

A STUDY ON THE REDUCTION OF HEXAVALENT CHROMIUM IN AQUEOUS SOLUTIONS BY VINASSE

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ABSTRACT

Hexavalent chromium introduced to the water ecosystem is an important issue due to the toxic effect it poses. The first step of conventional treatment of wastewaters containing hexavalent chromium is its reduction to chromium (III) which is less toxic. The use of industrial waste material for the reduction of chromium (VI) may be a new cost-effective alternative. In this study, Cr(VI) reduction characteristics of vinasse which is a waste material of alcohol production from sugar beet molasses was investigated. The parameters of pH, temperature, concentrations of initial Cr(VI) and vinasse on the reduction of Cr(VI) were examined as a function of time by applying batch tests. Cr(VI) was almost completely reduced within about 270 min in the concentrations of Cr(VI) and vinasse of 80 mg l⁻¹ and 200 ml l⁻¹, respectively, at pH 3.0 and 25°C. The results showed that reduction time can be shortened by increasing acidity and vinasse concentration or decreasing Cr(VI) initial concentration. Cr(VI) reduction process was found to obey first order kinetic model of homogenous phase reactions. The temperature was found to have a positive effect on the reduction process and the activation energy of process was calculated as 46.07 kJ mol⁻¹. Although the detoxification of wastewaters containing Cr(VI) via reducing it to Cr(III) by using vinasse seems to be cost-effective, the resulting effluent to be produced necessitates a further treatment to reduce organic pollution.

Key words: Hexavalent chromium, reduction, detoxification, vinasse, distillery waste.

INTRODUCTION

The widespread application of chromium compounds in industrial processes such as tanning, plating, alloying, manufacturing of pigments and chemicals, corrosion prevention etc. has led to its introduction into the environment. Chromium contamination of ecosystems is a significant problem worldwide. The most stable oxidation states of chromium are Cr(III) and Cr(VI) in aqueous systems. The hexavalent form of chromium is highly toxic, mutagenic and potentially carcinogenic to living organisms. [1,2] Trivalent chromium is quite immobile in the water environment because of limited solubility of its hydroxide which is readily formed in the pH range of natural waters. However, complexing agents may prevent hydroxide precipitation due to forming complex compounds [3, 4].

Due to the emphasis placed on protection of the environment, the detoxification of chromium has recently gained importance. Because of the benign character of Cr(III), detoxification and immobilization processes of Cr(VI) is based on its reduction to Cr(III). Conventionally, the reduction of Cr(VI) is performed by using SO₂ and sulfide salts and ferrous

sulfate in the processes practiced [4-7]. Besides using various inorganic materials, the reduction of hexavalent chromium by using organic substances [8-16], agricultural by-products [17-18] and microorganisms [19-23] has been widely investigated with various purposes of characterization, detoxification and removal. Finding the cost effective reductants requires further investigation in the field of natural materials, industrial and agricultural wastes or by-products. In recent studies, our efforts have been focused on Cr(VI) reduction by using low-cost materials [24-27].

The alcohol production from molasses, which is a by-product of the sugar industry, generates a dark brown effluent, called vinasse, with a high organic matter content frequently more than 50 g-COD l⁻¹. Unregulated disposal of this liquid waste causes environmental problems such as ground water contamination, strong smells, appearance of insects and other nuisances.

The vinasse loaded with organic matter in high level may reduce the Cr(VI), thus, the resulting wastewater could be treated altogether. As an introduction, in this study, Cr(VI) reduction by vinasse is aimed. For this purpose, the parameters of pH, temperature, initial Cr(VI) concentration and amount of vinasse on the reduction of Cr(VI) were

examined and kinetic evaluations were made.

MATERIALS AND METHODS

Vinasse was provided from the alcohol unit of a sugar factory located in Malatya, Turkey. The vinasse sample was stored at +4°C in a refrigerator during the experimental study. The chemical oxygen demand (COD) of vinasse was determined titrimetrically by means of the dichromate method [28, 29]. Total solid content of vinasse was determined by evaporating 100 ml of vinasse at 50-60°C and drying at 105°C until constant weight. The residue obtained after drying was incinerated at 550°C to determine fixed and volatile residue contents of the vinasse [28].

Stock Cr(VI) solution (1000 mg l⁻¹) was prepared by dissolving 2.837 g of 99.7 % K₂Cr₂O₇ in about 250 ml of distilled water and diluting to 1000 ml. The working solution of 100 mg-Cr(VI) l⁻¹ was prepared by diluting the stock solution with distilled water.

