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Hexavalent chromium removal from aqueous solutions by biosorbents (non-living activated sludge)

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ABSTRACT

The removal of hexavalent chromium from aqueous solution was examined by the adsorption process using non-living activated sludge as an absorbent. The kinetics of the hexavalent chromium removal were examined in batch experiments for the concentrations between 1 and 20 mg/L hexavalent chromium solutions. The adsorbent dosage applied was 0.1 g dry weight of adsorbent/250 mL for the non-living activated sludge. Four different mixing times ranging from 30 to 120 min and six different pH values between 2 and 7 were assessed to find out the optimum mixing time and pH value. The removal efficiencies were above 56% for all hexavalent chromium concentrations and mixing times. The 250-rpm shaker speed at pH 2 gave the highest removal efficiency. The adsorption kinetics can be described by the pseudo-first-order and pseudo-second-order kinetic models. The rate constants were evaluated for all hexavalent chromium concentrations. This study showed that the hexavalent chromium adsorption kinetics of the non-living activated sludge fitted quite well to the pseudo-second-order kinetic model than the pseudo-first-order kinetic model. This reveals that it is comparative to the square of the concentration of chromium adsorption rate. These results show that non-living activated sludge could be effectively used as a low-cost and alternative absorbent for the removal of hexavalent chromium from aqueous solution.

Keywords: Hexavalent chromium; Non-living activated sludge; Batch adsorption; Kinetic model; Cost-efficient adsorbent

1. Introduction

Chromium is a metal which naturally occurs and is present in little quantities. Recently, chromium pollution has increased in the environment by human activities, so adverse effects on human health and the environment could be observed, in particular for hexavalent chromium Cr(VI) and its compounds [1]. Water pollution caused by chromium is a significant concern due to the widespread use of chromium in leather, nuclear power plant, textile industries, and electroplating [2,3]. There are various oxidation states of chromium ranging from −IV to +VI. The chromium compounds exist in various distorted geometries such as square planar, tetrahedral, and octahedral [4]. The two main oxidation steps of chromium in water are Cr(III) and Cr(VI), and they vary by their toxicological

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and biological properties. Cr(VI) is reported as a strong oxidizing agent and is also toxic and carcinogenic for human and animals and is 500 times more poisonous than Cr(III), while Cr(III) is a crucial nutrient for the glucose metabolism of human [5–9]. Hexavalent chromium can cause serious skin sensitivity and also can origin sensitization of lungs [4,10].

Hence to avoid further impact on the environment, Cr(IV) has to be removed from the wastewaters before they are discharged into any type of water sources. Many methods and techniques have been investigated to remove the chromium from the water such as reverse osmosis, ion exchange, and adsorption [8,11]. All of these methods have been employed and have flourished in removing an impressive percentage of Cr(IV) from the wastewater, but the adsorption method stands out to be one of the most versatile methods due to its flexibility and simplicity [8,11]. Even though the removal of Cr(VI) with activated carbon is efficient, its use is partial owing to the expense of activated carbon [12]. So cost-efficient alternative adsorbents are required. The purpose of this study is to investigate the removal of hexavalent chromium using activated sludge as an absorbent in batch experiments.

2. Experimental

All of the chemicals used were of analytical reagent grade, free from chromium traces. Ultrapure water was used throughout the entire study. All chemical analyses were carried out according to the standard methods [13]. A UV–visible spectrophotometer (Hach Lange DR 5000 Model) was used for hexavalent chromium analysis at the wavelength of 543 nm. A pHmeter (Hach Lange HQ40D Model) was used to measure pH which is adjusted with 0.1 N NaOH and 0.1 H_2SO_4.

2.1. Stock chromium solution

A known weight of 282.8 mg of $K_2Cr_2O_7$ (Sigma-Aldrich, AR) was dissolved in water and diluted to 1,000 ml (1.00 ml = 100.0 μg Cr(VI)).

2.2. Biosorbents

Non-living activated sludge used for the study was collected from a laboratory-scale sequencing batch reactor (SBR) fed with glucose as the sole carbon source [14]. The biosorption performance can be controlled by the basis and character of the biosorbents such as their functional groups, physical structure, and chemical nature [12]. The Fourier transform infrared (FTIR) spectra of activated sludge in the range of 4,000–400 cm^{-1} were obtained to classify the functional groups in the biosorption using a FTIR spectroscope [14] (Perkin–Elmer Spectrum two FTIR spectrometer & ATR) (Fig. 1).

