The Utilization of Modified Rye Straws as Biosorbents for Cr (VI) Ions

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Abstract: The potential to remove Cr (VI) ion from aqueous solutions using modified rye straws *(MRS)*, through adsorption was investigated in batch experiments. Rye straws were collected from vicinity of Konya, Turkey and modified with various amount of citric acid (CA). The parameter for modification was selected by trying different parameters such as time, temperature and citric acid quantity. The rate of adsorption was studied under a variety of conditions including initial Cr (VI) concentration (1.10^{-4}-4.10^{-3}M), amount of adsorbent (0.05-0.4 g), pH (1.5 to 7), and contact time (5-240 min). Adsorption of Cr (VI) uptake is in all cases pH-dependent showing a maximum at equilibrium at pH values of 1.5-2.0 for *(MRS)*. The batch sorption kinetics has been tested and the applicability of the Langmuir and Freundlich adsorption isotherms for the present system has been tested at 25°C. The experimental results inferred that adsorption, electrostatic attraction, complexation and chelation are major adsorption mechanisms for binding Cr (VI) ion to the *(MRS)*.
Compared to the various other adsorbents reported in the literature, the *(MRS)* shows very good alternative adsorbent for practical applicability for waste streams and the results indicated that *MRS* can be employed as a low cost alternative in the removal of Cr (VI) ion from wastewater.

Introduction

The increasing contamination of urban and industrial wastewaters by toxic metal ions causes important environmental pollutions. These inorganic micro-pollutants are of considerable concern because they are non-biodegradable, highly toxic and have a probable carcinogenic effect (Madoni et al., 1996). The traditional techniques for the removal of toxic metals from aqueous effluents are incapable of reducing concentration to the levels required by law. Cr(III) and Cr(VI) are the chromium oxidation states usually encountered in the environment. The hexavalent form is of particular concern because of its greater toxicity.

Several other methods are utilized to remove chromium from industrial wastewater. These include: reduction, ion exchange, activated carbon adsorption, electrolytic removal, reverse osmosis, membrane filtration (Cimino et al., 2000; Gode and Pehlivan, 2003; Lu et al., 2006). There are other systems for treating wastewaters containing toxic metal ions is today the use of micro-organisms such as bacteria, fungi and algae but as yet not suitable for applications on a large scale (Ho et al.1995). Several studies have established the potential of peat and brown coal to capture dissolved metals from contaminated waters (McKay and Porter, 1997; Lakatos et al., 2002). Chromium, in its hexavalent form, is one of the undesirable heavy metals because it affects human physiology accumulates in the food chain and cause several ailments. Chromium exists in different oxidation states in aqueous solutions. Although Cr(III) is an essential element for humans, water soluble Cr(VI) is highly irritating and toxic to humans and animals. The main industrial sources of chromium pollution are leather tanning, electroplating, printing, mining, metal processing, wood preservatives, paint and pigments, particularly yellow road paints, textile, metallurgical engineering, battery manufacturing processes and as an anticorrosion agent in cooling waters (Raji and Anirudhan, 1996; Yu et al., 2003; Sharma and Forster, 1993).

Biosorption is an emergent and low cost option to treat heavy metal pollutants that would otherwise create serious environmental hazard. A wide range of physical and chemical processes is available for the removal of Cr(VI) from wastewater. The lignocellulosic waste materials are accomplished requirements for good adsorbent, they possess some adsorption capacities, and they are locally available and have a low cost. Several natural adsorbents, including rice bran, soybean and cottonseed hulls (Marshall and Johns, 1996), sawdust (Bryant et al.,

1992), straw (Aderhold et al., 1996) have been investigated for their ability to sequester metal ion from water. However, limited information exists on the removal efficiency of anions (Achari and Anirudhan, 1995). New economical, easily available and highly effective adsorbents are still needed.

The purpose of this research was aimed to gain a fundamental understanding of the chemical and physical phenomena associated with the binding of Cr(VI) to rye straw (RS) obtained as by-product from locally used wood. The modification of rye straws (RS) by citric acid with the highest sorption capacity was subsequently investigated for its potential as a sorbent for the removal of Cr(VI) from aqueous solutions. This study reports the use of citric acid modified MRS as a biosorbent to remove hexavalent chromium from aqueous solutions. The effects of solution pH, contact time, adsorbent concentration, and initial metal concentration on chromium (VI) adsorption were investigated in detail.

