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Adsorptive removal of Cr(VI) ions from aqueous solutions by H_2SO_4 modified oak (*Quercus* L.) sawdust

Duygu Özdeş[1*], İbrahim Yıldırım[2], Celal Duran[3]

[1]Gümüşhane University, Gümüşhane Vocational School, Department of Chemistry and Chemical Processing Technologies, 29100, Gümüşhane, Turkey
[2]Gümüşhane University, Institute of Science, 29100, Gümüşhane, Turkey
[3]Karadeniz Technical University, Faculty of Sciences, Department of Chemistry, 61080, Trabzon, Turkey

Abstract

In this study, the utilization of H_2SO_4 modified oak sawdust (*Quercus* L.) (HMOS) as a new and promising sorbent for the uptake of an extremely toxic inorganic pollutant, Cr(VI), from aqueous media by batch adsorption method has been investigated. The HMOS has been characterized by different methods such as Boehm titration, pH_{pzc}, and moisture content. Some of the process parameters including initial solution pH, equilibrium time, initial Cr(VI) concentration, HMOS amount, and salt effect were examined in detail in order to optimize the experimental conditions for the uptake of Cr(VI) ions onto HMOS. The maximum Cr(VI) uptake was achieved at initial solution pH of 2.5 and at equilibrium time of 240 min. The adsorption behaviors of Cr(VI) ions onto both natural oak sawdust (NOS) and HMOS were analyzed in terms of Langmuir and Freundlich isotherm models and the Cr(VI) adsorption was obtained to be compatible with both isotherm models. The Cr(VI) adsorption capacities of NOS and HMOS were calculated as 48.07 and 100.00 mg g^{-1}, respectively by utilizing the Langmuir model. As a result, H_2SO_4 modified oak sawdust provides a strong alternative to remove Cr(VI) ions from wastewaters.

Keywords: Adsorption, chromium, heavy metal, isotherm, Oak Sawdust

1. Introduction

Heavy metals, which occur naturally in the earth's crust, cause serious troubles to both the environment and all of the living organisms depending on their types and levels [1]. Chromium, which is a major heavy metal pollutant in aqueous media, is usually spread into both the environment and the water sources by virtue of several industrial activities such as metal plating, batteries, paper production, leather tanning, pesticides, mining and electroplating [2-4]. Although chromium is found at different oxidation states in nature, only two of them are stable: Cr(III) and Cr(VI). The solubility, mobility, and toxicity of these two chromium species are different from each other. Cr(III) has an important part in carbohydrate metabolism hence it is an essential element for the human body. Nevertheless, Cr(VI), which exists in aqueous solutions as chromate (CrO_4^{2-} or $HCrO_4^-$) and dichromate ($Cr_2O_7^{2-}$) depending on solution pH and its concentration, may cause serious damages to the living organism. Cr(VI) is a strong oxidizing agent and easily absorbed in the human body via digestion, respiratory system, skin, and mucous membrane. Eventually, it may induce many health problems such as skin irritation, lung cancer, gastric and liver damage, ulcer formation, and nervous system failure [5,6]. The permissible limit for Cr(VI) in drinking water is recommended as 0.05 mg L^{-1} by World Health Organization (WHO) [7]. That is why it is compulsory to develop economical and efficient methods for purification of waters contaminated with Cr(VI) ions by virtue of various industrial activities.

Several techniques including reverse osmosis [8], coagulation [9], ion exchange [10], advanced oxidation [11], and adsorption [12] have been carried out in order to remove Cr(VI) from water resources. Adsorption method, performed without causing a secondary waste generation, is commonly utilized in wastewater treatment due to its high selectivity, simplicity of design, low cost, and high efficiency

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***Author of correspondence:** duyguozdes@hotmail.com
Phone: +90 (456) 233 10 60, **Fax:** +90 (456) 233 10 67

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when compared with other conventional techniques. The choosing of adsorbents plays a significant role during the adsorption process. Adsorbents, used in developed processes should be inexpensive and easily available, which are not harmful to the environment. In addition, they should have a large specific surface area and have functional groups that can interact with the target pollutants [13].