The band at 3,265 cm^{-1} revealed N–H stretching vibrations of amine groups on the surface of the activated sludge, and the band at 2,913 cm^{-1} would be due to an asymmetric vibration of C–H [12]. The band 1,724 cm^{-1} was a product of the stretching vibration of C–H of aldehyde [12]. A distinct band at 1,621 cm^{-1} was the consequence of the stretching vibration of C–O and C–N (Amide I) peptidic bond of protein [12]. The 1,508 cm^{-1} band could be due to a combination of the C–N stretching and deformation of N–H (Amide II) protein peptide bond [12]. The band at 1,386 cm^{-1} could be assigned to the symmetrical stretching vibration of C–O of carboxylate and deformation vibration of O–H of alcohols. The band at 1,216 cm^{-1} implied the C–N stretching of Amide III. Bands at 1,031 and 1,018 cm^{-1} could be attributed to the stretching vibration of O–H of polysaccharides. The band at 870 cm^{-1} reflected C–O stretching vibrations [12].

The attraction of biosorbents to adsorbate is decided primarily by hydrophobic, π−π, H-bonding, and electrostatic contacts. Functional groups can change hydrophobicity, π–π, H-bonding, and electrostatic interactions of biosorbents [15]. For example, C=O, C–O, and O–H functional groups on non-living sludge surface have negative effects on adsorption. On the contrary, N–H and C–H functional groups on non-living sludge surface have positive effects.

2.3. Batch adsorption experiment

An orbital shaker (Heidolph, Unimax 1010 Model) was used for batch studies and various concentrations of hexavalent chromium prepared by the diluted stock chromium solution were tested. Standard solutions were placed in 100-mL conical flasks as final volume of 50 ml and were shaken [16]. The adsorbent dosage corresponding to 0.1 g dry weight was added into each conical flask during all experimental studies. The effect of pH on the removal efficiency of hexavalent chromium was studied by varying the pH from 2 to 7 [17]. There is no obtained result at pH values greater than 7 in this study because chromium ions tend to settle as chromium hydroxide at pH levels more than 7 [18]. To determine the effect of the shaker speed on the removal of hexavalent chromium, the experiments were carried out at different stirring speeds from 30 to 300 rpm. The equilibrium kinetic studies were carried

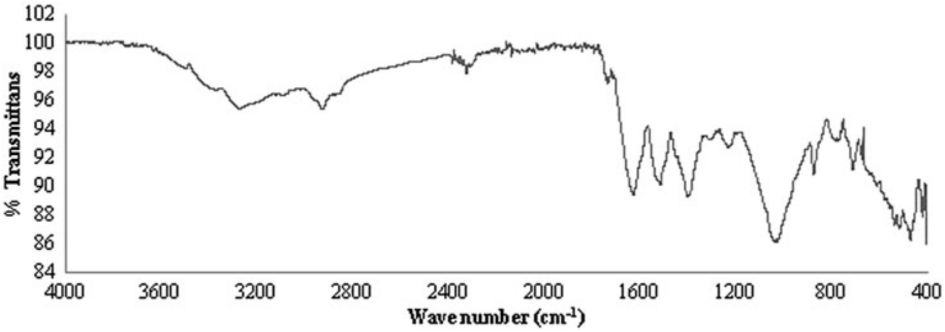

Fig. 1. FTIR spectra of non-living activated sludge.

out at five different concentrations of 1, 5, 10, 15, and 20 mg/L of chromium solutions whose pH values were adjusted to 2 [16].

3. Results and discussion

3.1. Effect of pH

The adsorption of heavy metals from wastewater is affected by pH in a great matter [19]. Removal efficiencies of Cr(VI) on the waste sludge at different pH values are shown in Fig. 2 (the initial concentration of Cr(VI) is 5 mg/L, the mixing time is 60 min, and the shaker speed is set to 200 rpm). The optimum pH was observed as 2 with 73% removal of Cr(VI) which showed the process was encouraged in an extremely acidic medium.

