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# Chrome (VI) Removal from Wastewater Using Water Treatment Plant Sludge as an Adsorbent

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## Abstract

**Background:** The extensive use of chromium in industries such as electroplating, steel production, wood preservation and leather tanning can result in release of chromium containing effluents. Hexavalent chromium in the environment has been often harmful and it should be treated before releasing into the environment. So far various wastewater treatment techniques have been used to remove heavy metals from industrial wastewater. Due to this, adsorbent with high removal capacity, low cost and easy accessibility will be a choice for industrial wastewater treatment option. This study aimed at removing chromium from wastewater using low cost alum based water treatment plant sludge, as an adsorbent.

**Methods:** The study was conducted on removal of Cr (VI) by alum based water treatment sludge through batch adsorption experimental study. Response surface methodology was applied in batch wise experiment to evaluate the process viable, Cr (VI) concentration, pH, adsorbent dose, time and temperature.

**Results:** Chrome (VI) concentration and pH increase was found to decrease chrome removal, while adsorbent dose and shaking time increase, increase chrome removal. Cr (IV) concentration with pH shows that maximum chrome removal 95.62% was obtained at Cr (IV) concentration of 2.4mg/l and pH 2.45, while the interaction of Cr (IV) concentration and adsorbent dose shows, 97.06% chrome removal was obtained at a chrome concentration of 3.3mg/L and adsorbent dose of 6.3g.

**Conclusion:** Alum based water treatment sludge is a suitable material from which a low-cost adsorbent for removal of Cr (VI) can be developed.

**Keywords:** *Alum Based Water Treatment Sludge; Batch Adsorption; Cr (VI); Response Surface Methodology*

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## Introduction

The risks posed by heavy metals in the environment have recently been driving the search for sustainable technologies. Soils, groundwater, sediments, and rivers at many locations have been exposed to the intense pollution from industrial activities. Whilst the industry has improved practices over time, the accumulated pollutants are, posing local and peripheral environmental risks. Those of heavy metals can adversely affect water resources and endanger the health of surrounding ecosystems and human populations. So, ecological remediation through cost-effective technology is necessary. The application of sorbents with high affinity for heavy metals, and in particular those derived from low-cost waste materials, is a promising and attractive remediation route (Chiang *et al*., 2012).

Cr (VI) is highly toxic, mutagenic and potentially carcinogenic to living organisms. Accumulation of Cr (VI) in waste streams is therefore of great concern. Chromium carcinogenicity to humans and other living organisms has promulgated extensive research on its treatment technologies with varying levels of success; generally, the most efficient methods come with a significantly higher cost burden (Kimbrough *et al*., 1999). Due to this cost effective and locally available material for Cr (VI) removal will be a choice.

Aluminum based water treatment sludge (Al-WTS) is an easily available by-product in towns, cities and metropolitan regions worldwide that utilize surface waters as a drinking water source. Since Al-WTS are derived from residual of treatment of raw water, which contains mainly turbidity, color, suspended clays and humic substances, it is unlikely to contain a substantial quantity of toxic substances. Moreover, it is a low-cost material that can be simply released as a

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byproduct from water treatment plants. Knowledge of its physicochemical characteristics and chromium adsorption capacity would be very useful for practical guidance in utilizing it as chromium adsorbent from industrial wastewater. Al-WTS can be obtained free-of-charge from drinking water treatment plants, and they have been successfully used to reduce soluble phosphorus, selenite, selenate, arsenite, arsenate, and perchlorate as well as the cations Pb (II), and Hg (II) (Ippolito *et al*., 2011).

However, its effectiveness and characteristics as an adsorbent for heavy metals like Cr (VI) have not been explored yet; hence this study was aimed at evaluating the chrome removal and adsorptive capacity of Alum sludge**.**

## Materials and Methods

### Characterization of Al-WTS

Freshly generated Al-WTS were collected directly from the sludge thickening unit of Legedadi water treatment plants, Addis Ababa, Ethiopia. Prior to characterization and utilization as an adsorbent, the sample was air-dried, grounded and sieved (< 1mm). The pH of WTS was determined in a 2:1 WTS to 0.01MCaCl. Accordingly, 2g of WTS sample was weighed and transferred into a 250 ml beaker and 100 ml of distilled water and 1 g of CaCl was added and stirred for 1h. Samples were allowed to stabilize and then pH was measured using an electronic pH/conductivity meter (Jenway 430 Model). Electrical conductivity (EC) was measured in a 1:5 sludge sample/water ratio (McLean, 1982).

The Isoelectric point or Zero-point charge ($PH_{zpc}$) of the Al-WTS samples were measured by using the pH drift method. A series of ten $NaNO_3$ solutions, 250 ml, having the initial pH values ranging from 1 to 10 was prepared by diluting with HCl and NaOH. All $NaNO_3$ solutions taken in ten different bottles were mixed with 0.5g WTS. Then the solutions were filtered off and the sludge was separated. The final pH values of the ten solutions were measured and thereby calculation of ΔpH was made by subtracting the initial pH values from final pH values (McLean, 1982).