The agroforestry wastes, which are the by-product of agricultural and forestry production, substantially composed of polyphenolic compounds and hydroxyl groups originating from tannin and lignin. These functional groups are known to be the active sites for the binding of heavy metal ions. Sawdust is a timber industry waste product and it is used as a fuel or a packaging material. It contains lignin and cellulose, and it is comprised of electron rich-functional groups [14]. Acid and alkali treatment of sawdust enhances the pollutant uptake capacity of them. Agricultural waste by-products have been used in the adsorption process as efficient adsorbents in the removal of both organic and inorganic pollutants recently since they are low cost and easily available. Until now, several agricultural wastes have been reported in the literature including date pit and olive stone [5], sugarcane bagasse [15], corncob [16], rice husk [17], Citrus limetta peel [18], peanut shell [19], and apple peel [20], etc. to uptake Cr(VI) from aqueous media.

In this study, H_2SO_4 modified oak (*Quercus* L.) sawdust (HMOS) was prepared and applied to remove Cr(VI) ions from aqueous solution. To our best knowledge, no study has been reported on the removal of any pollutant by using H_2SO_4 modified oak (*Quercus* L.) sawdust. The HMOS was characterized by different techniques. Subsequently, to achieve the optimum uptake conditions, the effects of various experimental parameters including initial solution pH, initial Cr(VI), and HMOS concentration and contact time on the process were evaluated. The adsorption isotherms were used to determine the Cr(VI) adsorption capacity of HMOS and to interpret the adsorption mechanism.

2. Materials and methods

2.1. Preparation and characterization of HMOS

For the modification of the oak sawdust with H_2SO_4, 20 g of the oak sawdust was taken without grinding, and 20 mL of concentrated H_2SO_4 was added and mixed well. The mixture was left on a hot plate at 200°C for 24 hours. After this period, the adsorbent was washed with boiled distilled water for several times to neutralize the carbonized sample. The adsorbent was then treated with a 1% $NaHCO_3$ solution for 24 hours to completely neutralize the acid residues. After the modified adsorbent was filtered, it was washed well with distilled water and finally dried in the oven for 24 hours at 105°C. The obtained adsorbent (HMOS) was used in the adsorption process after grinding to a particle size of 150 μm [21, 22]. The pH_{pzc} (point of zero charge) and moisture content of HMOS were determined according to standard methods [23] while the surface acidic groups of it were obtained by Boehm titration [24].

2.2. Adsorption method

Adsorption studies were performed by a batch method using 15 mL polyethylene centrifuge tubes which were shaken by using BOECO PSU-15i model mechanical shaker at room temperature. The initial pH of the Cr(VI) solution was adjusted to the desired values by the addition of 0.1 M HNO_3 and NaOH solutions using Hanna pH-2221 model digital pH meter. The adsorption studies were performed in duplicate, and the Cr(VI) levels in the dilute phase were analyzed by Perkin Elmer Analyst 400 model flame atomic absorption spectrophotometer (FAAS). The adsorption studies were performed by mixing Cr(VI) solutions (10 mL) in the concentration range of 100-2300 mg L^{-1} and in the pH range of 1.0-8.0 with 10-200 mg of HMOS amount. The mixtures were shaken in the contact time range of 1-360 min at 350 rpm. After enough shaking time, the mixtures were centrifuged at 3500 rpm for 10 min. The Cr(VI) amounts in the aqueous phase were analyzed by FAAS and the adsorption amount was calculated by using the following equation;

$$q_e = \frac{V(C_o - C_e)}{m_s} \qquad (1)$$

C_o (mg L^{-1}) and C_e (mg L^{-1}) is the initial and equilibrium Cr(VI) concentration in aqueous solution, respectively, V (L) is the aqueous solution volume, m_s (g) is the HMOS amount, and q_e (mg g^{-1}) is the amount of calculated Cr(VI) adsorption onto 1.0 gram of HMOS.

3. Results and discussion

3.1. Characterization of HMOS

The pH_{pzc} value of HMOS was determined as 2.6, which indicates that the surface acidic groups are more dominant than the basic groups. It is important to know the pH_{pzc} values of the adsorbents in order to have an idea about the pH values, at which maximum adsorption will occur of the species that may be found in an anionic or cationic form in aqueous solutions. At $pH>pH_{pzc}$, the surface charge of adsorbent is negative, whereas $pH<pH_{pzc}$ the surface charge of adsorbent is positive. Thus, in the studies conducted at pH lower than the pH_{pzc} value of the adsorbent, it is thought that the anionic species in the aqueous solution such as Cr(VI) will be better adsorbed [25].

