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EFFECT OF VARIOUS IONIC SALTS ON THE ADSORPTION OF CR(VI) USING HUMIC ACID AS AN ADSORBENT

Erol PEHLIVAN[1*], Şerife PARLAYICI[1], Masood HUSSAIN[2, 3], Ahmet AVCI[3]

[1] Selcuk University, Department of Chemical Engineering, Konya, Turkey

[2] National Centre of Excellence in Analytical Chemistry Sindh University, Jamshoro, Pakistan

[3] Selcuk University, Department of Mechanical Engineering, Konya, Turkey

Corresponding Author:

Erol Pehlivan
Selcuk University
Department of Chemical Engineering,
42079 Konya, Turkey

Phone : + 90 332 22321287
e-mail : erolpehlivan@gmail.com

ABSTRACT

Humic acids are a principal component of humic substances, which are the major constituents of soil (humas), peat and coal. It is a complex mixture of many different acids containing carboxyl and phenolate groups so that the mixture behaves functionally as a dibasic acid or, occasionally, as a tribasic acid.

Humic acid (HA) was tested in the aqueous medium to remove hexavalent chromium Cr(VI) during this study. The extent of adsorption of Cr(VI) on the surface of HA was examined on the basis of increasing quantity of humic acid. An ionic interference study was also performed in order to check the effect of various ionic salts on the adsorption process. Various salts of calcium chloride ($CaCl_2$), potassium chloride (KCl) and sodium chloride (NaCl) were tested on the adsorption of Cr(VI) while using humic acid as an adsorbent. Interactions between HA and Cr(VI) were confirmed by using Fourier transform infrared (FTIR) spectroscopy. Further characterization was also performed using UV-Visible spectroscopy and Scanning Electron Microscopy (SEM) analysis.

Keywords: Humic acid, Peat, Ionic interference, Characterization, Adsorbent

INTRODUCTION

Cr(VI) is one of the major pollutants which can contribute a huge burden on the environment and affect aquatic life [1]. Cr(VI) mostly existed in the form of CrO_4^{2-} and $Cr_2O_7^{2-}$ and considered as persistent organic pollutant [2]. Cr(VI) is a major component in soil and groundwater excreted from various industries such as wood preserving, electroplating, pigment production and chrome tannery industries [3,4]. It is a carcinogenic and refractory pollutant having huge environmental toxic effects [5].
When it enters into the blood it can create various diseases and also affect liver, kidneys and red blood cells by several oxidative processes [6,7]. In additions to human beings it can also affect plants life such as mutagenesis inhibiting, enzymatic processes and reduction in yields [1]. By considering all these parameters researchers divert their mind towards transport bioavailability and adsorption of Cr(VI) in water and soil [4,8].
Humic acids are the major components of the sediments and soils containing several functionalities such as phenyl, carboxyl, and phenolic hydroxyl and control the natural environments through various geometrical, physical and oxidative processes by using the functionalities [9-11]. In this regards several studies have been conducted to elaborate the various binding of humic functionalities with various toxic pollutants such as pesticides, organic pollutants and metal ions [12-16]. The literature showed many studies have been done on binding interactions of humic substances with Cr(VI) by using voltammetry techniques, UV-vis spectroscopy, and X-ray absorption. These results indicated the existence of Cr(VI) in soil and groundwater. Ohta et al. reported the interactions of humic acid with Cr(VI) using X-ray absorption[17]. Reductive properties of humic acid and oxidative behaviour of Cr(VI) attracted the attention of scientists towards the adsorption of Cr(VI) easily by using humic substances[18-21]. The reduction phenomena of Cr(VI) mostly affected by various parameters such as soil pH, sunlight, Fe (II) contents, organic matters and various dissolved sulphides. The previous studies investigated that Cr(VI) have a long lifetime when it has been adsorbed in the soil. The binding capabilities of humic acid with Cr(VI) are correlated with the reduction of Cr(VI) using humic acid as an adsorbent.
The undertaken study first time elaborates the binding capabilities of Humic acid with Cr(VI) and explains the effects of various ionic salts on the adsorption phenomena as well as interactions of humic functionalities with Cr(VI).

