

## REMOVAL OF CHROMIUM TRIVALENT IONS FROM AQUEOUS SOLUTIONS USING BYPASS CEMENT KILN DUST AND ITS APPLICATION TO TANNERY WASTEWATER TREATMENT

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The studies on adsorption of trivalent chromium *Cr(III)* onto bypass cement kiln dust (*BCKD*) were conducted by varying various parameters such as contact time, initial chromium ion concentration, *BCKD* dose and initial pH. Langmuir and Freundlich isotherm models were applied to the equilibrium data. The percentage adsorption increased with decrease in pH and showed maximum removal of *Cr(III)* at initial pH value 2.5. Thermodynamic parameters such as standard Gibbs energy  $\Delta G^\circ$ , heat of adsorption  $\Delta H^\circ$  and entropy  $\Delta S^\circ$  were calculated. These thermodynamic parameters showed the process to be endothermic in nature. Desorption of *Cr(III)* from the spent *BCKD* has also been investigated. Desorption process suggest that the adsorption of *Cr(III)* ions on *BCKD* involves physisorption mechanism. Removal of *Cr(III)* from tannery wastewater by *BCKD* was testified.

### 1. Introduction

Environmental pollution due to the development in technology is one of the most important problems of the century and the future. Heavy metals like chromium, copper, lead, cadmium, ..etc. in wastewater are hazardous to the environment. These metals cannot be degraded or readily detoxified biologically and have tendency to accumulate in living materials. Beside that, heavy metals discharge in the wastewater can be toxic to aquatic life and render natural waters unstable for human consumption.

Chromium is present in aqueous solutions mainly in two stable oxidation states, *Cr(III)* and *Cr(VI)*. *Cr(III)* is widely used as a tanning agent in the leather industry, and is an important source contamination due to the large volume of wastewater discharges and solid sludge's produced. There is no doubt that its compounds at higher concentrations are both accurately and chronically toxic and can generate serious trouble and diseases such as nausea, skin ulceration's and lung cancer, (Khan & Mohamad, 2007).

The main sources of *Cr* pollution are mining, leather tanning, cement industry, dyes, electroplating, production of steel, photographic material and corrosive paints. The principal techniques for recovering or removing *Cr* from wastewater are chemical reduction and precipitation, adsorption by several types of adsorbents; such as activated carbon, ion exchange and membrane technologies. Most of these methods suffer from some drawback such as high capital and operational costs. Therefore, there is a need for search and development of low cost, easily available materials, which can adsorb *Cr* economically.

The main objective of this study was to evaluate the possibility of using bypass cement kiln dust (*BCKD*) as adsorbent for the removal of *Cr(III)* from aqueous environment. *BCKD*, commercially available in Libya. The effect of contact time, initial chromium ion concentration, *BCKD* dose, pH value and temperature on *Cr(III)* adsorption are described here in detail.

### 2. Materials and Methods

The adsorbent is bypass cement kiln dust (*BCKD*) are collected from Al-Burg cement factory (Zliten city/Libya) which was undesired byproduct from the dry process of Portland cement manufacturing due to its high alkalinity content. The chemical composition of the *BCKD* constituents are shown in Table.1.

Table 1 X-ray analysis of *BCKD*

| Constituents            | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | CaO   | MgO  | K <sub>2</sub> O | Na <sub>2</sub> O | Cl   | SO <sub>3</sub> | O.C.#  |
|-------------------------|------------------|--------------------------------|--------------------------------|-------|------|------------------|-------------------|------|-----------------|--------|
| Composition *,<br>(wt%) | 12.47            | 3.58                           | 2.37                           | 39.35 | 1.67 | 3.08             | 0.865             | 5.31 | 6.31            | 24.955 |

\* Average value of six samples.

# Other Compounds, includes (free lime 13.108% and loss on ignition 11.9)

Stock solution 1000 mg/l of *Cr(III)* was prepared by dissolving of basic chromium sulfate salt ( $Cr_2(SO_4)_2OH_2$ ) into 1 liter of deionized distilled water (DDW) and stir *Cr(III)* solutions of different concentrations for sorption experiments were prepared by diluting stock solution with DDW.

