual amount (mg) of Cr (VI) respectively. M is the mass (g) of the adsorbent added. Batch adsorption tests were carried out by mechanical agitation (agitation speed: 90-100 rpm) at room temperature. The pH of the solution was maintained to 2.0 and 9.5. The pH of the system was adjusted using acetic buffer and ammonium chloride-ammonia buffer. The analysis was repeated at least thrice to determine the uncertainties values.

Results and discussion

FTIR analysis:

Immobilization of aniline onto functionalized silica gel was confirmed by the FTIR spectrum of FSG-ANI (**Figure 1 (a)**). The spectrum showed the characteristic peaks at 3429, 1502, 1230, and 795 cm^{-1} , which were absent in the spectra of both SG and FSG. The peaks at 3429, 1502, 1230 and 794 cm^{-1} may be assigned to N-H stretching, benzene ring vibration, C-N stretching and N-H bending respectively [19]. The characteristic new peaks thus provided to strong evidence of aniline immobilization on FSG.

The displacement of all the peaks (FSG@ANI) to a larger wave numbers can be observed for the FSG@ANI \rightarrow CuCl₂ (**Figure 1 (b)**) complex and the chromate loaded copper complex (FSG@ANI \rightarrow Cu (Cr₂O₇/CrO₄)) (**Figure 1 (c)**), due to the Cu (II)-N coordination. The wave number increases according to the force of interaction with the metallic ion observed by Santana et al. [20]. This is indicated that the coordination of the nitrogen center with cupric ion (FSG@ANI \rightarrow CuCl₂). This was further confirmed by the appearance of a new peak at 482 cm^{-1} in the spectrum of FSG@ANI \rightarrow CuCl₂ (**Figure 1(b)**). The new peak was very probably due to Cu (II)-N coordination in the copper complex [21].

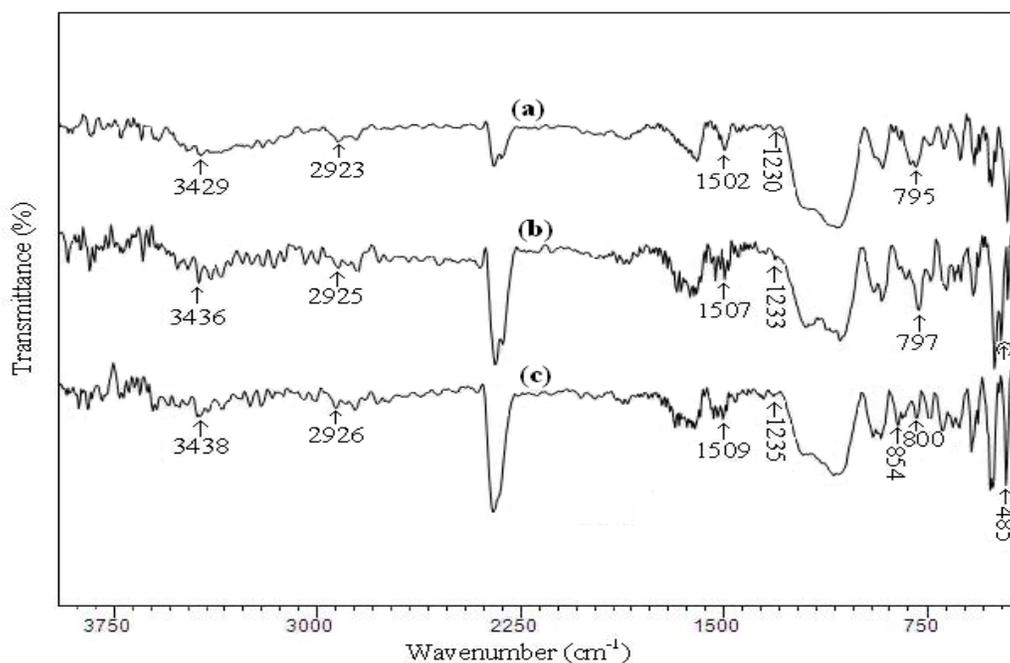


Figure 1 FTIR spectra of (a) FSG@ANI (b) FSG@ANI \rightarrow CuCl₂ and (c) FSG@ANI \rightarrow Cu (Cr₂O₇/CrO₄)