MATERIALS AND METHODS

Materials

HA was purchased from Shanghai Jufeng Company (BR, China). KCl, NaCl, and $CaCl_2$ were all of the high quality and analytic were obtained from Sigma-Aldrich. Deionized water has been used during all experimentation. Humic Acid (HA) solution was prepared by dissolving 100mg HA in 100 mL of 0.1M KOH. The solution was vigorously stirred for 2hrs and then 100 mL of 1M HNO3 was added. After that, the above HA solution was brought to 1000 mL using deionized water to obtain 100 mg/L HA solution. The HA solution was next filtered to use in further experimentation. Similarly, KCl, NaCl, and $CaCl_2$were prepared in 0.1 M concentration and used directly during experiments.

Instrumentations

Various instruments were used to study the effect of various ionic salts on adsorption of Cr(VI). An optimization study was conducted to optimize several reaction parameters using U-3900 spectrophotometer. In order to study the interactions between humic acid and Cr(VI) Fourier Transform Infrared (FT-IR) study was performed using Bruker model vertex-70. The morphological changes were studied using Scanning Electron Microscopy (SEM).

RESULTS AND DISCUSSION

Different amount of HA (10-100 ppm) were added in order to analysis the adsorption phenomena for complexation of Cr(VI). This spectral profile elaborates that by increasing the concentration of HA the adsorption of Cr(VI) increases linearly. This means that HA adsorbs Cr(VI) from aqueous solutions in a better manner as depicted in Fig.1.

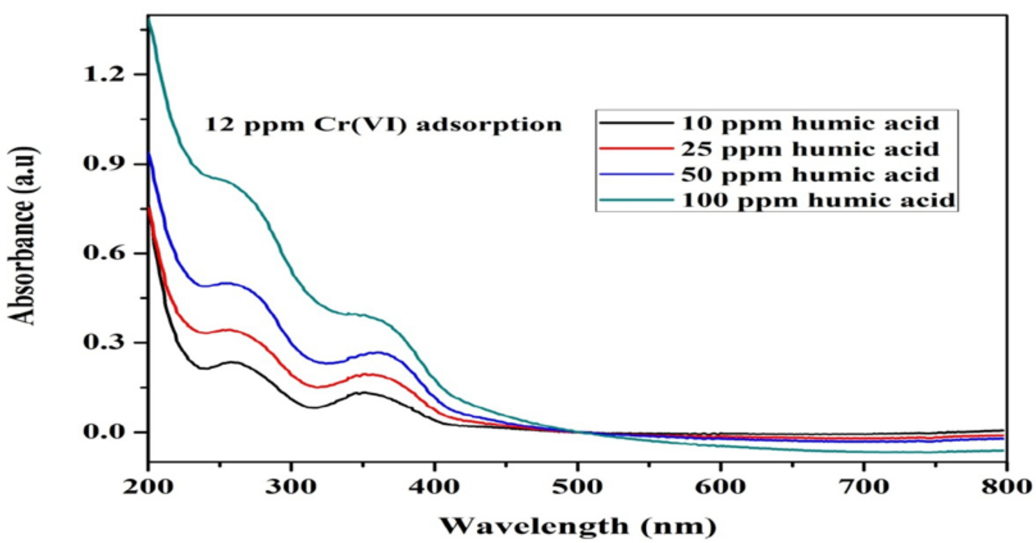

Fig. 1. Complexation of Cr(VI) with HA under different concentrations

Several ionic interference studies were conducted to study the influence of various salt solutions on the adsorption phenomena. For this purpose, initially, 0.1 M $CaCl_2$ solution was mixed in HA-Cr(VI) complex solution. The UV-Vis spectral profile showed that there is less adsorption occurs as compared to pure HA. This indicates that the salt influence in the stop the active sites for adsorption phenomena. Another thing is that the adsorption occurs slowly at a low level. Initially there is no effect by increasing the concentration of HA 10 to 25 ppm but after that, the adsorption increases abruptly and then become constant. This concluded that the salt of $CaCl_2$ interferes on the complexation phenomena between HA and Cr(VI).