The values of the carboxylic and phenolic groups on the surface of HMOS were determined as 8.72 and 7.34 mmol g^{-1}, respectively, and the total acidic group amount was obtained as 16.06 mmol g^{-1}. It is seen that HMOS is rich in terms of total acidic groups and especially the amounts of carboxylic groups are higher than the phenolic groups. Besides, the moisture content of HMOS was determined as 9.5%.

3.2. Effect of initial solution pH

The influence of initial solution pH on the adsorptive removal of Cr(VI) ions by HMOS was investigated in the pH range of 1.0-8.0 by using 50 mg L^{-1} of initial Cr(VI) concentration and 5.0 g L^{-1} of HMOS. From Fig. 1, it is seen that the adsorption efficiency of Cr(VI) ions rises from 74.0% to 99.2% when pH increases from 1.0 to pH 2.5 and it decreases prominently after pH 2.5. Cr(VI) ions exist in the form of acid chromate ($HCrO_4^-$), chromate (CrO_4^{2-}), and dichromate ($Cr_2O_7^{2-}$) depending on the pH of the aqueous solution. In acidic pH values, the dominant form of Cr(VI) is $HCrO_4^-$, and the surrounding of HMOS is wrapped with H_3O^+ ions to make the surface functional groups positively charged. Thus at low pH values, an increase in the adsorption efficiency was observed because of occurring an electrostatic interaction between the $HCrO_4^-$ ions and the positively charged HMOS surface. At higher pH values the adsorption efficiency decreases because of the competitive effect of OH^- ions with $Cr_2O_7^{2-}$ ions, the dominant form of Cr(VI), to adsorb the active adsorption sites on the HMOS surface. Besides, the electrostatic repulsion between the same charged Cr(VI) ions and the HMOS surface decreases the adsorption efficiency at high pH values. The pH effect on the adsorption of Cr(VI) ions onto HMOS can also be explained by the pH_{pzc} value of the adsorbent. The pH_{pzc} value of HMOS was determined as 2.6. In the case of $pH<pH_{pzc}$, the net surface charge of HMOS is positive and the adsorption efficiency of Cr(VI) ions is expected to be high [25].

In subsequent experimental studies, the optimum pH value was determined as 2.5 for the adsorption of Cr(VI) ions onto HMOS (Fig. 1).

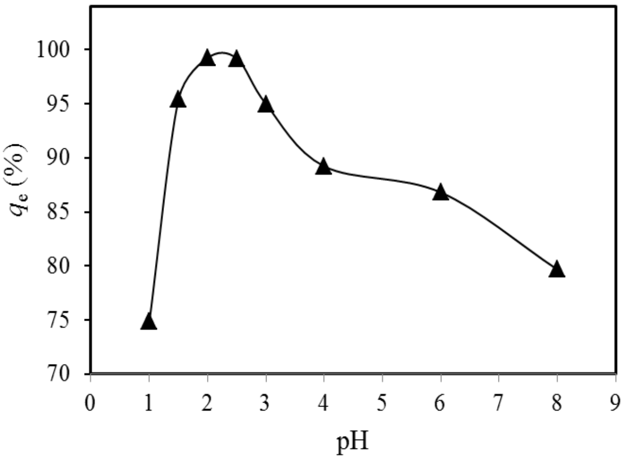

Figure 1. Effect of initial pH on Cr(VI) adsorption onto HMOS (initial Cr(VI) concentration: 50 mg L^{-1}; HMOS concentration: 5.0 g L^{-1})

3.3. Effect of contact time

In order to investigate the sufficient equilibrium time, the adsorption studies were carried out in the shaking time range of 1-360 min by mixing 230 mg L^{-1} of initial Cr(VI) concentrations containing 5.0 g L^{-1} of HMOS at initial pH 2.5. In the first stages of the adsorption (in the 1-30 minute time interval), the uptake of Cr(VI) ions onto HMOS occurs very quickly since the active adsorption sites are completely open. Subsequently, the adsorption rate gradually decreases due to the diffusion of Cr(VI) ions towards HMOS pores, and finally, the equilibrium occurs due to the saturation of the HMOS surfaces [12].

In the light of the results obtained in this parameter, the appropriate contact time for the adsorption of Cr(VI) ions onto HMOS was determined as 240 minutes (Fig. 2). No notable increases were noticed in the Cr(VI) uptake amount after this period.