Reduction experiments were carried out using a continuously shaken batch system. To do this, predetermined volumes of Cr(VI) solution and vinasse were mixed in a 500 ml glass bottle and if required, the distilled water was used as diluent to obtain desired Cr(VI) and vinasse concentrations ranging from 20 to 80 mg l⁻¹ and 40 to 200 ml l⁻¹, respectively. To obtain different initial pH values for each working mixtures, a required amount of sulfuric acid was added to the Cr(VI) solution before mixing. Following the mixing, if required, dilution was made with distilled waters the pH of which was finely adjusted and then the time was commenced. The flasks containing reaction mixture were shaken at constant rate (200 cycle min⁻¹) using a flask shaker with a thermostatic water bath (Clifton). At the end of the predetermined time, 10 ml of mixture was automatically pipetted and then analyzed for Cr(VI). The reduction yield of Cr(VI) was calculated by difference in initial and final concentrations of mixture. The analysis of Cr(VI) was carried out colorimetrically with the 1,5 diphenyl carbazide method [28] by a UV-1201V Model Shimadzu spectrophotometer. All experiments were conducted in duplicate and average values were reported.

RESULTS AND DISCUSSION

Characterization tests show that vinasse contains a high amount of organic matters. Because of quite transparent appearance and low turbidity value, it can be noted that most of the organics are in soluble form in the vinasse. The characteristics of vinasse sample used in the study are presented in Table 1. Preliminary tests showed that the reduction of Cr(VI) by vinasse occurred more rapidly in acidic medium. The following general equation can be written to describe the reduction phenomenon.

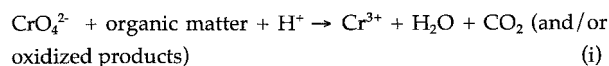


Table 1. Characteristics of vinasse.

Characteristics	Values
pH	5.28
Turbidity, NTU	0.83
Density, g cm ⁻³	1.094
COD, mg-O ₂ l ⁻¹	63200
Total residue (105°C), g l ⁻¹	104.10
Fixed residue (550°C), g l ⁻¹	31.40
Volatile residue (105-550°C), g l ⁻¹	72.70
Na, mg l ⁻¹	2300
K, mg l ⁻¹	9100

Effect of pH

Firstly, the effect of the pH of the solution on the reduction yield was investigated. In a series of experiments, the reduction of Cr(VI) was systematically tested in the solutions having initial pHs 1.5, 2.0, 2.5 and 3.0 (± 0.05). The Cr(VI) and vinasse concentration in these solution were taken as 80 mg l⁻¹ and 200 ml l⁻¹, respectively. The experiments were conducted until chromium (VI) concentration drops below the detection limit of 0.1 mg-Cr(VI) l⁻¹. This value corresponds to 99.88 % of Cr(VI) reduction for a 80 mg l⁻¹ initial Cr(VI) concentration. The results of these experiments are shown in Figure 1.

In order to determine the reduction rate constants, first order kinetic model was applied to the experimental data. This kinetic model can be expressed as follows.

$$-\ln(1-x) = k t \quad (\text{ii})$$

where, x is the fraction of conversion of Cr(VI) at the end of any time t (min); k (min⁻¹) is rate constant for the reduction process.

The pH dependence of rate constants is depicted in Figure 1b. It can be said that the plots of -ln(1-x) versus t display a good linear relation since the correlation coefficients (r²) calculated are high enough. The first order rate constants (k) calculated from the slopes of plots were found to be 0.1067, 0.0880, 0.0527 and 0.0249 min⁻¹ for pHs 1.5, 2.0, 2.5 and 3.0, respectively. It is clearly seen that increasing acidity shortens the time required for the reduction of whole Cr(VI) in the solution. For example more than 99.88 % of Cr(VI) was reduced to Cr(III) within about 62, 75, 130 and 270 min for initial pH 1.5, 2.0, 2.5 and 3.0 (±0.05), respectively. In a study carried out by soil fulvic acid to reduce Cr(VI), it has been reported that the rates of reduction were strongly pH dependent and increased with decreasing pH [11]. Elovitz and Fish [9] have pointed out that reaction rates increased as much as 4 orders of magnitude from pH 5 to 1 in the study where the reduction of Cr(VI) by substituted phenols was investigated. Yurkow et al. [16] have observed that more