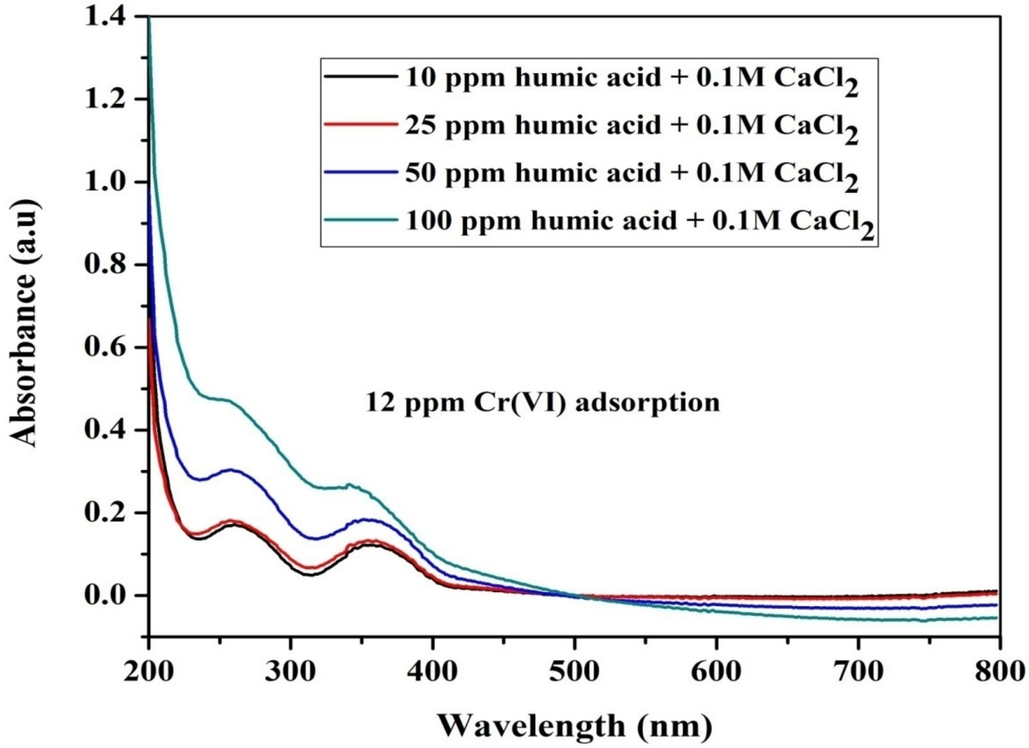

Fig. 2. The effect of 0.1 M $CaCl_2$ salt solution on the complexation of HA with Cr(VI).