The graph was drawn by plotting the final pH values against ΔpH. From the graphs plotted, the $pH_{zpc}$ of the Al-WTS was determined. The elemental metal composition was carried out by carefully weighing 0.5g of the air-dried Al-WTS samples into clean vessels followed by the addition of 8 ml $HNO_3$ + 400ml HF + 8 ml of distilled water. Samples were then digested using a low volume microwave digestion technique (Sandroni *et al*., 2003) and the digestates was analyzed for dissolved metals using a UV spectrophotometer (Perkin Elmer lambda 950 UV VIS Spectrometer). Humic acid expressed as total organic carbon (TOC) content of WTS was determined by HACH DR2800 spectrophotometer, method 10128 (HACH, 2007).

### Preparation of chromium stock solution

Potassium dichromate ($K_2Cr_2O_7$) was used as the source for a chromium stock solution. All the required solutions were prepared with analytical grade reagents and distilled water. The chromium (VI) stock solution (1000mg/L) was made by dissolving 2.835g of 99% $K_2Cr_2O_7$ in 1.0 L distilled water. From stock solution, subsequent standard and working solutions were prepared according to desired concentration for this study (0.5mg/l, 2mg/l, 6mg/l, 10mg/l, 15.5mg/l) (Chemiasoft, 2011).

### Chromium analysis, diphenylcarbazide method

250mg 1, 5-diphenylcarbazide was dissolved in 50mL acetone solution. Fifty milliliter (50 mL) sample was taken and 2mL of 3M $H_2SO_4$ and 1mL of diphenylcarbazide was added. Cr (VI) concentrations were estimated by the intensity of the red-brownish color complex formed, and was measured using a UV spectrophotometer (Perkin Elmer lambda 950 UV-VIS Spectrometer) at 540nm, following the 1, 5-diphenylcarbazide method. To estimate the percentage removal of chromium (VI), the following equation was used.

$$\text{Percentage removal} = \frac{Co-Ce}{Co} \qquad \text{(Eqsn 1)}$$

Where, $C_o$ and $C_e$ are the concentrations of Cr (VI) at the beginning and at the end of the adsorption process. The metal uptake ($q_e$) at equilibrium time was calculated from the following equation.

$$q_e = \frac{Co-Ce}{1000w} V \qquad \text{(Eqsn 1)}$$

Where $q_e$(mg/g) is the amount of chromium adsorbed per unit weight of adsorbent, $C_0$ and $C_e$ are the initial and equilibrium chromium ion concentration (mg/L), v is the volume of aqueous solution (ml), and w is the adsorbent weight (g) (APHA, 1998).

**Batch adsorption experimental procedure**

For each experimental run 200mL of known chrome concentration (0.5, 2, 6, 10, 15.5mg/L) of an aqueous solution with a known adsorbent dose (0.2, 2, 6, 10, 15.5g) was placed in a 250ml conical flask. The desired pH (1, 2, 3.5, 5, 7) was adjusted by adding 0.2N $H_2SO_4$ and then the flask is placed in a thermal shaker at required temperature (15, 25,32.5, 40, 50$^oC$) and speed of shaking was adjusted at 200rpm for a time period of (0.15, 1, 3.5, 6, 9hr). The adsorbate was decanted and separated from the adsorbent using filter paper (Whatman No-1). The final Cr (VI) concentration was determined according to diphenylcarbazide method. The amount of chrome adsorbed onto unit weight of the adsorbent was calculated using equation 2.

**Data quality control**

The study was conducted in Addis Ababa university laboratory, Ethiopia in 2015/16. To keep the quality of the experiment, all reagents used were analytical grade. In addition, the equipment used were calibrated before any experimental runs were conducted and experimental methods used were standard approved methods, which are all cited in the document.

**Batch adsorption experimental design**

A batch adsorption experiment study was conducted to check the influence of the study variables (pH, adsorbent dose, chrome concentration, temperature and contact time). Response surface methodology, with the initial design of central composite was applied to generate factor combination using Design of Expert (DOE) software version 7.0.0 (Montgomery andWiley,2001).

**Table 1:** Experimental range and levels of the independent variables in terms of actual value on Cr (VI) removal from waste water using Alum based water treatment sludge, 2015/16, Addis Ababa, Ethiopia

| Variable | | Low axial (-α = -2) | Low factorial (-1) | Center point (0) | High factorial (+1) | High axial (+α = +2) |
|---|---|---|---|---|---|---|
| Initial Cr(VI)concentration (mg/L) | A | 0.5 | 2 | 6 | 10 | 15.5 |
| pH | B | 1 | 2 | 3.5 | 5 | 7 |
| Adsorbent dose (g) | C | 0.5 | 2 | 6 | 10 | 15.5 |
| Time (h) | D | 0.25 | 1 | 3.5 | 6 | 9.5 |
| Temperature ($^o$c) | E | 15 | 25 | 32.5 | 40 | 50 |

**Bach Adsorption Isotherm Study**

The isotherms models of Langmuir and Freundlich were fitted to describe the equilibrium adsorption. These equations of isotherms were,

Langmuir isotherm $$q = \frac{Q_{max}K_LC_e}{1+K_LC_e} \qquad \text{(Eqsn 1)}$$

Where *Ce* is the supernatant concentration after the equilibrium of the system (mg/L), $K_L$ the Langmuir affinity constant (L/mg), and $Q_{max}$ is the maximum adsorption capacity of the material (mg/g) assuming a monolayer of adsorbate uptaken by the adsorbent.