3.4. Effect of HMOS amount

The influence of HMOS amount on the adsorption of Cr(VI) ions was investigated in the HMOS concentration range of 1.0-20.0 g L^{-1} by using 230 mg L^{-1} of initial Cr(VI) concentration at initial pH 2.5. When the amount of HMOS was increased from 1.0 to 20.0 g L^{-1}, the removal percentage increased from 29.3 to 86.0% as a result of the increase in the active adsorption surfaces. Conversely, the higher HMOS amount causes a decrease in total surface area due to the formation of agglomerates and of unsaturated adsorption surfaces [26], and thus the adsorption amount decreased from 67.5 to 9.9 mg g^{-1} as increasing the amount of HMOS from 1.0 to 20.0 g L^{-1} (Fig. 3).

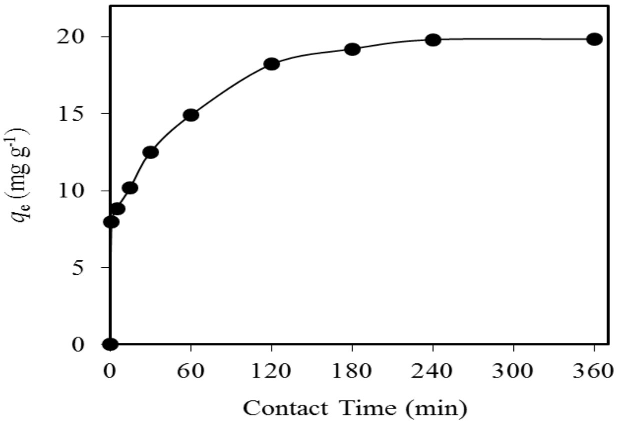

Figure 2. Effect of contact time on Cr(VI) uptake by HMOS (initial Cr(VI) concentration: 230 mg L^{-1}; HMOS concentration: 5.0 g L^{-1}; initial pH: 2.5).

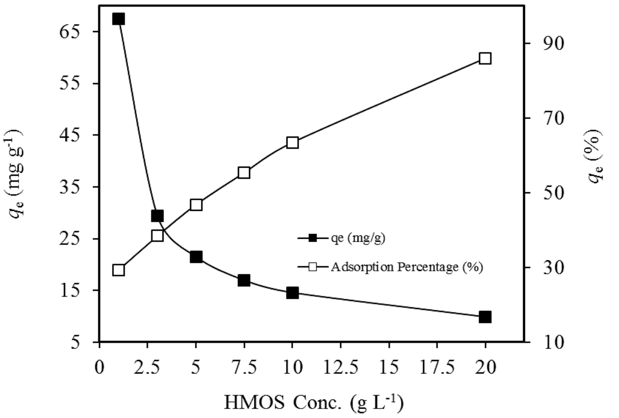

Figure 3. Effect of adsorbent amount on Cr(VI) uptake by HMOS (initial Cr(VI) concentration: 230 mg L^{-1}; initial pH: 2.5; contact time: 240 min).

3.5. Effect of initial Cr(VI) concentration and adsorption isotherms

The data obtained as a result of the investigation of the influence of initial metal concentration on the uptake of heavy metal ions is applied to various adsorption isotherms to have an idea about the capacities of the adsorbents. Therefore, to examine the change in Cr(VI) uptake capacity of oak sawdust due to the modification with H_2SO_4, the effect of increasing initial Cr(VI) concentration was evaluated for both natural oak sawdust (NOS) and H_2SO_4 modified oak sawdust (HMOS).

In order to evaluate the effect of initial Cr(VI) ions concentration on the adsorption efficiency of NOS and HMOS, a series of Cr(VI) solution at initial concentrations of 100-2300 mg L^{-1} were added to the centrifuge tubes containing 0.05 g NOS or HMOS, separately, and the mixtures were shaken until the equilibrium reached. After centrifugation, the Cr(VI) concentrations remaining in the solutions were determined by FAAS and from the obtained data the relationship between the adsorbed Cr(VI) amounts (q_e) and the adsorption percentages (%) against initial Cr(VI) concentrations were plotted in Fig. 4 (for NOS) and in Fig. 5 (for HMOS).