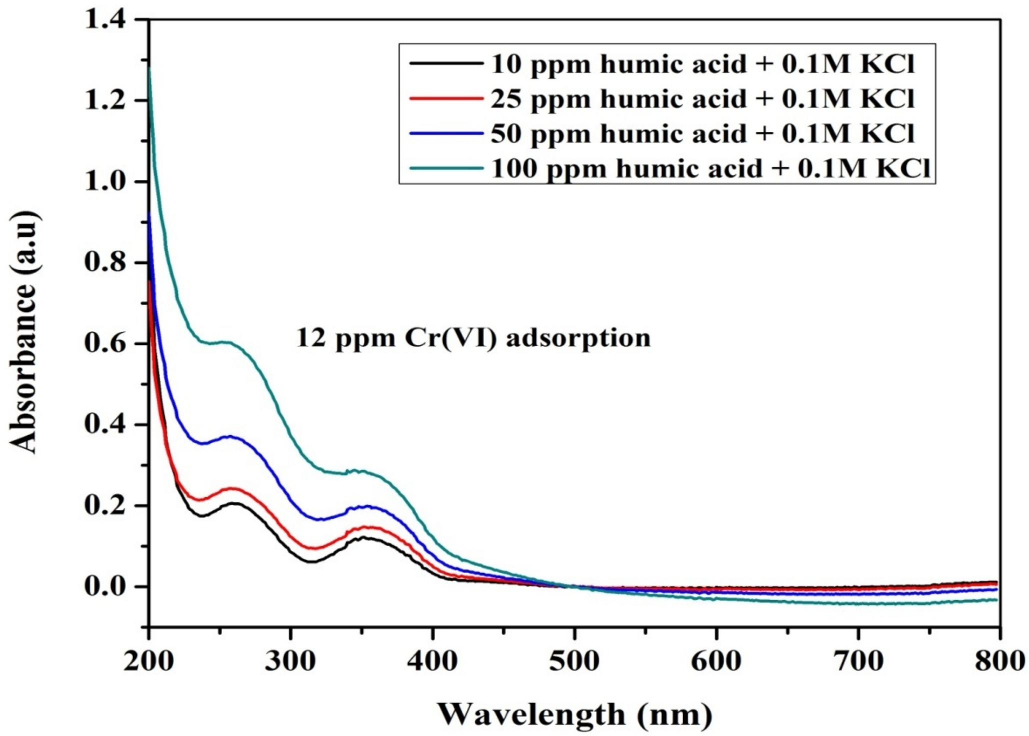

Fig. 3. The effect of 0.1 M KCl salt solution on the complexation of HA with Cr(VI).

Further, the study was extended to elaborate the interferences by taking a different concentration of HA. 0.1 M KCl and 0.1 M NaCl solution were mixed in HA-Cr(VI) complex solutions. The spectral profile after addition of these salts indicated that the adsorption affected by foreign interfering ions (Fig. 2 and Fig. 3).The foreign salts easily affect the process of adsorption. After addition of these salts, the percent adsorption decreased. Another idea is that the ionic radii can influence the interaction of Cr(VI) with HAs. Because by increasing the ionic radii of nucleuses causes the chelating between Cr(VI) and HA. By increasing the sizes of the ions the interaction forces decreases that is why complexation decrease between HA and Cr(VI) ion. These salts affect linearly on the adsorption by increasing the concentration of HA 10 to 100 ppm. It concluded that the both of KCl and NaCl salts affected slightly complexation study between the HA and the Cr(VI).