Materials and Methods

Materials

(RS) was collected from vicinity of Konya-Turkey. Straws were ground with Retsch RM 100 model grinding machine. They were ground and sieved to obtain size of 100 μm. Before the use, all the sorbents were washed thoroughly with deionized water and dried in air oven at 120°C for 24 h. All chemicals were of an analytical grade. Double distilled water was used to prepare all solutions throughout the experiments. Cr (VI) stock solution (from Merck) was prepared by dissolving $K_2Cr_2O_7$ salt in double distilled water. Solutions were stored in plastic sealed beakers. Solutions of 0.01 M NaOH and HCl (from Merck) were used for pH adjustment.

Modification of Rye Straws (Rs) with Citric Acid (Ca)

First citric acid (10 g) was dissolved in water (50 ml), added over 100 μm 10 g (RS) thoroughly mixed and allowed to soak for 24 hours at 60°C in the oven. At this period, all surface moisture was removed and (RS) particles were coated with CA. Then, the dry sample was reacted for 2 hours by elevating oven temperature at 120°C. The oven temperature and reaction time were raised to the desired level (120°C) for 2 to 24 hours and mixtures were allowed for reacting. Reaction products were mixed with distilled water for 30 min, filtered and washed with water and the product was dried in the oven. Finally, the modified straws were vacuum oven dried for 24 h at 45 °C. The thermally treated sample was then cooled to room temperature and then ground.

IR Spectra of RS and MRS

To decide whether citric acid was esterified into RS, IR spectroscopic analysis of both untreated RS and MRS were studied. The two major changes in the IR spectrum of MRS could be observed by comparing it with that of MRS: a) a quite evidently increase in the carbonyl (C=O) stretching vibration absorbance in the range of 1730-1750 cm^{-1}; b) a reduction in the hydroxyl (O-H) stretching band in the range of 3430-3440 cm^{-1}. It reflected the result of citric acid etherification. For high amounts of introduced free carboxyl groups, it can be concluded that CA modified (MRS) presented an adequate physical and chemical characteristics to adsorb Cr (VI) ions.

Carboxyl Determination

0.1 g dry sample was slurried in water and 0.1 N NaOH was added and stirred for 24 h. The mixture was back-titrated with 0.1 M HCl until the phenolphthalein end point. Conversion factors were determined using citric acid as standards. Untreated RS was used for comparison in carboxyl determination. Carboxylic acid (%) has been calculated as 11% for (RS)$_l$ and 17% for (MRS) respectively.

Preparation of Cr(VI) solution

An accurately weighed quantity of the $K_2Cr_2O_7$ (purchased from Merck Company) was dissolved in double-distilled water to prepare a stock solution (500 mg/L). Experimental solutions of the desired concentrations were obtained by successive dilutions ($1x10^{-4}$- $4x10^{-3}$ mol/L). Experiments were carried out at initial pH values ranging from 1.5 to 7.0; initial pH was controlled by addition of dilute HCl or NaOH solutions. 0.1 M KNO$_3$ solution is used for ionic strength. All chemicals used were of analytical reagent grade.

Adsorption Experiments

The sorption mixture was consisted of 0.1 g of sorbent in 50 mL of chromium solution from $1x10^{-4}$-$4x10^{-3}$ mol/L $K_2Cr_2O_7$ for 2 h at 25 °C. After equilibration, the sorbent-solution passed through a filter and was analyzed for Cr(VI) ion content using an UV- spectrometer. The sorbent dosage was changed in the range of 0.01-0.4 g. The chromium concentration ($1x10^{-4}$-$4x10^{-3}$ mol/L) was adjusted in the batch experiments. Contact time adsorption experiments were conducted at 25°C in a well-mixed Pyrex glass vessel with a cover. Cr(VI) removal is built up; equilibrium conditions are attained after nearly 2 h.
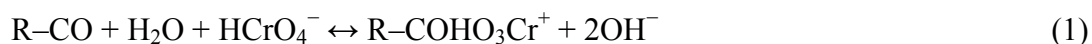
To study the effect of pH on sorption, the pH of the chromium solution was adjusted to values in the pH range of 1.5-7.0 by the addition of 0.1 M HC1 or 0.1 M NaOH prior to experiment. All pH measurements were performed with a Crison Basic 20 Model pH meter. Time dependent experiments were carried out by shaking the adsorption mixture at various predetermined intervals and analyzing the Cr(VI) content at the end of the contact time.