Chromium, in aqua solutions, exists commonly in two oxidation states, Cr(VI) and Cr(III), and the pH of the solution affects the constancy of these types [17]. It is well known that the principal form of Cr(VI) at pH 2.0 is $HCrO_4^-$ [20]. An increase in the pH shifts the concentration of $HCrO_4^-$ to other forms, such as CrO_4^{2-} and $Cr_2O_7^{2-}$. Maximum adsorption at pH 2 showed that the dominant species of Cr(VI) was $HCrO_4^-$.

Previous studies demonstrated that the overall pH effects were dependent on the balance between all positive and negative interactions [21,22]. In this study, both the positive effect of low pH and the negative effect of high pH were observed for the adsorption. The surface of waste sludge might become more negatively charged as the pH increases, leading to the increase in the electrostatic repulsion between adsorbates and waste sludge [21,23–27]. This observation can be attributed to that increasing pH made possible deprotonation of acidic functional groups of waste sludge, which encouraged π–electron donor ability of the waste sludge surface (–O– is a stronger electron donor than –OH), which was reduced greatly with increasing pH due to increase in electrostatic repulsion [21].

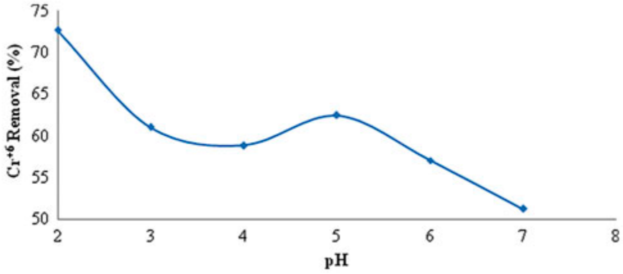

Fig. 2. The pH effect on chromium removal efficiency.

3.2. The effect of shaker speed

The speed of the shaker has a significant part in the mass transfer of chromium for the adsorption process [16]. The effect of speed on chromium removal efficiency was shown in Fig. 3.

The maximum removal efficiency of hexavalent chromium was found using 250-rpm shaker speed. This could be due to the fact that higher speeds influence the desorption rate [16].

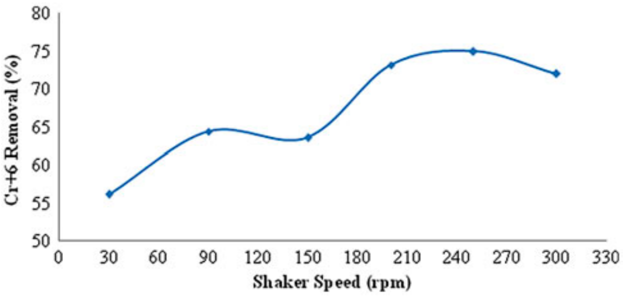

Fig. 3. The shaker speed effect on chromium removal efficiency.

3.3. Adsorption kinetics

Removal efficiencies of Cr(VI) by the non-living activated sludge at various mixing times, the initial concentrations at pH 2, and the shaker speed of 250 rpm are shown in Fig. 4.

The experimental adsorption kinetic data were fitted with pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetic models.

The adsorption kinetics explained by PFO equation is generally given as [16]:

$$\log(q_e - q) = \log q_e - (k_1/2.303)t \tag{1}$$

where q_e and q are the amounts of Cr(VI) adsorbed (mg/g) at time t (min) and at equilibrium time, respectively, and k_1 is the equilibrium rate constant of PFO adsorption (1/min) [16]. The Eq. (1) was plotted for all concentrations (1–20 mg/L).

All five concentrations showed almost linear plots (Fig. 5). The kinetic constants, k_1, obtained from the slopes of the plots are shown in Table 1. The minimum correlation coefficient attained from the PFO kinetic was 0.6830 while the biggest one was 0.9820.

The adsorption kinetics explained by PSO equation is given by the following equation [15]:

$$dq/dt = k_2(q_e - q)^2 \tag{2}$$

where k_2 is the rate constant in g/mg min. Integration of Eq. (2) for the boundary conditions, $t = 0$ to $t > 0$ and $q = 0$ to $q > 0$, and then rearrangement yield the following linear form [16]:

$$1/q_t = 1/k_2 q_e^2 + t/q_e \tag{3}$$

This model can be applied by the linear plot of (t/q) vs. t for adsorption kinetics of Cr(VI) and is presented in Fig. 6. The values of k_2 were determined from the intercepts [17]. The minimum and the maximum correlation coefficients taken from the PSO kinetics were 0.9351 and 0.9999, respectively, and they are better than the correlation coefficients of the PFO kinetics (Table 2).