By increasing the initial Cr(VI) concentration from 100 mg L^{-1} to 2300 mg L^{-1}; at constant NOS amount, the amount of adsorption increased from 7.7 mg g^{-1} to 40.0 mg g^{-1}, the percentage of adsorption decreased from 33.5% to 8.8% (Fig. 4) and at constant HMOS amount, the amount of adsorption increased from 11.9 mg g^{-1} to 78.4 mg g^{-1}, and the percentage of adsorption decreased from 52.0% to 17.3% (Fig. 5). At constant NOS and HMOS amount, the increase in initial Cr(VI) concentration causes a driving force to overcome mass transfer resistance for Cr(VI) transportation between the solution and the surface of NOS and HMOS, which increases the adsorption amount. Conversely, at high Cr(VI) concentrations, a saturation occurs on the active adsorption sites of NOS and HMOS surface which makes them less available for Cr(VI) binding thus the adsorption percentage decreases [27].

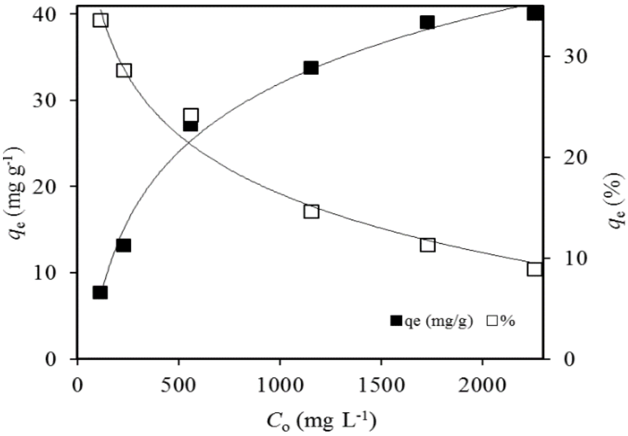

Figure 4. Effect of initial Cr(VI) concentration on its uptake by NOS (initial pH: 2.5; NOS concentration: 5.0 g L^{-1}; contact time: 240 min).

The Langmuir and Freundlich isotherm models were fitted to the experimental data in order to have an opinion about the mechanism of the adsorption of Cr(VI) ions onto NOS and HMOS. According to Langmuir isotherm model, the adsorption process occurs as a monolayer on homogeneous surfaces, and all active binding sites on the adsorbent surface have equal energy [28]. In contrast, the Freundlich isotherm model is based on the idea that the multilayer adsorption occurs on heterogeneous adsorbent surfaces [29].

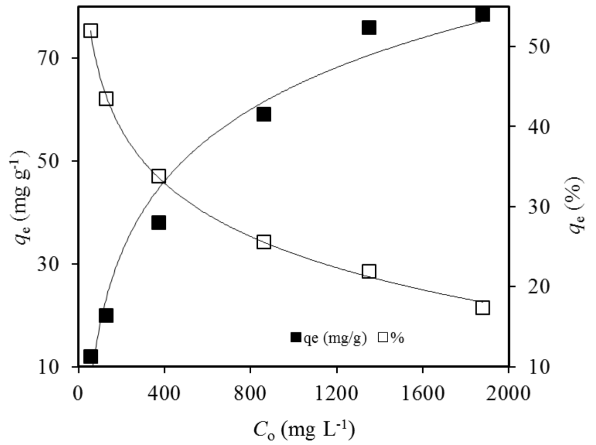

Figure 5. Effect of initial Cr(VI) concentration on its uptake by HMOS (initial pH: 2.5; HMOS concentration: 5.0 g L^{-1}; contact time: 240 min).

The linear forms of Langmuir and Freundlich isotherm models are given in Eqs. 2 and 3, respectively.

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{bq_{max}} \qquad (2)$$

$$ln\, q_e = ln\, K_f + \frac{1}{n} ln\, C_e \qquad (3)$$

where q_e (mg g^{-1}); Cr(VI) adsorption per unit mass of NOS and HMOS at equilibrium, C_e (mg L^{-1}); equilibrium concentration of Cr(VI) ions in solution, q_{max} (mg g^{-1}); maximum adsorption capacity of NOS and HMOS, b (L mg^{-1}); adsorption energy, K_f (mg g^{-1}); sorption capacity, and n; sorption intensity.