Results and discussion

Effect of pH on Cr(VI) Removal

There are methods available for contacting sorbent materials with solutions contacting metal ions. Batch contacting process has been employed to investigate the performance of the modified straws in removing Cr(VI) from aqueous solution. Lignocelluloses resources and the cell walls of RS mainly consist of polyphenolic compounds, hydroxyl groups such as tannin and lignin, which are believed to be the active sites for attachment of heavy metal cations. All those components are active ion exchange compounds. The lignin content of woods is usually in the range of 18–35%. Tannins are complex polyhydric phenols that are soluble in water and they occur chiefly in hardwoods, and are present in many barks, including softwoods barks. Lignin molecule is built up from the phenyl propane nucleus, i.e. an aromatic ring with a three-carbon side chain. Natural tannins are classified as either hydrolysable or condensed tannins. The hydrolysable tannins are esters of glucose with one or more polyphenolic acids, commonly gallic, digallic, or ellagic acid.

The interactions of Cr(VI) ions with RS surface molecules are complex, dominated by adsorption, ion exchange and chelation. Hunt (1986) notes as a generalization the binding of Cr(VI) ions involved two mechanism, the first of these being simple ion exchange and the second through the formation of complexes, which may be chelates. According to the mechanism and the discussion of pH effect, the adsorption will lead to a decrease in pH as equivalent H^+ will be released along with the adsorption. Hexavalent chromium existing as negative species in solution may release hydroxide (OH^-) instead of proton (H^+) when they are adsorbed by RS, and therefore result in an increase in pH. This is the case for most metal adsorption, but there is always exception. Because of the complexity of most biomaterials, it is very likely that both of these processes of Cr(VI) binding will take place in a system at the same time. The following equation (1) describes the chemical adsorption involving exchange with hydroxyl ions:

$$R–CO + H_2O + HCrO_4^- \leftrightarrow R–COHO_3Cr^+ + 2OH^- \tag{1}$$

The effect of pH is presented in Fig. 1. The effect of pH on adsorption of Cr(VI) was studied at room temperature be varying the pH of metal solution–MRS suspension from 1.5 to 7.0. The percent adsorption decreases in the pH range of 2.0–7.0, showing the maximum adsorption at pH 1.5. The pH dependence of adsorption may suggest that Cr(VI) ions are adsorbed according to the ion-exchange mechanism, and deacetylation dependence of adsorption may indicate the chelation mechanism. The pH increase was lesser at lower initial pH values. It may be due to hydrolysis of the adsorbent in water, which will create positively charged sites (Dakiky et al., 2002). Percentage removal of Cr(VI) was maximum at the initial pH of 1.5 (92.21%, by MRS) and decreased at higher initial pH values. As described in Eq. (1), hydroxyl species are released from the process of Cr(VI) adsorption instead of hydrogen ions.
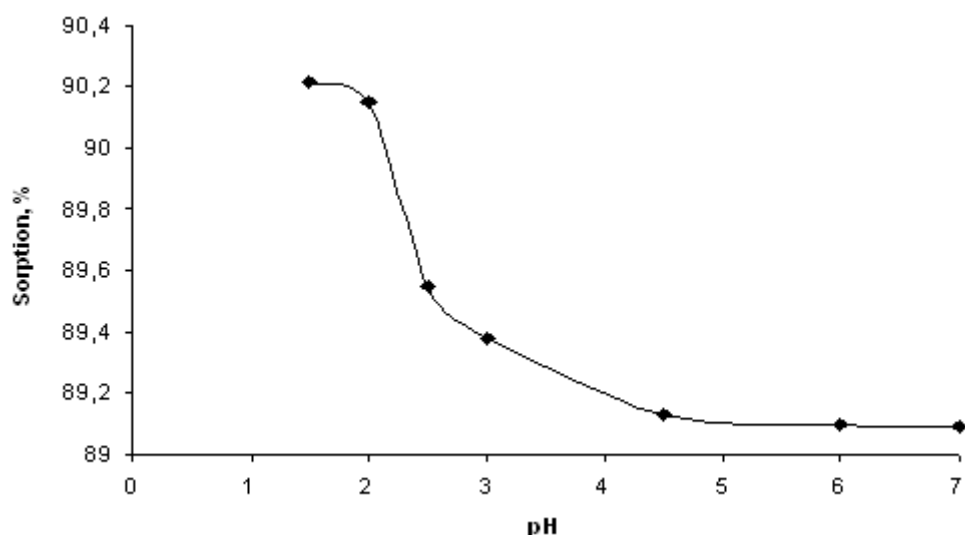
Fig. 1. Effect of pH on the adsorption of Cr(VI)