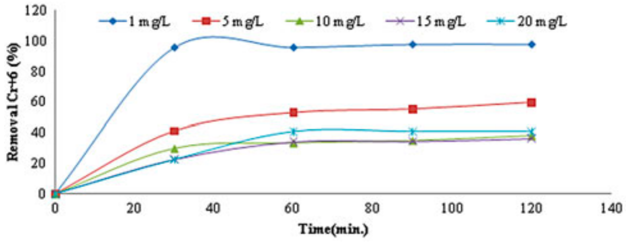

Fig. 4. Removal efficiency of Cr(VI) by the non-living activated sludge at various mixing times and initial concentrations.

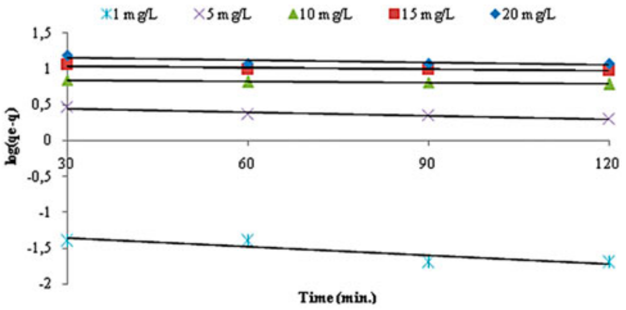

Fig. 5. PFO kinetics of non-living activated sludge (pH 2).

Table 1
PFO rate constants for 1–20 mg/L initial concentrations

Initial Concentration (mg/L)	k_1 (min^{-1})	R^2
1	0.0092	0.8000
5	0.0040	0.9210
10	0.0014	0.9820
15	0.0020	0.7390
20	0.0027	0.6830

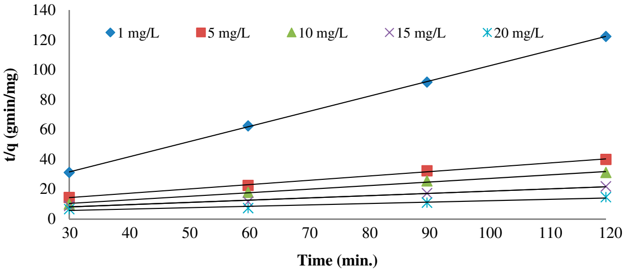

Fig. 6. PSO kinetics of non-living activated sludge (pH 2).

Table 2
PSO rate constants for 1–20 mg/L initial concentrations

Initial Concentration (mg/L)	k_2 (g/mg min)	R^2
1	0.7941	0.9999
5	0.0143	0.9978
10	0.0172	0.9947
15	0.0061	0.9849
20	0.0028	0.9351

4. Conclusion

The removal of hexavalent chromium by biosorption was studied using some kinds of tree dusts, leaf dusts, and saw dusts which was found to be an effective biosorbent for the removal of hexavalent chromium at acidic pH from contaminated water [28–31]. In this study, the adsorption of hexavalent chromium with non-living sludge was stated as an effective method and the results obtained are similar to ones in these studies. It has a capability of removing 56% of hexavalent chromium at concentrations of 1–20 mg/L for all mixing times. The adsorption process was greatly affected by the pH of the adsorbate solution. The adsorption kinetics were well classified by PSO kinetics instead of the PFO kinetics. In addition, functional groups on non-living sludge surface were considered to have effects on the adsorption processes. The activated sludge can act as a good adsorbent for the adsorption of chromium from industrial effluents such as electroplating industries.

List of symbols

q_e — the amount of Cr(VI) adsorbed (mg/g) at time
q — the amount of Cr(VI) adsorbed (mg/g) at equilibrium time
k_1 — the equilibrium rate constant of pseudo-first-order adsorption (1/min)
k_2 — the equilibrium rate constant of pseudo-second-order adsorption (g/mg min)
t — time (min)

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