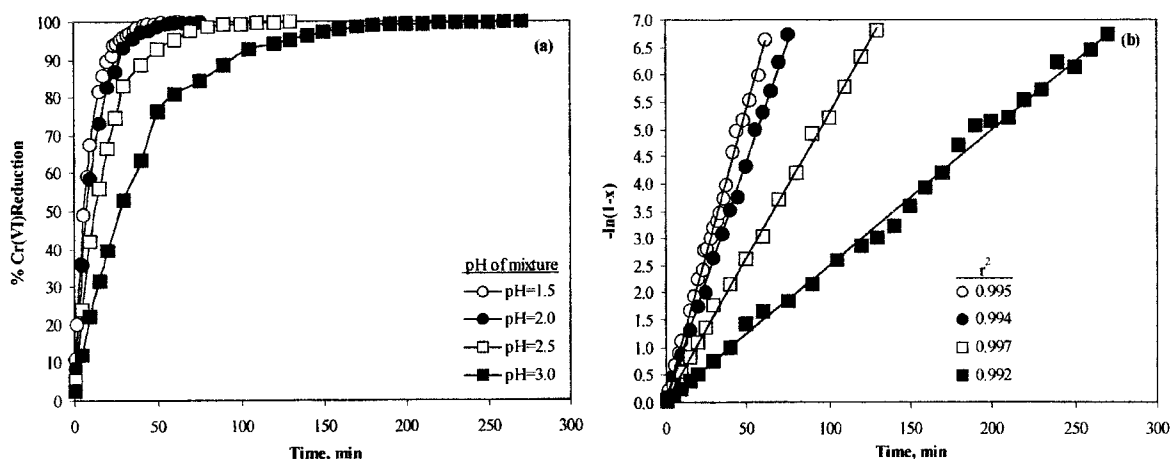


Figure 1. Effect of pH on the Cr(VI) reduction by vinasse (vinasse conc.: 200 ml l⁻¹; Initial Cr(VI) conc.: 80 mg l⁻¹; temperature: 25 °C).

hexavalent chromium was reduced by glycerol in acidified medium than neutral one. It has been stated that certain primary alcohol groups can chemically reduce Cr(VI) in reactions containing strong acids to produce Cr(III). [30] In our recent study [27], Cr(VI) reduction by sugar beet pulp press water was also found to be pH dependent, however, the reduction process obeyed second order kinetic model and reaction rates were slower compared to those of vinasse. Although the reduction of Cr(VI) by vinasse has not been characterized or described in detail, it can be stated that the functional groups of reductant such as alcohol, aldehyde etc. in the compounds present in the vinasse may govern the Cr(VI) reduction.

Effect of Temperature

Figure 2 shows the results of the experiments carried out at 25, 40 and 60°C. The data presented in the figure were obtained from the experiments conducted by processing a Cr(VI) solution-vinasse mixture in the concentrations of 80 mg l⁻¹ Cr(VI) and 200 ml l⁻¹ vinasse at pH 3.0 (±0.05). It is clearly seen that the temperature of the mixture has a positive effect on the reduction of Cr(VI). At the end of reaction time of 30 min, the reduction yields of Cr(VI) were found to be 52.62 %, 82.08 % and 99.48 % for the temperatures of 25, 40 and 60°C, respectively. The time required for the concentration of Cr(VI) in the mixture to drop to the