At initial pH of 1.5, the adsorbent surfaces might be highly protonated which favor the uptake Cr(VI) in the predominant anionic form (HCrO$_4^-$) (Srinivas Rao et al, 1992). With increase in pH from 2.0 to 7.0, the degree of protonation of carbon surfaces reduced gradually and hence removal was decreased. The rate of adsorption of Cr(VI) ion on (*MRS)* was great for pH changes from 1.5 to 2.0 for Cr(VI) ion. An increase in pH above pH 2 shows a slight decrease in adsorption in which the surface of the adsorbent is negatively charged. Decrease in adsorption at higher pH is due to the formation of soluble hydroxyl complexes.

Different mechanisms, such as electrostatic forces, ion exchange, chemical complexation, must be taken into account when examining the effect of pH on Cr(VI) sorption. One of the common proposed mechanisms is electrostatic attraction/repulsion between sorbent and sorbate. Thus, the increase of Cr(VI) sorption at acidic pH should be due to the electrostatic attraction between positively charged groups of biomaterial surface and the HCrO$_4^-$ anion, which is the dominant species at low pH. Moreover, the decrease of the sorption with increasing pH could be due to the decrease of electrostatic attraction and to the competitiveness between the chromium anionic species (HCrO$_4^-$ and CrO$_4^{2-}$) and OH$^-$ ions in the bulk for the adsorption on active sites of the sorbent. From these assumptions it can be suggested that Cr(VI) removal also takes place by physical adsorption.

Speciation studies of Cr(VI) in aqueous solution, on the basis of spectrophotometer, electrochemistry, indicates the existence of the following equilibrium;

$$H_2CrO_4 \;=\; H^+ + HCrO_4^- \tag{2}$$
$$HCrO_4^- \;=\; H^+ + CrO_4^{2-} \tag{3}$$
$$2HCrO_4^- \;=\; Cr_2O_7^{2-} + H_2O \tag{4}$$

Equilibrium is dependent on pH, with HCrO$_4^-$ and Cr$_2$O$_7^{2-}$ existing primarily in acidic media and CrO$_4^{2-}$ being the lone species of Cr(VI) above pH 7.0. At higher pH range, the fraction of Cr$_2$O$_7^{2-}$ species rapidly decreases with increasing pH above 5. In the removal of Cr(VI) process, the anion is not a simple monovalent anion but rather a series of chromate anions depending upon the pH and concentration of the solution. The total chromate species will be represented as Cr(VI). In the neutral solution at low concentrations, Cr(VI) will be present in the form of HCrO$_4^-$ and CrO$_4^{2-}$. At acidic pH, HCrO$_4^-$ is the predominant Cr(VI) species in the aqueous phase. The decrease in adsorption at high pH values may be due to the competitiveness of the oxyanion of chromium and OH$^-$ ions in the bulk. Processes of oxo group protonation and Cr(VI) reduction were lowering because both these reactions require protons.

The decrease in the adsorption with increase of pH may be due to the decrease in electrostatic force of attraction between the sorbent and sorbate ions. At lower pH ranges, due to the high electrostatic force of attraction, the percentage of Cr(VI) removal is high. At very low pH value, the surface of sorbent would also be surrounded by the hydronium ions which enhance the Cr(VI) interaction with binding sites of the biosorbents by greater attractive forces. A decrease in adsorption above pH 4.5 may be due to occupation of the adsorption sites by anionic species like HCrO4$^-$, Cr$_2$O$_2^{7-}$, CrO$_2^{4-}$, etc., which retards the approach of such ions further toward the sorbent surface (Donmez and Aksu, 2002).