The suitability of the adsorption process can be evaluated by using the separation factor (R_L) related to Langmuir isotherm which is given in the following equation [30];

$$R_L = \frac{1}{1 + b.Co} \qquad (4)$$

where b (L mg^{-1}) is the Langmuir constant and C_o (mg L^{-1}) is the initial Cr(VI) concentration. R_L values should be in the range of 0-1 for favorable adsorption.

q_{max} and b values belong to Langmuir isotherm model were calculated from the slope and intercept of the linear plot of C_e/q_e versus C_e, respectively (Fig. 6(a) and (b)) and K_f and n values belong to Freundlich isotherm model were determined from the intercept and slope of the linear plot of lnq_e versus lnC_e, respectively (Fig. 7a and b). All of the isotherm constants were given in Table 1. The correlation coefficients calculated from the figures drawn by applying the linear equations are compared to determine which of the two models is more suitable for explaining the surface structure of the adsorbents. The correlation coefficients obtained from both the Langmuir and Freundlich isotherm models for the adsorption of Cr(VI) ions onto NOS and HMOS are greater than 0.95. This indicates that the active adsorption sites on the NOS and HMOS surface exhibit both the homogeneous and heterogeneous distribution [13].

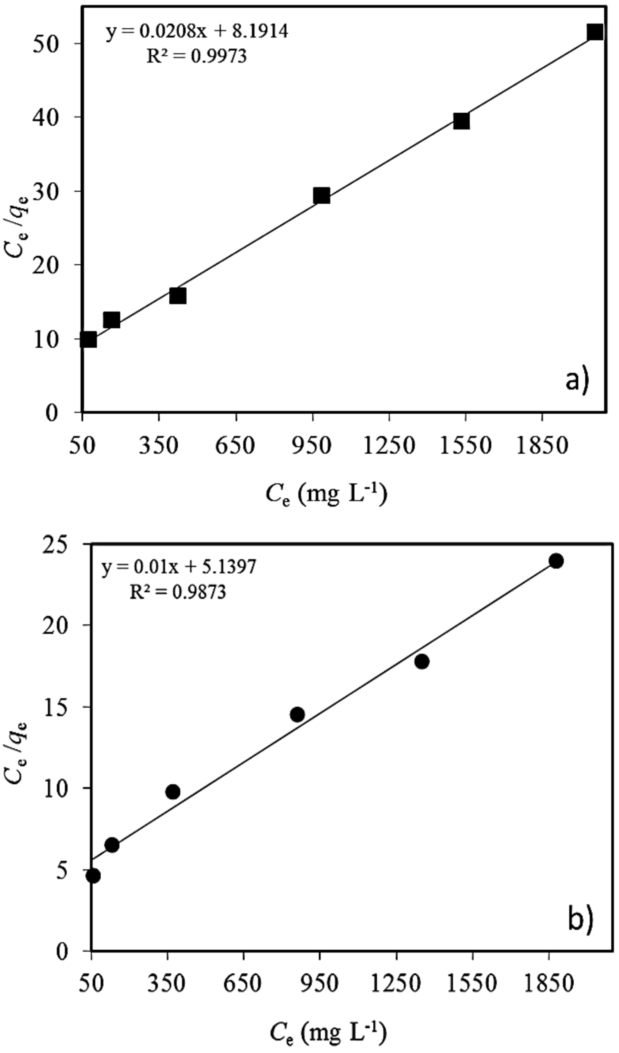

Figure 6. Langmuir isotherm model plotted for a) NOS b) HMOS.

One of the most important benefits of the Langmuir isotherm model is that it can be applied in the calculation of the maximum adsorption capacities of the adsorbents. By using the Langmuir isotherm model the maximum Cr(VI) adsorption capacity of NOS and HMOS has been calculated as 48.07 and

100.00 mg g^{-1}, respectively. As can be noticed from these values, as a result of the modification process of oak sawdust with H_2SO_4, Cr(VI) adsorption capacity has increased by about 100%. The maximum Cr(VI) adsorption capacity of NOS and HMOS has also been compared with the adsorbents previously used in the removal of Cr(VI) ions in the literature (Table 2). As seen in Table 2, the maximum Cr(VI) adsorption capacity of NOS and HMOS is better than many adsorbents given in the literature [31-39]. This comparison showed that NOS and HMOS can be utilized as effective and low-cost adsorbents in the removal of Cr(VI) ions from aqueous media.

Table 1. The isotherm parameters of Cr(VI) adsorption.