A comparison between the spectrum of copper complex and chromate loaded copper complex shows that a new peak at 854 cm^{-1} appears in the spectrum of chromate loaded copper complex but the peak is absent in the spectrum of copper complex. The peak at 854 cm^{-1} due to Cr=O bond [21]. Thus the spectral comparison suggests the replacement of the chloride ion by chromate ion.

Role of Cu^{2+} on the Physico-chemical and thermal properties

Surface area, ion exchange capacity, bulk density and zero point charge of the developed material (FSG@ANI \rightarrow CuCl₂) were evaluated following the procedure as described earlier by P. Chowdhury et al. [22] and the results were presented in **Table 1**. The exchange capacity of the synthesized material changes remarkably due to the presence of cupric ion, because it has counter anion (chloride) which is exchangeable. It is noteworthy to mention here that the Chromate binding capacity (mg g^{-1}) (at trace level of chromium), Rate constant, Chromate selectivity, pH range for chromium binding, Thermal stability and Redox property discuss later systematically. The Magnetic susceptibility data shows that the material (FSG@ANI \rightarrow CuCl₂) was diamagnetism because it has contained the less amount of cupric ion.

Table 1 Comparison of some physical and chemical properties of FSG@ANI and FSG@ANI \rightarrow CuCl₂

| Materials / Properties | FSG@ANI | FSG@ANI \rightarrow CuCl ₂ | Measurement method |
|--|--------------------------|---|---------------------------|
| Composition (weight %) | FSG=0.1564 ANI=0.1341 | FSG=0.1564 ANI= 0.1341 CuCl ₂ =0.058 | TGA analysis |
| Surface area ($\text{m}^2\text{ g}^{-1}$) | 63.94 | 72.46 | Methylene blue adsorption |
| Ion exchange capacity ($\text{meq. Cl}^{-1}\text{ g}^{-1}$) | Nil | 1.55 | Volhard's method |
| Bulk density (g mL^{-1}) | 1.11 | 1.23 | Specific gravity bottle |
| Zero point charge | 6 | 8 | Chromate titration |
| Chromate binding capacity (mg g^{-1}) (trace level of chromium) | 0.4 | 23.3 | Batch method |
| Rate constant ($\text{mg g}^{-1}\text{ min}^{-1}$) (Pseudo second order) | Nil | 12.9×10^{-2} | Batch method |
| Chromate selectivity | Nil | Positive | Batch method |
| pH range for chromium binding | Nil | 1 to 2 & 6 to 9.5 | Batch method |
| Thermal stability | More | Less | TGA analysis |
| Redox property | Nil | Positive | Cyclic voltammetry |
| Magnetic property | Diamagnetism | Diamagnetism | Magnetic susceptibility |

TGA analysis

The TGA tracing of four samples, FSG, FSG@ANI, FSG@ANI→CuCl₂ and FSG@ANI→Cu (Cr₂O₇ / CrO₄) are shown in **Figure 2**. In the temperature zone 45-100°C, FSG undergoes 1.780% weight loss, while the immobilized FSG's (FSG@ANI, FSG@ANI→CuCl₂ and FSG@ANI→Cu (Cr₂O₇ / CrO₄)) were 1.601, 1.524 and 4.040% respectively. The first step (45-100°C) weight loss is due to loss of loosely bound moisture as revealed from DTA data (S. P. Bayen and P. Chowdhury [6]) (sharp endothermic peak around 85°C for all the samples). Thus it may be inferred that the FSG's derivatives contain less amount of moisture after immobilization. FSG loses 0.648% weight in the temperature region 100-280°C, while other samples lose more than that. The more weight loss within 100-280°C is mainly due to evaporation of chemically bound aniline (**Scheme 1**). On the other hand, FSG@ANI→CuCl₂ has loses more (2.123%) weight loss within this temperature region. This observation may be explained on the basis of complex formation. Aniline coordinated with the cupric ion in the material FSG@ANI and formed FSG@ANI→CuCl₂ (**Scheme 2**).