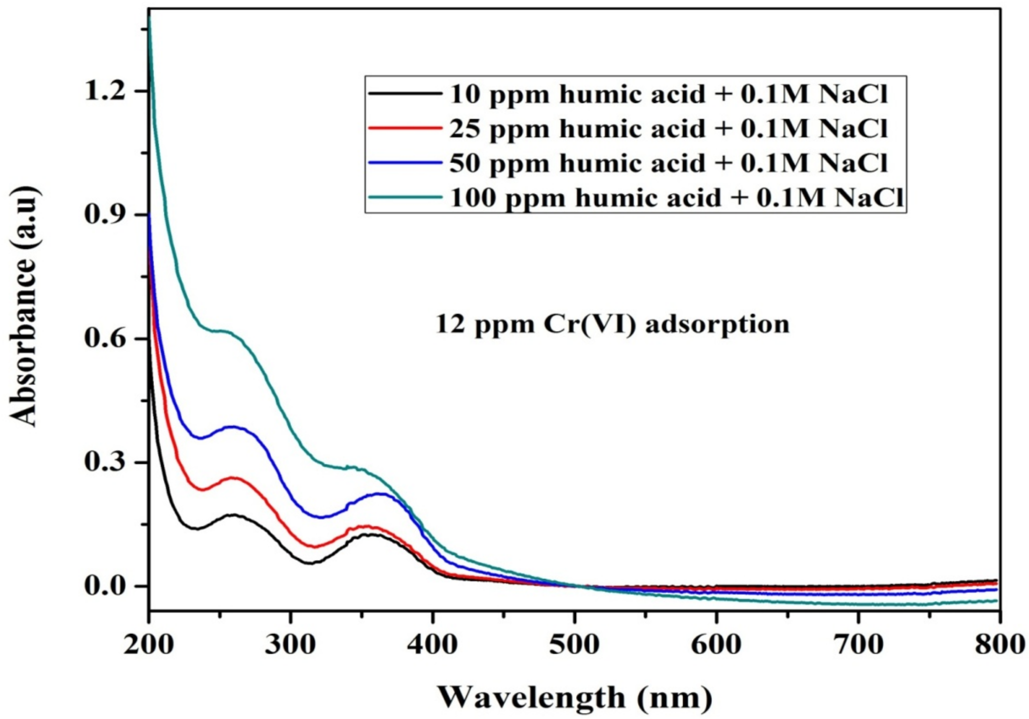

Fig. 4. The effect of 0.1 M NaCl salt solution on the complexation of HA with Cr(VI).

In order to study the extent of interference of various salts on adsorption of Cr(VI) a simultaneous graph was interpreted as depicted in Fig. 5. This plot clearly indicates the extent of adsorption on Cr(VI) complexation with humic acid. The extent of adsorption was found to be more affected in case of $CaCl_2$ and less affected in case of NaCl. This figure also indicated that by increasing the concentration of humic acid more complexation occurs between humic acid and Cr(VI) that why adsorption increases and humic acid acts as a good adsorbent without a presence of various ionic solution.

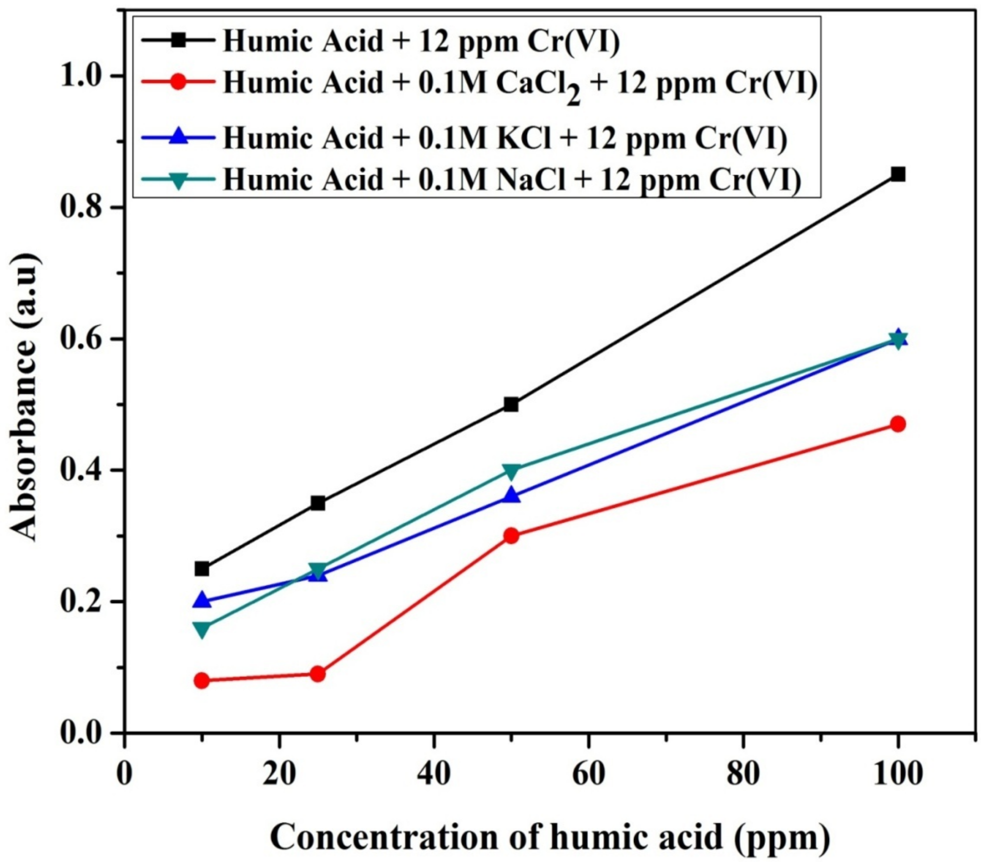

Fig. 5. Plot between absorbance versus concentration of HA in various ionic salts.