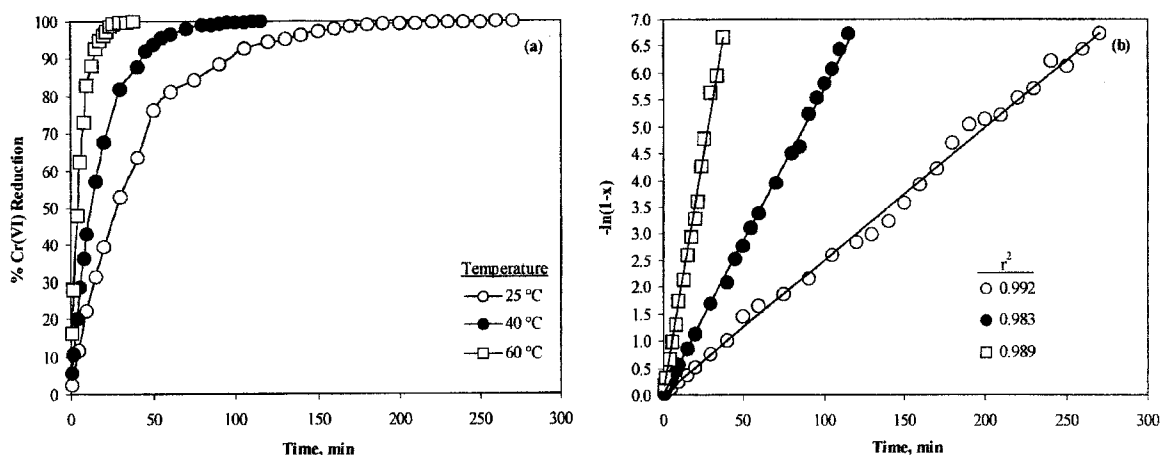


Figure 2. Effect of temperature on the Cr(VI) reduction by vinasse (vinasse conc.: 200 ml l⁻¹; Initial Cr(VI) conc.: 80 mg l⁻¹; pH: 3.0).

detection limit was observed as 38 min at 60°C. However, by an extrapolation, the time required for reduction of whole Cr(VI) in the mixture can be calculated as about 79 min. The increase in the reduction yield with temperature indicated that this process is endothermic. In our previous studies, the reduction process of Cr(VI) by sugar beet pulp press water [27] and synthetic iron sulfide [26] were also reported as endothermic.

In addition, the data obtained at different temperatures were analyzed according to the first order kinetic model (Figure 2b). The values of rate constants calculated from the slopes of the lines were 0.0249, 0.0573 and 0.1752 min⁻¹ for 25, 40 and 60 °C, respectively. That the values of rate constants increased with temperature show the applicability of reduction process more effectively at higher temperatures.

Activation energy of the reduction process was determined using Arrhenius equation [31] given as:

$$k = k_0 e^{-E_a/RT} \quad (\text{iii})$$

where T is absolute temperature, E_a is the activation energy and R is the perfect gases constant. Activation energy of the process was calculated as 46.07 kJ mol⁻¹ by plotting lnk versus 1/T at the temperature range examined (Figure 3). In our previous study, it has been reported that the value of

activation energy was about 64 kJ mol⁻¹ for the Cr(VI) reduction process conducted by sugar beet pulp press water at even strong acidic condition (pH 2.0) and lower Cr(VI) concentration (20 mg l⁻¹). That the vinasse has a lower value of activation energy compared to that of sugar beet pulp press water, can be stemmed from the high organic matter content and high reducing ability of vinasse.

Effect of Initial Cr(VI) Concentration

The influence of initial Cr(VI) concentration on the reduction process and the first order kinetic model evaluations are given in Figure 4. These results were obtained from a series of the mixtures which contain Cr(VI) in the concentrations ranged from 20 to 80 mg l⁻¹ and 200 ml l⁻¹ vinasse at pH 3.0 (±0.05) and 25°C. As seen from Figure 4a, for the mixture with a concentration of 20 mg l⁻¹ Cr(VI), the required time to achieve detection limit, corresponding to 99.5 % of reducing yield, was found to be about 10 min. The reaction time required to reach the detection limit for the mixtures in the Cr(VI) concentration of 40, 60 and 80 mg l⁻¹ are about 85, 205 and 270 min. That the reduction of Cr(VI) was not completed at higher Cr(VI) concentration for a shorter period of time, can be attributed to insufficient concentration of vinasse, since the amount of vinasse added to the Cr(VI) solution is not proportional to the Cr(VI) concentration.