The Langmuir equation can be presented to linear form for the convenience of plotting and calculating the Langmuir constants ($K_L$). The values of $q_m$ and $K_L$ can be calculated from the linear plot of $Ce/q_e$ versus *Ce*. Eq.4.

$$\frac{C_e}{q_e} = \frac{1}{q_mK_L} + \frac{1}{q_m}.C_e \qquad \text{(Eqsn 2)}$$

The essential characteristics of the Langmuir isotherm may also be expressed in terms of a dimensionless separation factor of equilibrium ($R_L$) which may be calculated from Eq. 5

$$R_L = \frac{1}{1+K_LC_O} \qquad \text{(Eqsn 3)}$$

The parameter ($R_L$) is related to the shape of the isotherm according to the following characteristics: $R_L > 1$ represents unfavorable adsorption; $R_L = 1$

corresponds to a linear relationship; 0 < RL < 1 is favorable adsorption and $R_L = 0$ is irreversible.

Freundlich isotherm $q = K_F C_e^{1/n}$ (Eqsn 1)

Where $K_F$ is the Freundlich constant related with adsorption capacity (mg/g) and $n$ is the Freundlich exponent (dimensionless): Equilibrium constants evaluated from the intercept and the slope, respectively, of the linear plot of log $q_e$ versus log $Ce$ based on experimental data. A linear form of the Freundlich expression will yield the constants $K_F$ and $1/n$ Eq. (7) (Langmuir, 1919).

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad \text{(Eqsn 2)}$$

## Results

### Characteristics of Alum based water treatment sludge (Al-WTS)

Table 2 presents major physico-chemical constituents and composition of Al-WTS. The sludge produced is high in its Aluminum content which is 196.45 mg/g. The sludge was also characterized with high amount of TOC (humic acid) which is resulted from turbid nature of Legedadi reservoir.

**Table 2**: Physicochemical characteristics of Alum based water treatment sludge sampled from Legedadi Water Treatment plant, 2015/16, Ethiopia

| Parameters | Value | Unit |
|---|---|---|
| pH | 6.56 | - |
| $pH_{PZC}$ | 5.82 | - |
| EC | 1.3 | mS/cm |
| Aluminum | 196.45 | mg/g |
| Calcium | 4.21 | mg/g |
| Chromium (VI) | 0.06 | mg/g |
| TOC (humic acid) | 98.68 | mg/g |

### Mathematical model development and evaluation

Experimental result of batch adsorption was feed to DOE software for multiple regressions. Quadratic polynomial model was fitted with backward elimination regression with alpha to exit 0.10. The sequential model sum of squares is presented in Table 3. Analysis of variance is presented in Table 4.

**Table 3:** Sequential Model Sum of Squares

| Source | Sum of Squares | df | Mean Square | F Value | p-value Prob > F | |
|---|---|---|---|---|---|---|
| Mean vs Total | 288860.80 | 1 | 288860.80 | | | |
| Linear vs Mean | 6508.38 | 5 | 1301.67 | 17.642 | < 0.0001 | |
| 2FI vs Linear | 880.10 | 10 | 88.01 | 1.264 | 0.288 | |
| ***Quadratic vs 2FI*** | ***1085.19*** | ***5*** | ***217.03*** | ***4.913*** | ***0.00223*** | ***Suggested*** |
| Cubic vs Quadratic | 608.48 | 15 | 40.56 | 0.844 | 0.627 | Aliased |
| Residual | 672.60 | 14 | 48.04 | | | |
| Total | 298615.58 | 50 | 5972.31 | | | |

Sequential Model Sum of Square selects the highest order polynomial where the additional terms are significant and the model is not aliased. From sequential model sum of squares it was found that quadratic model was the most suitable model to describe effect of selected process condition in removal of Cr (VI) by Al-WTS. The final obtained model equation for prediction of response variables based on coded factor was as follows;

**Chrome Removal (%) =**
72.48 - 3.97 * A - 3.81 * B + 8.46 * C + 6.91 * D- 2.73 * A * B + 2.08 * A * C + 3.12 * B * C + 3.05 * A2 + 2.50 * B2 - 1.47 * D2
Where: A is initial Cr (VI) concentration, B is pH, C is adsorbent dose, D is contact time.