Effect of time on the removal of Cr(VI)

Cr(VI) adsorption by (*MRS*) was studied by mixing for a predetermined time interval. An initial concentration of Cr(VI) 2.10^{-3} M was tried and the concentration of Cr(VI) remaining in the equilibrated solution was plotted as a function of the equilibration period for the (*MRS*). The plots for Cr(VI) sorption (%) versus time for (*MRS*) **(Fig. 2)** showed that equilibrium was attained in 90 min for the adsorption of Cr(VI). The uptake of Cr(VI) is initially rapid then continues at a much slower rate. The concentration of Cr(VI) in the solution increased rapidly within 60-90 min and the sorption was virtually completed within 90-110 min.
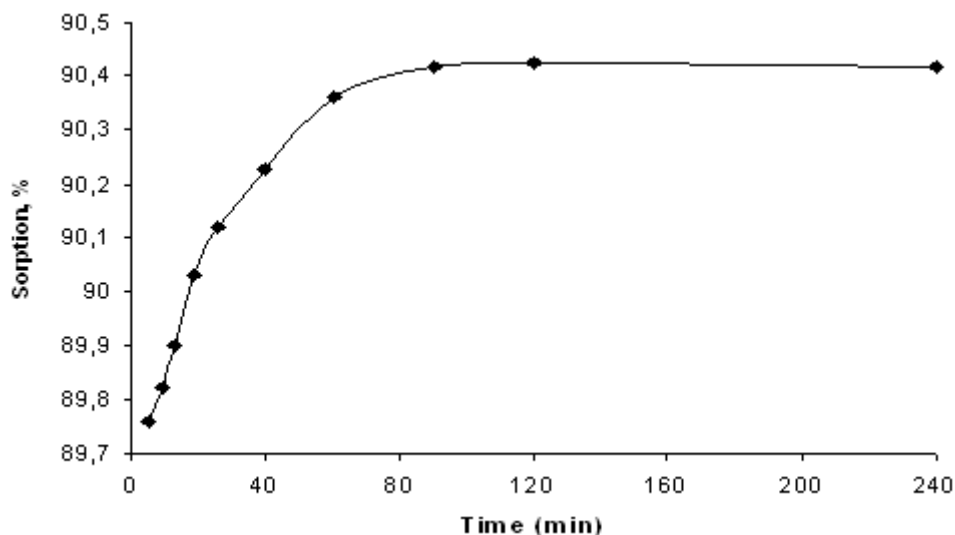

Fig. 2. Effect of contact time on the sorption of Cr(VI)

The metal uptake versus time curves was single, smooth and continuously leading to the saturation suggesting the possible monolayer coverage of metal ions on the surface of the adsorbent. The capacity of (*MRS*) reached in this study is 0.89 mmol Cr(VI) per gram of (*MRS*) at pH 2.0. Therefore, in addition to other some natural sorbents, (*MRS*) provides relatively cheap alternatives for Cr(VI) ion removal .

Effect of initial Cr(VI) ion concentration

The effect of Cr(VI) concentration on the sorption by the (*MRS*) sorbents was investigated by varying the concentration (1.10^{-4} M to 4.10^{-3} M) at a pH of 2 for 120 min equilibrium time. The percent Cr(VI) ion removal efficiency of (*MRS*) increased with increasing metal concentration. At higher concentrations, more Cr(VI) ions are left unabsorbed in solution due to the saturation of binding sites. Langmuir and Freundlich isotherms have both been used to describe observed sorption phenomena of various metal ions on sorbents (Madoni et al. 1996). The sorption data of Cr(VI) ion have been correlated with Langmuir and Freundlich models [Eqs. (5) and (6)]. These isotherms relate metal uptake per unit weight of resin q_e to the equilibrium metal ion concentration in the bulk fluid phase C_e.

Langmuir equation:

$$\frac{C_e}{q_e} = \frac{1}{K_b A_S} + \frac{C_e}{A_S} \tag{5}$$

where, A_s and K_b are coefficients, q_e is the weight adsorbed per unit weight of adsorbent and C_e is the metal concentration in bulk solution at equilibrium. Fig. 4 conforms to the Langmuir and Freundlich models.