In order to study various functional groups interactions between HA and Cr(VI) Fourier Transform Infrared (FT-IR) study was performed as depicted in Fig. 6. FT-IR study showed that the peak intensity of -OH group at 3250 cm^{-1} present in FT-IR spectrum of HA decreases after addition of 12 ppm Cr(VI) which indicated the interaction of Cr(VI) with HA. But after addition of salt the peak intensity again increases indicated that salts affect the adsorption of Cr(VI) using HA as an adsorbent. Similarly, the peak at 1100 cm^{-1} appeared due to -CO moiety which is present in HA. After addition of Cr(VI) the intensity decreases indicating the interaction of Cr(VI) with HA. But, after addition of ionic salts, this peak disappeared in the case of KCl and become smaller in case of other ionic salts. This information supported the information provided in Fig. 5.

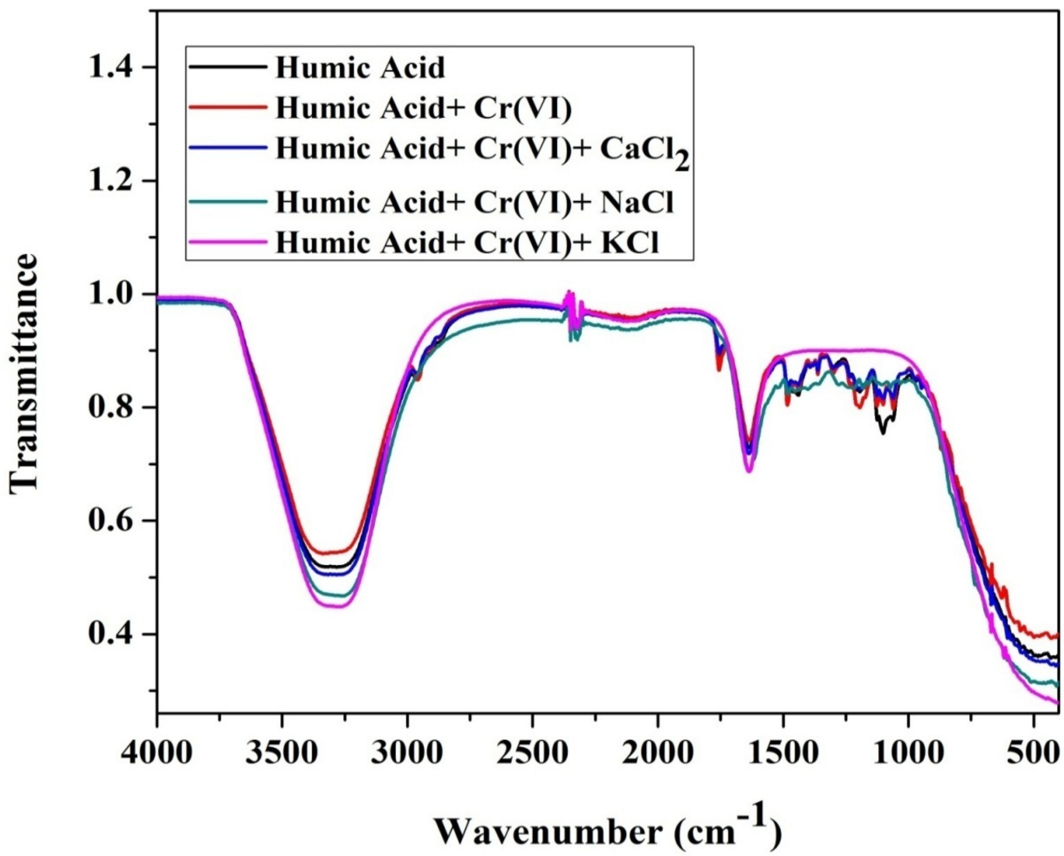

Fig. 6. FT-IR study in adsorption of Cr(VI) by HA in the presence of various ionic salts.