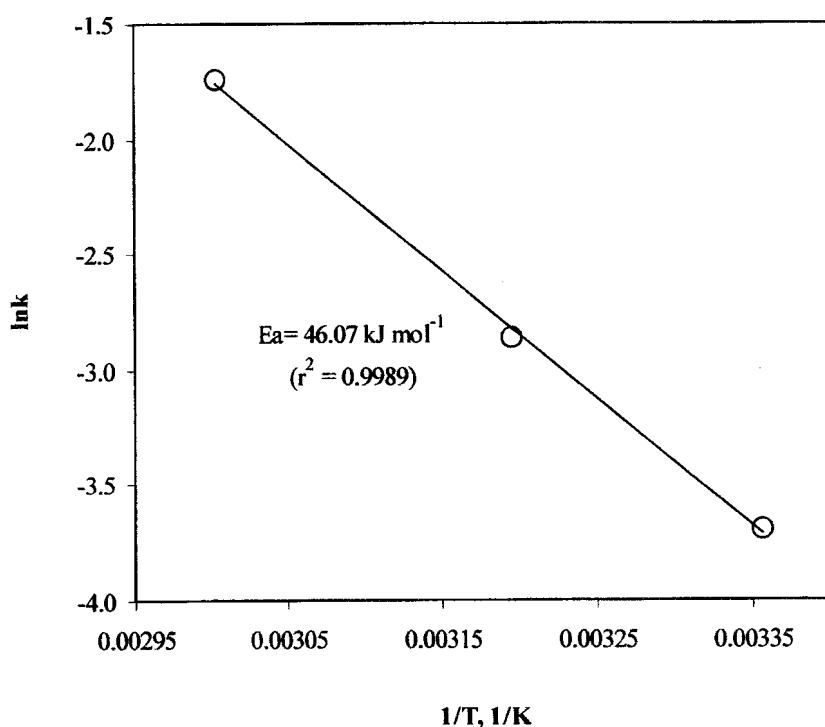


Figure 3. Arrhenius plot for Cr(VI) reduction by vinasse (vinasse conc.: 200 ml l⁻¹; Initial Cr(VI) conc.: 80 mg l⁻¹; pH: 3.0).

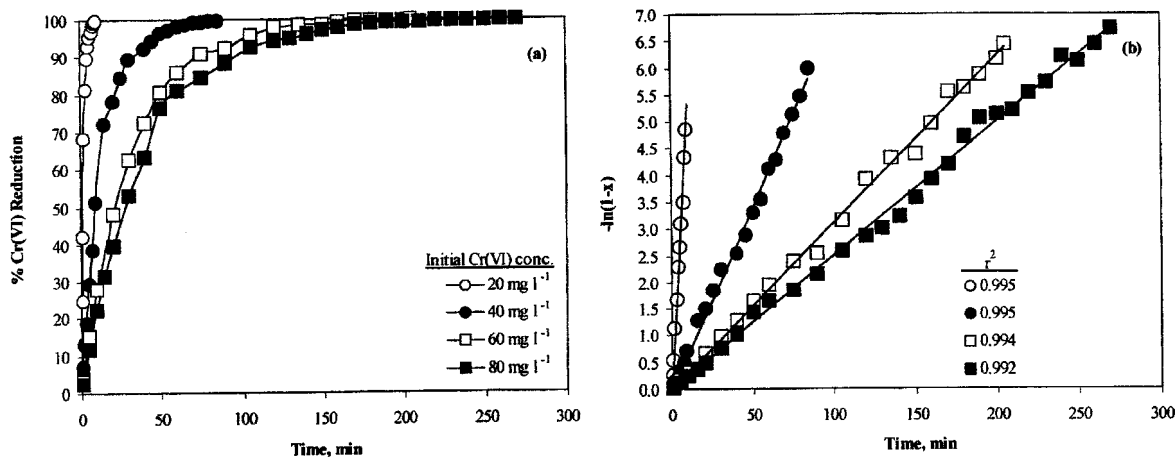


Figure 4. Effect of initial Cr(VI) concentration of mixture on the Cr(VI) reduction by vinasse (vinasse conc.: 200 ml l⁻¹; pH: 3.0 ; temperature: 25 °C).

The variation of reduction rate with initial Cr(VI) concentration is given in Figure 4b. As expected, the reduction rate for the process decreased with increasing initial Cr(VI) concentration. The rate constants were found to be 0.5327, 0.0681, 0.0312 and 0.0249 min⁻¹ for the initial Cr(VI) concentrations of 20, 40, 60 and 80 mg l⁻¹, respectively. As clearly seen, a four fold decrease in initial Cr(VI) concentration can cause about 21 fold increase in reduction rate.

Effect of Vinasse Concentration

The effect of vinasse concentration on the reduction process was examined by combining a certain amount of

Cr(VI) solution (100 mg l⁻¹) with varying amount of vinasse and, if required, with calculated amount of distilled water to obtain initial Cr(VI) concentration of 80 mg l⁻¹ and vinasse concentration ranged from 40 to 200 ml l⁻¹. The results of Cr(VI) reduction percentages as a function of time are presented in Figure 5a. The reduction rate of Cr(VI) increased with vinasse concentration.