**Table 4:** The Analysis of variance (ANOVA)

| Source | Sum of Squares | df | Mean Square | F Value | p-value Prob > F | |
|---|---|---|---|---|---|---|
| **Model** | **8215.82** | **10** | **821.58** | **20.82** | **< 0.0001** | **significant** |
| A-initial Cr (VI) concentration. | 682.91 | 1 | 682.91 | 17.30 | 0.0001 | |
| B-pH | 628.37 | 1 | 628.37 | 15.92 | 0.0002 | |
| C-Adsorbent dose | 3102.36 | 1 | 3102.36 | 78.62 | < 0.0001 | |
| D-shaking time | 2069.98 | 1 | 2069.98 | 52.45 | < 0.0001 | |
| AB | 335.63 | 1 | 335.63 | 10.93 | 0.0053 | |
| AC | 239.25 | 1 | 239.25 | 6.06 | 0.0183 | |
| BC | 139.02 | 1 | 139.02 | 3.52 | 0.0580 | |
| $A^2$ | 534.09 | 1 | 534.09 | 13.53 | 0.0007 | |
| $B^2$ | 356.99 | 1 | 356.99 | 9.04 | 0.0045 | |
| Residual | 1538.94 | 39 | 39.46 | | | |
| **Lack of Fit** | **1048.64** | **32** | **32.77** | **0.46** | **0.932** | **not significant** |

The ANOVA table shows linear terms, initial Cr(VI) concentration, pH, adsorbent dose and shaking time; interaction term, initial Cr (VI) concentration and pH, initial Cr (VI) concentration and adsorbent dose, pH and adsorbent dose and second order terms of initial Cr (VI) concentration, and pH (A, B, C, D, AB, AC, BC, $A^2$, $B^2$) are significant model terms.

### Effect of Independent Variables

In this study, chrome removal decrease with increasing initial chrome concentration and pH, while removal increase with increase in adsorbent dose and shaking time. Temperature has insignificant effect according to ANOVA result. Perturbation plot shows factors (A, B, C, D) have effect on response variable (chrome removal). It can be seen that chrome removal increase with increasing adsorbent dose and contact time (C,D), while it decreases with increasing concentration and pH (A,B). This can be also evidenced by ANOVA result.

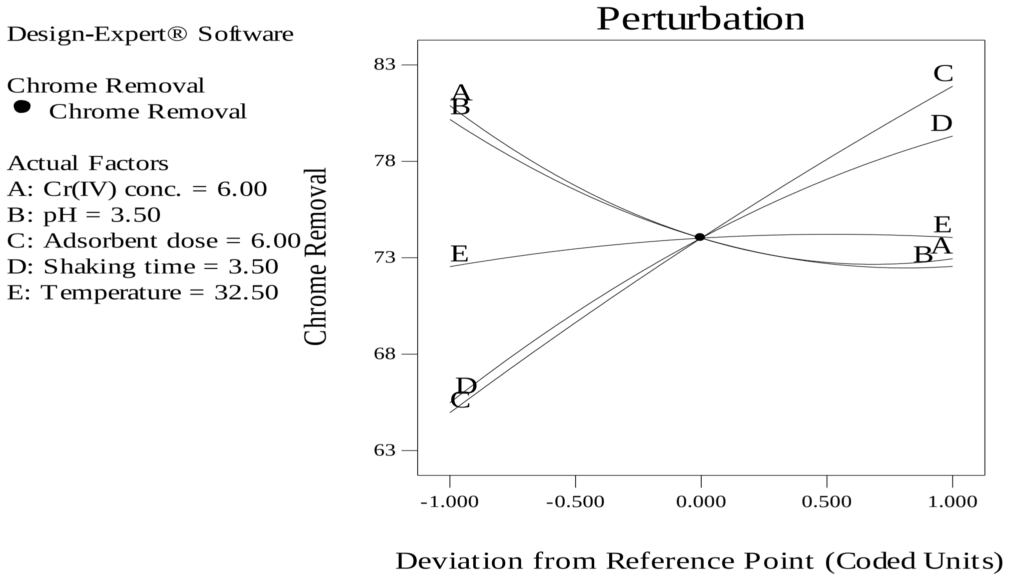

**Figure 1:** Perturbation plot showing effect of factors on chrome removal from waste water using Alum based water treatment sludge, 2015/16, Addis Ababa, Ethiopia

**Effects of factor interaction**

In order to study the interaction among different independent variables and their corresponding effect on the response variable, contour plots were drawn. A contour plot is a graphical representation of a three dimensional response surface as a function of two independent variables, maintaining all other variables at fixed or different level. These plots can be helpful in understanding both the main and interaction effects of the independent variables on the response variable. Interaction effect of initial Cr (VI) concentration and pH (AB) was shown in contour plot of Figure 2.