However, again a comparison of the weight loss in the region 280-700°C reveals that immobilized FSG's (FSG@ANI, FSG@ANI→CuCl₂ and FSG@ANI→Cu (Cr₂O₇ / CrO₄)) suffers more weight loss compared to FSG. But it was evident that the product FSG@ANI showed better thermal stability than FSG (the former undergoes less weight loss than later). FSG contains covalent chlorine, which is probably responsible for its relatively higher weight loss in this region. Thus, the greater weight loss in the region 280-700°C is due to evaporation of aniline and chlorine for the materials FSG@ANI→CuCl₂ and FSG@ANI→Cu (Cr₂O₇ / CrO₄). The coordination renders the materials (FSG@ANI→CuCl₂) less thermally stable, the degradation temperatures being dependent on the anion, with a more significant variation for the materials with the chloride ion investigated by Santana et al. [20]. The sample, FSG@ANI→Cu (Cr₂O₇ / CrO₄) undergoes more amount of total weight loss (14.532%) than that of other materials during heating up to 700°C. The result suggests that the potential oxidant chromate ion may leads to oxidative polymerization to some extent.

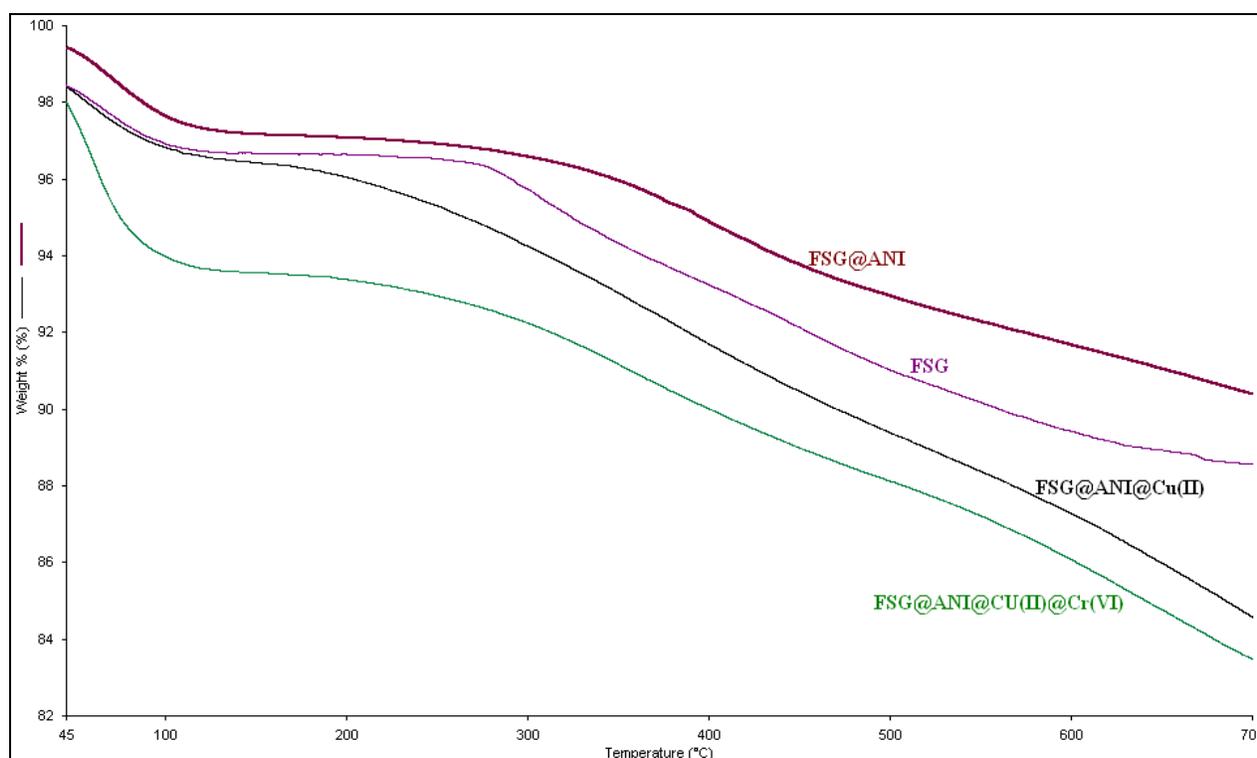


Figure 2 TGA curves of FSG, FSG@ANI, FSG@ANI→CuCl₂ and FSG@ANI→Cu (Cr₂O₇ / CrO₄)

Cyclic voltammogram

Figure 3(a) shows a complete cyclic voltammogram of functionalized silica gel containing aniline/cupric ion solid phase complex (FSG@ANI→CuCl₂). The voltammogram shows two distinct separate steps. The step (I) corresponds to the Cu(II)/Cu(I) redox couple having cathodic and anodic peak potentials at $E_{pc(I)} = +0.16$ V and $E_{pa(I)} = +0.23$ V (with respect to SCE) respectively. The $\Delta E_{p(I)}$ value (07mV) clearly indicates a quasi-reversible behavior of the system. Similarly the step (II) corresponds to the Cu (I)/Cu (0) redox couple (cathodic peak potentials, $E_{pc(II)} = -0.35$ V vs SCE, anodic peak potentials, $E_{pa(II)} = -0.15$ V vs SCE, and $\Delta E_{p(II)} = 20$ mV). The results are compared with that of well known aniline / cupric ion complex (studied Pollet et al. [23]) in absence of silica (**Figure 3(b)**). A close result with respect to peak potentials has been observed. Thus cyclic voltammetry confirms the formation aniline / cupric ion complex on the silica surface.