Langmuir isotherm model	**NOS**	**HMOS**
q_{max} (mg g^{-1})	48.07	100.0
b (L mg^{-1})	0.0025	0.0019
R^2	0.9973	0.9873
Freundlich isotherm model		
K_f (mg g^{-1})	0.99	1.36
n	1.98	1.81
R^2	0.9514	0.9930

The Langmuir and Freundlich isotherm models are also used to give an idea about the suitability of the studied adsorption system. For this purpose, the R_L values, indicating whether the adsorption process is suitable for the adsorbent-adsorbate pair, have been calculated using the Langmuir isotherm constant b. By increasing the initial Cr(VI) concentration from 100 mg L^{-1} to 2300 mg L^{-1}, the R_L values for NOS and HMOS varied between 0.81-0.18 and 0.18-0.01, respectively, suggesting that the adsorption of Cr(VI) ions onto both NOS and HMOS is favorable. Besides, n values calculated from the Freundlich isotherm model were determined as 1.98 and 1.81 for the adsorption of Cr(VI) ions onto NOS and HMOS, respectively. This result also supports the suitability of the adsorption process [40].

3.6. Effect of salt concentration

Industrial wastewaters contain various salts that generate ionic strength as well as toxic organic or inorganic pollutants. Such salts cause various effects by increasing or decreasing the pollutant removal efficiency. For this reason, it is significant to investigate the influence of ionic strength in order to evaluate the applicability and efficiency of the adsorption process applied to remove the heavy metal ions from waters and wastewaters.

The NaCl and $BaCl_2$ were chosen as model salts to evaluate the effects of ionic strength on the uptake of Cr(VI) ions by HMOS. For this purpose; the Cr(VI) solutions at an initial concentration of 230 mg L^{-1} (at initial pH of 2.5) containing 0.05 g HMOS were treated with NaCl and $BaCl_2$ solutions in the concentration range of 0.05-0.5 M, separately at optimized equilibrium time.