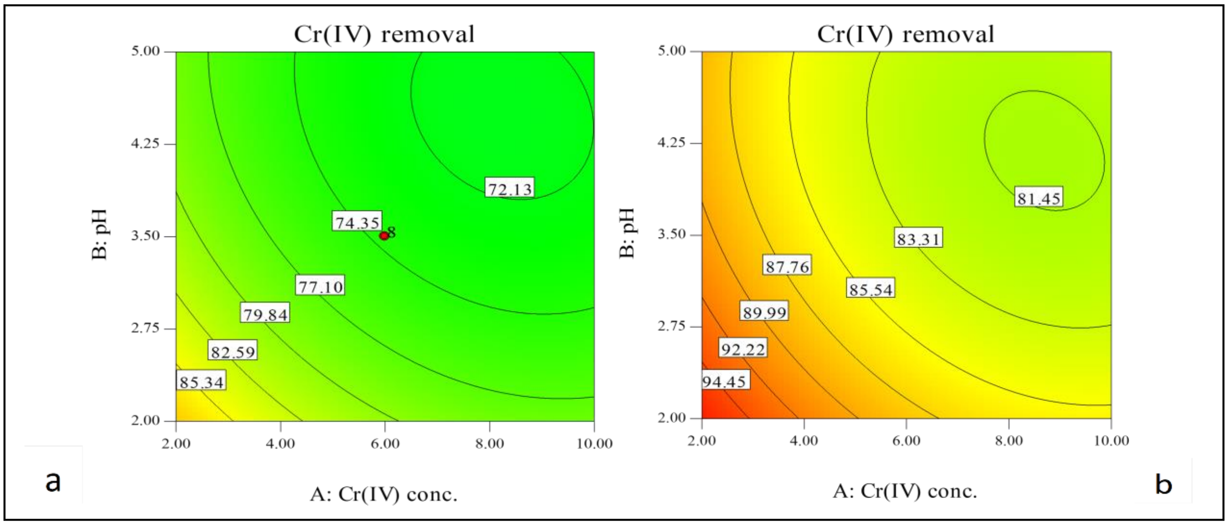

**Figure 2:** Contour plot showing the combined effect of Cr(VI) concentaration and pH (AB), at adsorbent dose 6g, shaking time 3.5hrs. temperature 32.5$^{o}$C (a) and at optimized adsorbent dose of 10g, shaking time 6hrs. and temperature 32.5$^{o}$C (b).

The combined effect of Cr (VI) concentration and adsorbent dose (AC) is shown in contour and 3D plot of Figure (3). Chrome removal increase with; adsorbent dose increase and Cr(VI) concentration decrease. The interaction of both factors (Cr (VI) concentration and adsorbent dose) can be analyzed by checking the hot spotted formed in contour and 3D plot of Figure 3.

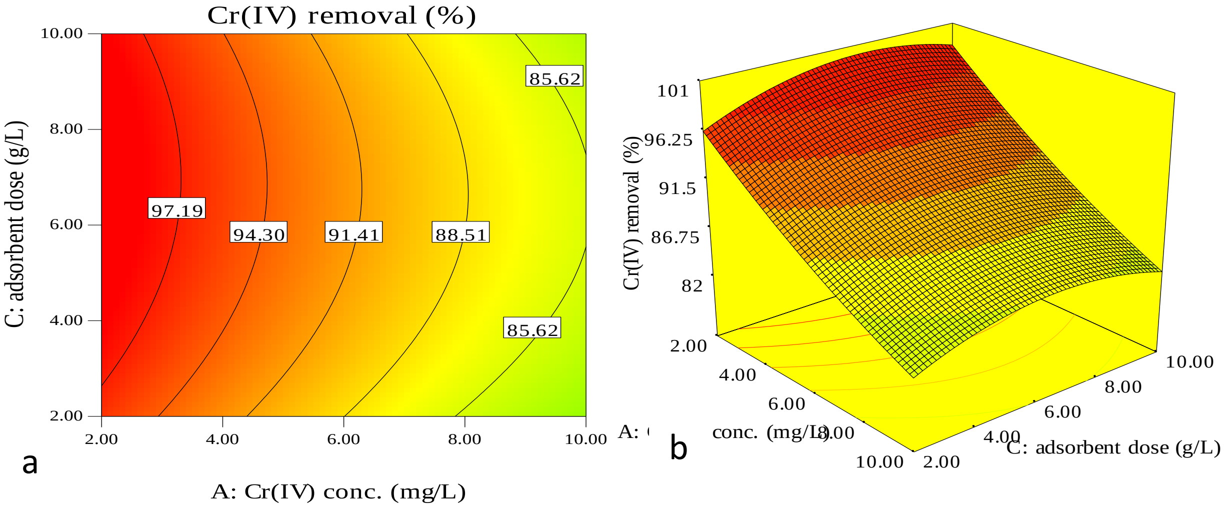

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**Figure 3**: Contour (a) and 3D (b) plot showing combined effect of Cr (VI) concentration and adsorbent dose (AC) at pH 2, shaking time 6h and temperature 32.5$^{o}$C.

Figure (4) represents the effect of pH and adsorbent dose (BC) on removal of Cr(VI). The graph shows that the maximum adsorption (92.35%) occurs under acidic condition, pH 2.4 and adsorbent dose of 6g.