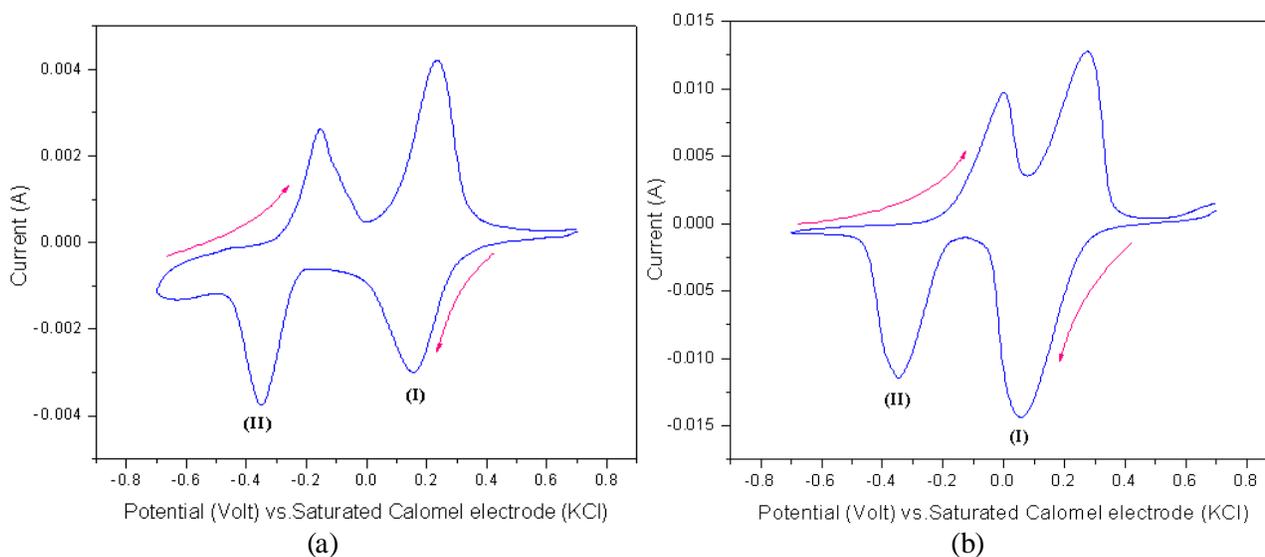


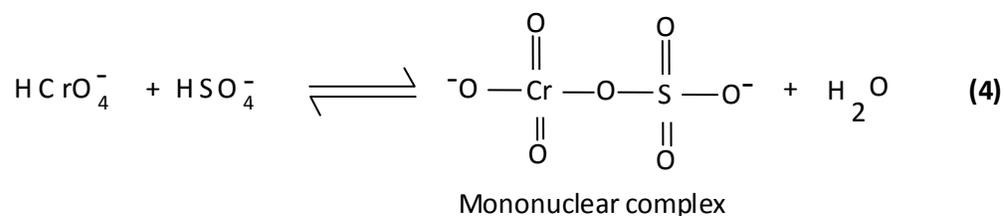
Figure 3 Cyclic voltammogram of (a) FSG@ANI→CuCl₂ and (b) CuCl₂·2(aniline) in 0.5M KCl solution vs. SCE at the scan rate of 5 mV s⁻¹

Selective binding of chromate in competitive condition

The selectivity value was found to be 0.87 with respect to sulfate in the pH range 1-5. The results suggest that the material is highly selective toward chromate. The order of selectivity was $\text{CrO}_4^{2-} > \text{SO}_4^{2-}$. However, the commercially available anion exchanger showed Dreesa et al. [24] the reversal order as: $\text{SO}_4^{2-} > \text{CrO}_4^{2-}$.

The selectivity order may be explained on the basis of aqueous chemistry of chromate. Chromate remains as dichromate (dimer) in acidic medium. The size and structure of dichromate are suitable for electrostatic attraction with the FSG@ANI→CuCl₂. Dimerization of sulfate did not occur at low level of sulfate ion. Thus, at low level of sulfate, degree of anionic polymerization played an important role in anion selectivity.

However, at very high concentration of sulfate (400 fold molar excess of sulfate compared to chromate), the aqueous chemistry of chromate differs studied by P. Chowdhury et al. [22]. In this condition, probably a mononuclear Cr(VI) complex (Eq.4) was formed. The complex has similar in size with dichromate. As a result, it is likely to be present in the solid phase through electrostatic interaction. Hence, only after complete capture of the complex, the diverse anion sulfate passed onto solid phase. Thus, at high level of sulfate, mononuclear complex formation directed the selectivity order.