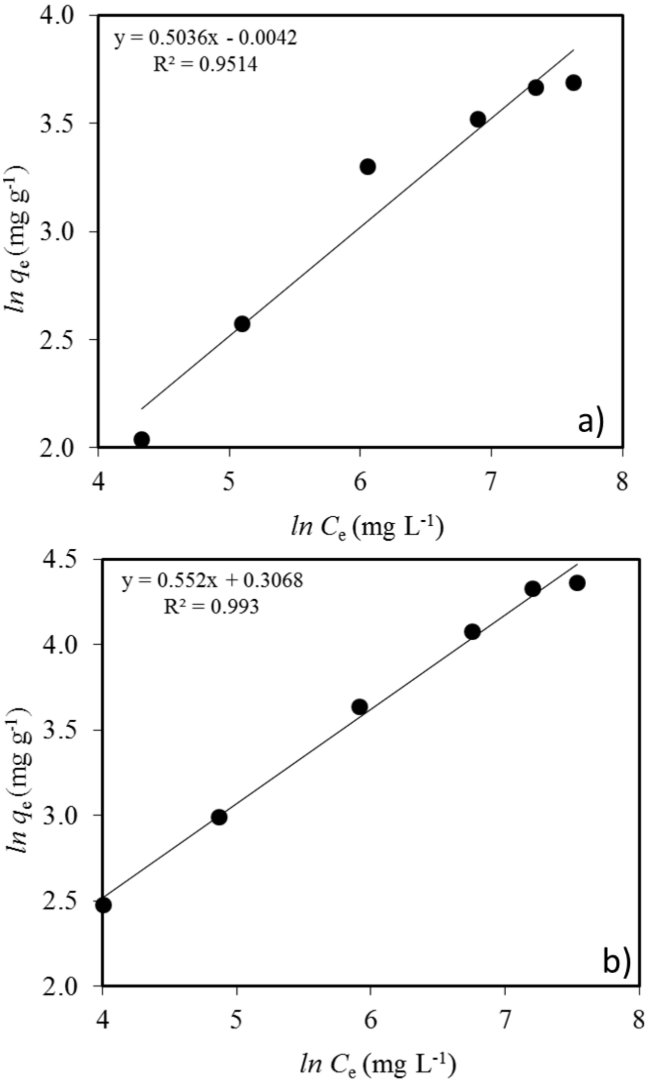

Figure 7. Freundlich isotherm model plotted for a) NOS b) HMOS

By increasing the NaCl and $BaCl_2$ concentrations from 0.05 M to 0.50 M; the Cr(VI) adsorption efficiency on HMOS decreased from 19.8 mg g^{-1} to 10.14 mg g^{-1} and from 14.12 mg g^{-1} to 7.66 mg g^{-1}, respectively (Fig. 8). It is clearly seen that a significant decrease in Cr(VI) adsorption amount occurs by increasing the salt concentration. This decrease in Cr(VI) adsorption as a result of the increase in salt concentration is thought to be caused by two reasons: i) The competition effect of salt anions (Cl^-) with Cr(VI) ions which present in an anionic form in aqueous solution to adhere the active adsorption surfaces of HMOS. ii) The screening of the electrostatic interaction between the Cr(VI) ions and the active adsorption sites of the HMOS due to the presence of ions in the adsorption medium [41,42].

Table 2. Comparison of the Cr(VI) uptake capacities of the different sorbents in the literature.

Adsorbent	**Adsorption capacity (mg g^{-1})**	**Reference**
Cetylpyridinium chloride modified montmorillonite	43.84	[31]
Magnetic phoenix tree leaves-derived biochar composite	55.0	[32]
Chemically modified date pits	82.63	[5]
Chemically modified olive stone	53.31	[5]
Fe_3O_4@ chitosan composite	21.04	[33]
Longan seed activated carbon	35.02	[34]
Apple peels activated carbon	36.01	[35]
Waste newspaper	59.88	[36]
Almond shell	3.4	[37]
HCl treated sawdust	6.34	[38]
Eucalyptus camaldulensis sawdust	35.58	[39]
Natural oak sawdust	48.07	This work
H_2SO_4 modified oak sawdust	100.0	This work

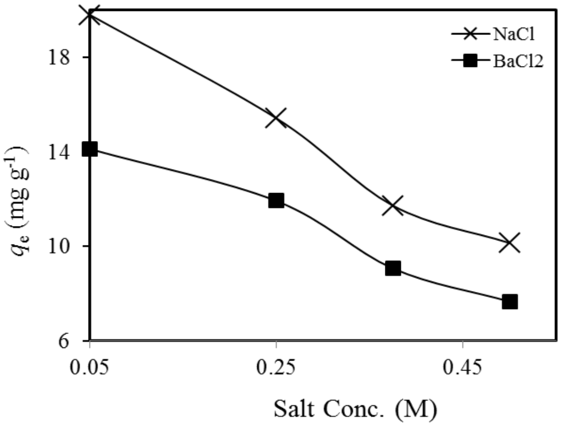

Figure 8. Effect of salt concentration on the adsorption of Cr(VI) ions onto HMOS (initial Cr(VI) concentration: 230 mg L^{-1}; initial pH: 2.5; HMOS concentration: 5.0 g L^{-1}, contact time: 240 min).

4. Conclusions

In the present research, the usage of the waste material, H_2SO_4 modified oak sawdust (HMOS), to remove Cr(VI) ions from waters and wastewaters has been evaluated. Although there are some studies in the literature that natural or modified oak sawdust have been used as sorbents for the uptake of different pollutants from aqueous media, the H_2SO_4 modified oak sawdust has been used for the first time in the removal of Cr(VI) ions in this investigation. The experimental results indicated that the process is highly pH-dependent and the optimum Cr(VI) uptake was observed at initial solution pH 2.5. The equilibrium was reached within 240 min of shaking time. Although the presence of other ions (Na^+, Cl^-, Ba^{2+}) in aqueous solutions has remarkable effects on Cr(VI) adsorption, approximately in the rate of 100% of adsorption efficiency has been achieved under the optimized conditions. The equilibrium adsorption data have been evaluated in terms of Langmuir and Freundlich isotherm models and both model fitted well to the experimental data which indicating the homogeneous and heterogeneous distribution of the active adsorption sites on the natural oak sawdust (NOS) and HMOS surface. The maximum adsorption capacities of NOS and HMOS have been obtained as 48.07 and 100.0 mg g^{-1}, respectively with the application of the Langmuir isotherm model. As a result, it has been concluded that the HMOS appears to be an effective, low cost and promising adsorbent for the removal of Cr(VI) ions as compared to many other adsorbents previously reported in the literature.

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