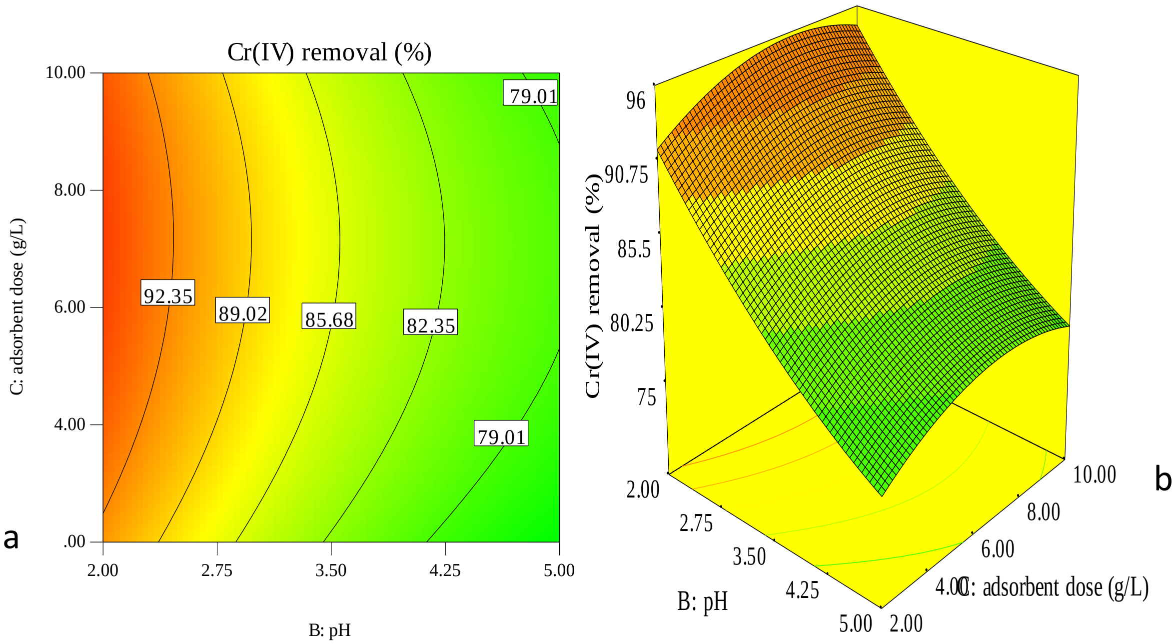

**Figure 4**: Contour (a) and 3D (b) plot showing the combined effect of pH and adsorbent dose (BC) at Cr (VI) concentration 2mg/L, shaking time 6h and temperature 32.5$^{o}$C.

**Adsorptive capacity of Al-WTS**

The equilibrium data of Cr (VI) sorption were evaluated by the linearized form the Langmuir and Freundlich sorption isotherms. The Langmuir constants, KL and monolayer sorption capacity, qm were calculated from the slope and intercept of the plot between Ce/qe and Ce (Figure 5).The results of fitting the equilibrium data to Langmuir isotherm are shown that the values of qm and KL are 33.4 and 0.164 respectively and the R2 is 0.984. The results of fitting the equilibrium data onto Freundlich isotherm are presented that values of n and KF are 0.43 and 2.49 respectively and the R2 is 0.969.

Figure (5) shows, the fitted equilibrium data in Langmuir and Freundlich isotherms. The fitting results, i.e. isotherm parameters and the coefficients of determination, R2 are shown in Table (5). It can be seen that Langmuir isotherm fits the data better than Freundlich isotherm. This is also confirmed by high value of R2 in case of Langmuir (0.9841) compared to Freundlich (0.9698).

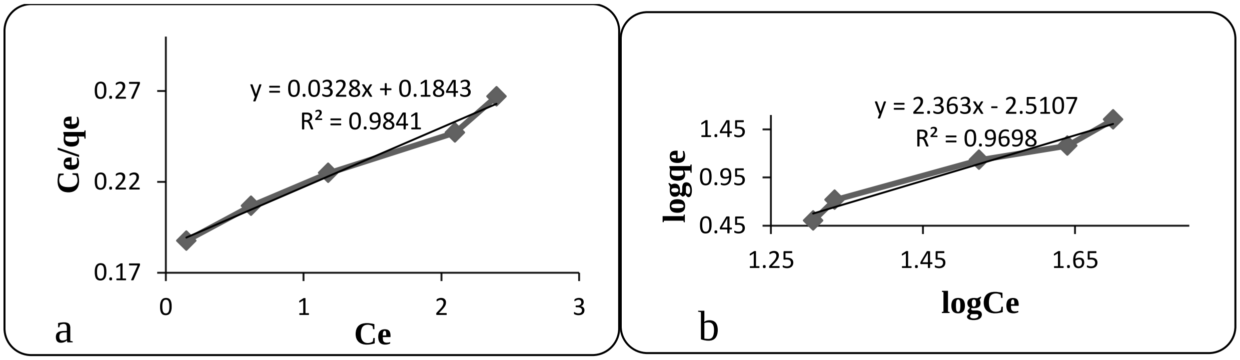

**Figure 5**: Langmuir (a) and Freundlich (b) isotherm plots

According to Langmuir and Freundlich isotherm study Al-WTS has excellent Cr (VI) removal capacity compared to other low-cost, locally available by-products. The fitting results, i.e. isotherm parameters and the coefficients of determination, $R^2$ are shown in Table (5).