Effect of pH on Cr (VI) binding capacity

The Cr (VI) binding capacity (**Figure 4**) of the prepared material (FSG@ANI→CuCl₂) increased from pH 1 to 2 and then decreased gradually up to pH 6. Then it again increased up to pH 9.5. This type of behavior is unlike to common exchangers. The figure suggest that the synthesized material functions well both in acid and basic mediums, and water may acts as good eluting agent. The observed pH dependent behavior of Cr (VI) binding may be explained with the help of aqueous chemistry of Cr (VI) and ion exchange mechanism (Eq.5). At very low pH (<1), the chromate remains mainly as non-ionic form (H₂CrO₄), which accounts for its low binding capacity. With the increase of pH from 1 to 2, the Cr (VI) remains mainly as dichromate (Cr₂O₇²⁻), which attributes higher binding capacity through electro static attraction. Dichromate is converted into monomeric hydro chromate (HCrO₄⁻) within the pH 2-6. The decreasing negative charge is responsible for its low capacity in this region. Hydro chromate changes to chromate (CrO₄²⁻) beyond pH 6. The double negative charge results into higher attraction between sorbate and sorbent. The aniline immobilized silica gel (FSG@ANI) (without cupric ion) has little chromate binding capacity. The appearance of chloride and disappearance of chromate (Cr₂O₇²⁻ and CrO₄²⁻) in the aqueous phase was tested by qualitative analysis same phenomena was observed P. Chowdhury et al. [22]. Thus the chemical analysis supports the ion exchange mechanism (Eq.5).