Freundlich equation:

$$q = K_f C_e^n \tag{6}$$

where, n is the Freundlich constant, and K_f is the adsorption coefficient, q is the weight adsorbed per unit weight of adsorbent and C_e is the equilibrium metal concentration in fluid. Taking logs and rearranging the equation (6), equation (7) was obtained.

$$\log q = \log K_f + n \log C_e \tag{7}$$

The linear plots of C_{eq}/q vs C_{eq} show that adsorption follows the Langmuir adsorption model and the correlation coefficients are calculated 0.97 for (MRS). The Langmuir-type sorption isotherm was suitable for equilibrium studies suggesting the formation of monolayer coverage of the adsorbate on the surface of adsorbent in the concentration studied. The data for the uptake of metal ions by the resin has been processed in accordance with a linear form of the Langmuir isotherm equation.

Effect of Ionic Strength

Ionic strength is one of the important factors influencing aqueous phase equilibrium. Generally, adsorption decreases with increasing ionic strength of the aqueous solution. The effect of the interfering ion KNO_3 was evaluated. The electrostatic attraction at low ionic strength appears to play a negligible role in the removal of Cr(VI) for sorbents. The results indicate that there was no significant decrease in the removal of Cr(VI) ion for the interval of (0.0001-0.001M) KNO_3 ionic concentration.

Amount of sorbent

The effect of variation of (MRS) amount on the removal of chromium by (MRS) is shown in Fig. 3. It is apparent that the equilibrium concentration in solution phase decreases with increasing (MRS) amount for a given initial chromium concentration. The fraction of metal removed from the aqueous phase increases as the sorbent amount is increased in the batch vessel with a fixed initial metal concentration (Fig. 3). This result was anticipated because for a fixed initial solute concentration, increasing amount of adsorbent provides greater surface area (or adsorption sites).
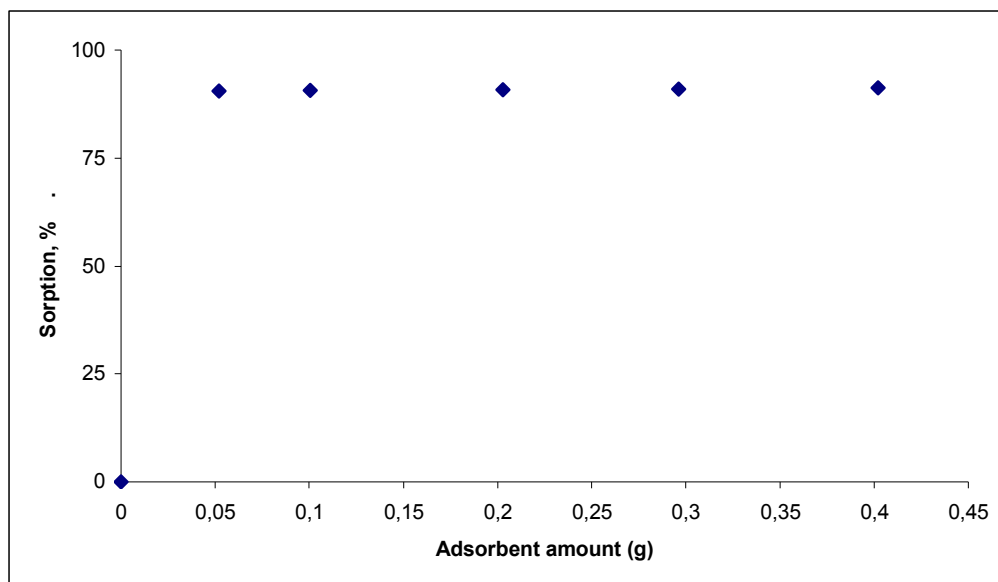

Fig. 3. Effect of sorbent dosage on the sorption of Cr(VI)

Conclusion

The studies indicated that equilibrium in the adsorption of Cr(VI) on (MRS) was reached in 90 min of contact time between the (MRS) and the solution. The optimum pH corresponding to the maximum adsorption was found to be at pH 2.0 for (MRS). Cr(VI) adsorption on the (MRS) was described by the Freundlich isotherm model. The adsorption of Cr(VI) increased with an increase in the concentrations of these metals in solution.

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