Table 5: Langmuir and Freundlich isotherm constants

| **Langmuir isotherm constants** | | | **Freundlich isotherm constants** | | |
|---|---|---|---|---|---|
| $q_m$ (mg/g) | $K_L$(L/mg) | $R^2$ | $K_F$(mg/g) | n | $R^2$ |
| 33.33 | 0.164 | 0.9841 | 2.49 | 0.43 | 0.9698 |

## Discussion

In this study the maximum chrome removal 97.06 % was obtained at chrome concentration of 3.3 mg/L and adsorbent dose of 6.3 g. Chrome concentration and pH increase was found to decrease chrome removal, while adsorbent dose and shaking time increase, increase chrome removal

### Characteristics of Al-WTS

The Al-WTS has a residual pH of 6.56, compared with a pH range of 5.1-8.0 for water treatment residuals reported by Dayton and Basta. The main concern about the pH effect is on Aluminum toxicity due to the quantity of Aluminum present in Al-WTS. However, given the nearly neutral pH of Al-WTS, it is expected that this will pose no problem. It is well known that Aluminum speciation is highly pH dependent, with soluble species present in higher concentrations at pH levels less than 6 (Dayton and Basta, 2001).

The solution pH at which the surface of a soil particle carries no charge is called the zero point of charge (ZPC). The ZPC values of Al-WTS obtained in this study is 5.8. At pH below ZPC value, the adsorbent carry the overall positive surface charges in suspension (Kumar and Chakraborty, 2009). Chromium below pH 6 exists as an ionic form of Cr (VI). So adsorption occurs below the PZC were the adsorbent will develop positive surface charges.

TOC of Al-WTS is 98.86mg/g. These values may be attributed to humic substances contained in the raw water being treated (Yang *et al*., 2006).

### Model evaluation

The ANOVA result shows that the Model F-value of 20.82 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. The ANOVA table also shows a term for residual error, which measures the amount of variation in the response data left unexplained by the model. Lack of Fit test shows the "Lack of Fit F-value" of 0.46 which implies the Lack of Fit is not significant relative to the pure error. There is a 93.2% "Lack of Fit F-value" this large could occur due to noise.

### Effect of Independent Variables

The percentage removal decreases with increasing Cr (VI) concentration beyond 6 mg/L. This is due to the fact that the adsorbent has a definite capacity and can adsorb only a maximum specific amount. Therefore, additional adsorbate does not get adsorbed and hence the percentage removal decreases (Hasani *et al*., 2015).

The stability of Cr (VI) is dependent on the pH of the system. Cr (VI) in aqueous solution can present in different ionic forms, which are closely related to the pH of the solution. It was determined that at pH 2, removal efficiency increases. This is due to the Cr (VI) found in aqueous solution in HCrO4- form. Increasing the pH will shift the concentration of $HCrO_4^-$ to other forms, $Cr_2O_4^{2-}$ and $Cr_2O_7^{2-}$. The maximum percent removal of Cr (VI) was obtained at pH 2. Maximum adsorption at pH 2.0 indicates that it is the $HCrO_4^-$ form of Cr (VI) which is the predominant species and adsorbed preferentially on Al-WTS (Cimino *et al.*, 2000, Mohan *et al.*, 2005).

Adsorbent dosage is an important parameter, because this determines the capacity of an adsorbent for a given initial concentration, separation cost and consequently the overall water treatment cost (Ouazene and Sahmoune, 2010). It was seen that removal increase with increasing adsorbent dose, the change in adsorbent dose from 2g to 10g can increase removal from 64.96% to 81.89% keeping other factors at the center. This trend was due to increase in surface area and adsorption sites available for adsorption.

Equilibrium time is an important parameter for economical wastewater treatment. As the contact time increases, the rate of adsorption decreases depending on the chemical characteristics of the surface (Chergui *et al*., 2007). In the study removal percent increase with in increasing shaking time.

**Effects of factor interaction**

The removal percentage increases with decreasing both initial Cr (VI) concentration and pH. Chrome removal of 85.35% is achieved at Cr (VI) concentration of 2.5mg/L, pH 2.4, adsorbent dose of 6g and contact time 3.5hrs. The effect of AB can also be optimized by increasing adsorbent dose and contact time. Chrome removal of 94.45% can be attained at Cr (VI) concentration of 2.4, pH 2.45, adsorbent dose 10g and shaking time of 6hrs.

In general, at higher Cr (VI) concentration, the Cr (VI) removal decreased as pH increased from 2 to 5, while at lower Cr (VI) concentration, removal increases first and then decreases. Possible explanations may lie in the states of the chromium ion, protonation level and surface charge of the adsorbent. The predominant Cr (VI) species were $HCrO_4^-$ and $CrO_4^{2-}$. Below pH 4.0, the $HCrO_4^-$ complex was the major form, while at pH above 4.0, the most abundant species were $CrO_4^{2-}$ (Mohan *et al*., 2005).