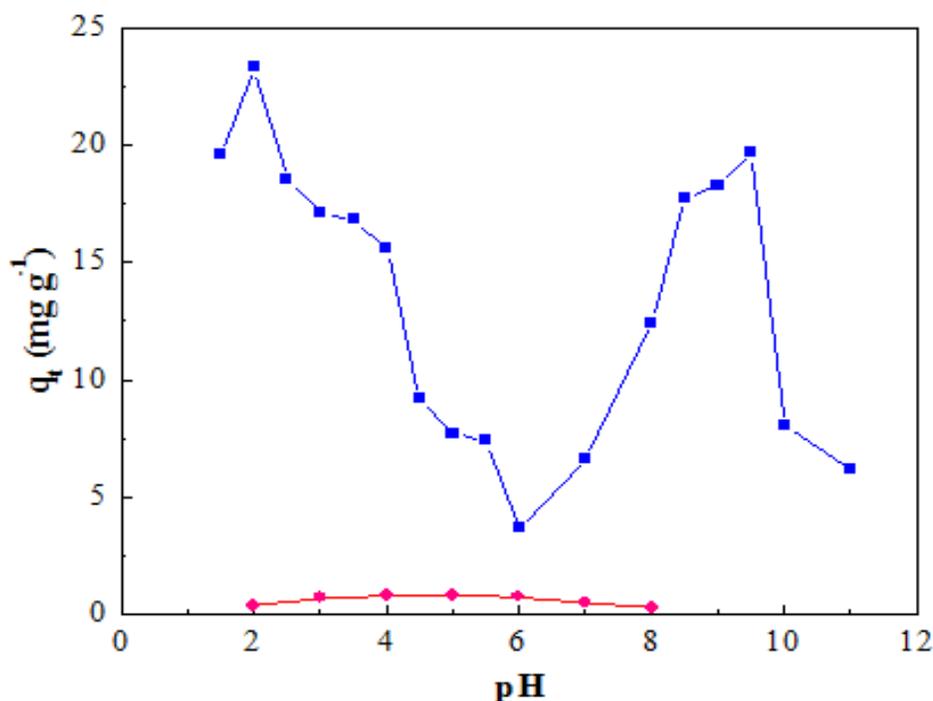


Figure 4 Variation of binding capacity (q_t) with pH
 —■—: FSG@ANI→CuCl₂; —●—: FSG@ANI
 [Adsorbent = 7.5 g L⁻¹, C₀ = 50 mg L⁻¹, Temperature = 27±1°C, Time = 1 h]

The high anion exchange capacity (1.55 meq Cl/g) of prepared material favors its high chromate binding capacity. The chromate binding capacity of the material was found to be 23.3 mg g⁻¹, which is higher than the commercially available exchangers like Amberlite IRA 743 has been studied Gandhi et al. [25], Lewatit M 62 and Lewatit MP 610 observed by F. Gode and E. Pehlivan [26].



Conclusions

A new organic-inorganic hybrid material based on coordination of cupric ion with immobilized aniline has been synthesized. Coordination of cupric ion with immobilized aniline (FSG@ANI) improve its surface area, ion exchange capacity, bulk density, zero point charge chromate binding capacity, metal ion binding rate, selectivity and redox properties.

The synthesized material functions well both in acid and basic mediums, which are usually found in tannery effluent and electroplating waste respectively. So the material is suitable for removal and recovery of Cr (VI) in these industries.

The chromate binding capacity was found to be 23.3 mg g⁻¹ (at trace level of chromium), which is higher than the commercially available exchanger. Thus the material has immense analytical aspect.

The present work reveals that immobilized of aniline on to silica nano particles followed by coordination of copper sulfate (CuSO₄) may leads to many agricultural application, because the bonded CuSO₄ is not readily washed out by rain.

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