The relation between Cr(VI) conversion and reaction time is illustrated in Figure 5b. The rate constants calculated from the slopes of plots were found to be 0.0004, 0.0010, 0.0028, 0.0071 and 0.0249 min⁻¹ for vinasse concentration of 40, 80, 120, 160 and 200 ml l⁻¹, respectively, at pH 3.0, and 25°C. While vinasse in the concentration of 200 ml l⁻¹ could reduce 80 mg l⁻¹ Cr(VI) to the detection limit (0.1 mg l⁻¹) in the

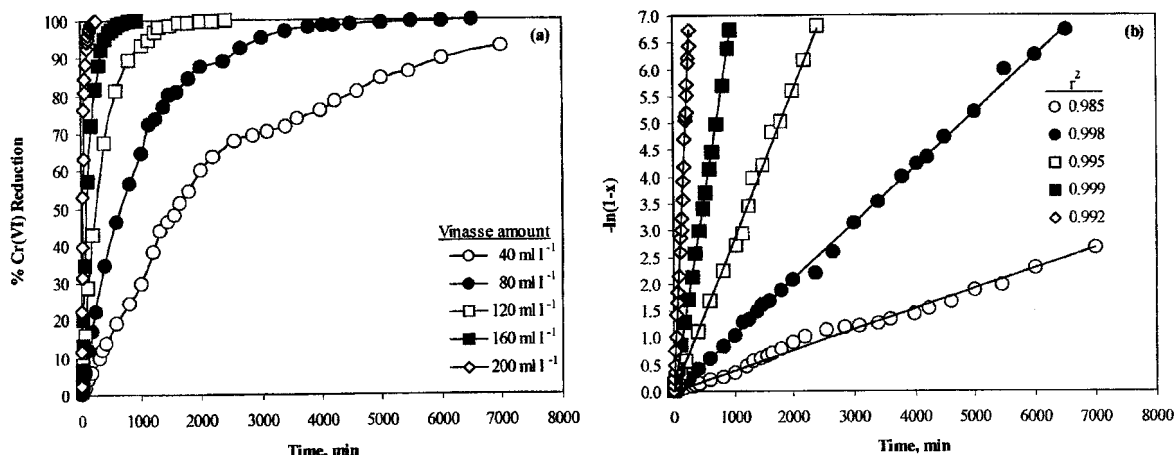


Figure 5. Effect of vinasse concentration on the Cr(VI) reduction by vinasse (initial Cr(VI) conc.: 80 mg l⁻¹; pH: 3.0; temperature: 25 °C).

reaction period of 270 min, reduced amount of vinasse, for example, 40 ml l⁻¹ gives a final concentration of 4.88 mg l⁻¹ within the period of 7000 min studied. However, the required time for obtaining detection limit (or 99.88 % Cr(VI) reduction), can be calculated as 17500 min by extrapolation for 40 ml l⁻¹ vinasse concentration under the conditions mentioned. Additionally, by a simple calculation made as in the former section, it can be found that reaction rate increased about 18 order of magnitude from 40 to 160 ml l⁻¹ of vinasse amount.

CONCLUSION

The data presented here shows that vinasse, the major effluent from the ethanol industry from molasses, can be effectively used for the reduction of Cr(VI) from aqueous solutions. The reduction extent of Cr(VI) is dependent on Cr(VI) and vinasse concentrations, acidity and temperature of mixture. The data obtained at different conditions for the reduction reaction was fitted to the first order kinetic model and rate constants were calculated. In the mixture with the concentrations of 80 mg l⁻¹ Cr(VI) and 200 ml l⁻¹ vinasse, the reduction of Cr(VI) could be almost completed in a period of 270 min at pH 3.0. When the pH of the mixture was decreased

from 3.0 to 1.5, the reduction time of Cr(VI) shortened as much as about 4 fold. By decreasing Cr(VI) initial concentration from 80 to 20 mg l⁻¹, the time required for a practical completion of reduction decreased from 270 to 10 min. When the concentration of vinasse was increased from 40 to 160 mg l⁻¹ for an initial Cr(VI) concentration of 80 mg l⁻¹, the decrease in the time needed for the reduction of Cr(VI) up to the detection limit exhibited a similar trend. On the other hand, with a rise in the temperature of the mixture, the reduction extent of Cr(VI) increased and the time required to reduce the whole Cr(VI) shortened. The activation energy of reduction process was found to be 46.07 kJ mol⁻¹.

As a conclusion, it can be stated that the detoxification of wastewater containing Cr(VI) can be accomplished by vinasse with no-cost reducing the Cr(VI) to Cr(III) which is a benign form of chromium. However, the final effluent with high COD from the reduction process will need further treatment.

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