From low adsorption obtained at high pH, it can be inferred that the amount of Cr (VI) adsorbed by other adsorption mechanism was limited, which confirmed that at low pH, the electrostatic attraction played an important role in the removal of Cr (VI) by Al-WTS. This might be due to the reason that at low concentration, the ratio of available surface to Cr (VI) concentration is high, so the removal is higher. However, in case of higher concentrations, this ratio is low; hence the Cr(VI) removal percentage is also low (Jain *et al*., 2011).

From the interaction of AC, chrome removal rises when adsorbent dose increases and Cr (VI) concentration decreases. Chrome removal of 80.3% chrome removal was obtained at Cr (VI) concentration of 3.5mg/L, adsorbent dose 7.4g, pH 3.5, and shaking time 3.5h. But, removal increases up to 97.19% at Cr (VI) concentration of 3.3mg/L, adsorbent dose 6.3g, pH 2 and shaking time 6h.

The combined effect of Cr (VI) concentration and adsorbent dose (AC) indicates, the maximum adsorption (92.2%) occurs under acidic conditions, pH 2.4 and an adsorbent dose of 6g. Increasing the pH from 2 to 5, decreases removal to 78.87%. The higher adsorption at acidic pH range is mainly due to ionizable surface charge of the adsorbent. Perusal of literature on Cr (VI) shows that dominant species are $HCrO_4$- which leads to electrostatic attraction between positively charged adsorbent surface and negatively charged Cr (VI) species HCrO4-.

Meanwhile, at lower pH, the adsorbent surfaces might be highly protonated which favor the uptake of Cr (VI) anion. Besides, as the pH was lowered, the overall surface charge on the adsorbent became positive or less negative, which will promote a stronger columbic attraction towards negatively charged Cr (VI) complex ions in the solution. Hence, adsorption increased with an increase in the acidity of the solution. In this study, the $pH_{PZC}$ value of alum sludge was 5.86. So at the low pH adsorbent surface acquires a positive charge, making the electrostatic attraction towards Cr (VI) anion better.

**Adsorptive capacity of Al-WTS**

The Langmuir isotherm fits the data better than Freundlich isotherm. This is also confirmed by the high value of $R^2$ in case of Langmuir (0.9841) compared to Freundlich (0.9698) and this indicates that the adsorption of Cr (VI) on Al-WTS takes place as mono layer adsorption on a surface that is homogenous in adsorption affinity.

The essential characteristics of the Langmuir isotherm may also be expressed in terms of a dimensionless separation factor of equilibrium ($R_L$). The parameter ($R_L$) is related to the shape of the isotherm according to the following characteristics, $R_L > 1$ represents unfavorable adsorption, RL = 1 corresponds to a linear relationship, $0 < R_L < 1$ is favorable adsorption and $R_L = 0$ is irreversible. In the present study, $R_L$ is 0.0296, which indicates that alum sludge are good adsorbent for Cr (VI) ion removal (Attia *et al*., 2010).

In this study the maximum adsorptive capacity of Al-WTS is 9.86mg/g. Ya-Feng, Z and Richard, H, 2010 As a low cost adsorbent, Al-WTS in this study has an appreciable adsorptive capacity in removing Cr (VI). Moreover, compared to other low cost adsorbents it can be freely available without charge from water treatment plants and it can be easily used as an adsorbent without further complicated preparation modification procedure.

### Limitation of the study

The study assesses Cr (VI) adsorptive capacity of Al-WTS through batch adsorption experiment. Only five major factors indicated are considered and other factors which might affect Cr (VI) adsorption and the Toxicity level of Al-WTS are not studied.

## Conclusion

This work has demonstrated the application of water treatment sludge for chromium removal through batch and fixed bed column study. The results of confirmation experiment were found to be in good agreement with the values predicted by the model. The Langmuir and Freundlich isotherms are subjected to adsorption data and the result gained were well described by the theoretical Langmuir equation. Generally, the capacity of water treatment sludge for Cr (VI) removal from wastewater is appreciably high when compared with other low-cost adsorbents. Therefore, water treatment sludge is a promising suitable material to develop a low-cost adsorbent for removal of chrome.

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used alum derived water treatment sludge for sorption of Pb (II), Cr (III) and Cr (VI) from aqueous solution in one factor at a time batch adsorption study (Ya-Feng and Richard, 2010). They obtained adsorptive capacity of Cr (VI), 0.22 mg/g. Adsorptive capacity obtained in this study is higher, compared to Ya-Feng, Z and Richard, H, 2010. This might be from the difference in adsorbent characteristics and adsorbent affinity towards the adsorbate.

## Contribution of Authors

AT involves in method development, data and lab analysis. WD involved in conceiving the idea, developing methods and data analysis. Both authors read and approved the final manuscript.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

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