In order to study the surface behaviours and morphological changes, SEM analysis was conducted. The results of adsorption of Cr(VI) only in the presence of HA Fig. 7(a) and in the presence of HA with mixtures of ionic salts $CaCl_2$, $NaCl_2$ and KCl Fig. 7(b). These images showed that the interaction of HA with Cr(VI) in the presence of ionic salts affect the adsorption phenomena in different modes. Hence the ionic salts affect the adsorption phenomena.

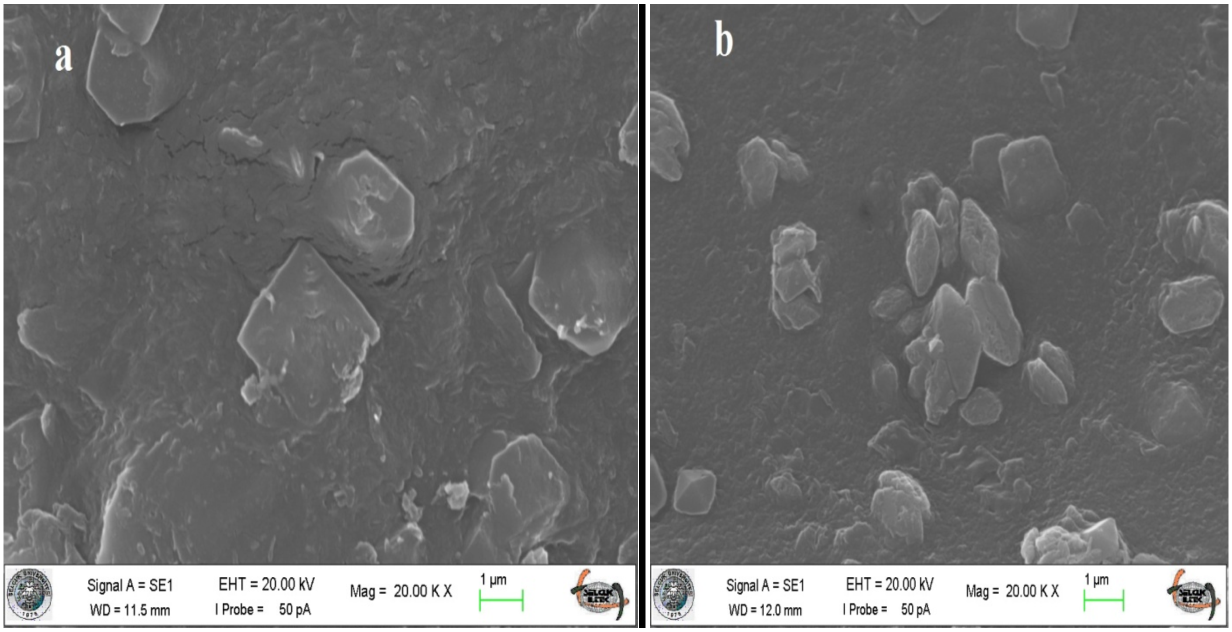

Fig. 7(a). SEM images of adsorption of Cr(VI) in the presence of only HA (a), and in the presence of HA with NaCl, $CaCl_2$ and KCl (b).

CONCLUSIONS

Humic acid was used as an adsorbent for adsorption of Cr(VI). The effect of various ionic salts on adsorption of Cr(VI) with the help of HA as an adsorbent was investigated. Various salts of $CaCl_2$, KCl and NaCl were studied to check the extent of interference of various salts on adsorption process. We concluded from results that these salts decreases the complexation between humic acid and Cr(VI) and also decreases the adsorption of Cr(VI). Finally, we interpret simultaneous effects and concludes that $CaCl_2$ highly affect the adsorption of Cr(VI) whereas NaCl decreases an adsorption phenomena to a little extent.

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