All experiments were carried out by batch system using a definite volume of *Cr(III)* ion solution with known initial concentration in 250 ml Erlenmeyer flasks, then mixed with a definite amount of BCKD. The mixture was agitated for a certain time at known temperature using a controlled temperature shaker bath.

The *Cr(III)* ion suspension at equilibrium time were centrifuges for 5 minutes at 200 rpm, the residual concentrations of *Cr(III)* ions for the supernatant solutions were measured by Atomic Absorption Spectrophotometer (AAS) SpectrAA 50, (Varian model) to studying parameters effect on adsorption process (Contact time, initial concentration, adsorbent dose and pH). The analysis on the AAS was carried out according to standard methods (Rand et al., 1995). The experiments were triplicate for quality control and statistical purposes.

Adsorption isotherms were obtained by batch method with a known initial concentration ranged (200-1000 ppm). The equilibrium adsorption data obtained are analyzed by the Langmuir and Freundlich isotherms.

Desorption studies were carried out after adsorption experiments for various initial concentration of *Cr(III)* ions (200, 400, 600, 800 and 1000 ppm) then the chromium-laden adsorbent samples, separated by centrifuge, were gently washed with DDW to remove any unadsorbed *Cr(III)*. The spent adsorbent samples were then agitated with 250 ml of DDW and sulfuric acid (98% wt.) was added to samples to various pH ranging from 0.25 to 2.0 and desorbed *Cr(III)* was estimated by analyzing the acid solutions by AAS.

The tannery effluent contained very high concentration of *Cr(III)*. Tanning solutions obtained from two different national tanneries effluents wastewater. The wastewater samples obtained from these tanneries after the tanning operation was filtered to obtain a tanning solution then reduction process for their content of *Cr(IV)* to *Cr(III)* which done (Ibrahim, 2010), the produced solution is to be further treated for *Cr(III)* removal. *Cr(III)* content in the filtrate (tanning solution) was determined using AAS. The initial concentrations of *Cr(III)* in tanning solutions were treated were 2336 and 4320 mg/l respectively.

### 3. Results and Discussion

#### 3.1 Parameters effect on adsorption process

The residual concentration of *Cr(III)* ions decrease with increase a contact time between *Cr(III)* ions and BCKD, sharply decreases occur through period (1 to 10 minutes) then a sluggish decrease in residual concentration of *Cr(III)* ions in a solution through the period (10-15 minutes), then the concentration values remain a constant in the range (15-60 minutes). This behavior refer to that the system reaches to equilibrium very fast and reached to equilibrium at 15 minutes. Similar results were reported.

*Cr(III)* removal percentage increases as the dose of the BCKD increase (ranged 0.1–0.5 g). This was attributed to increased BCKD surface area and availability of more number of adsorption sites (Arivoli et al., 2008).

The initial *Cr(III)* concentration is important parameter since a given amount of BCKD can adsorb a certain amount of *Cr(III)*. Variation effect of initial *Cr(III)* concentration (ranged 200-1000 ppm) on the percentage removal were done. It was found that, the removal increases by decreasing the initial concentration of *Cr(III)*.

pH equal to 1, 2, 3, 4 and 5 are studied. It was found that the removal percentage increases by increasing pH values in which were 47, 90.4 and 99.99% in cases pH values 1, 2 and 3 respectively. Then the opposite trend occurs in which the removal percentage decreases by increasing pH values from 4 to 5 as 88 and 81% respectively.

To explain this behavior a plot of removal percentage by adsorption/precipitation of *Cr(III)* done as shown in Figure (1). A maximum adsorption of 99.99% was attained at an initial pH= 2.5 (Final pH=3.1). For kinetic and isotherm studies care was taken that no tests were performed at an initial pH > 4 [Figure (1), because *Cr(III)* precipitation could occur] in order to find out the ability of BCKD to remove *Cr(III)* by adsorption rather than precipitation.

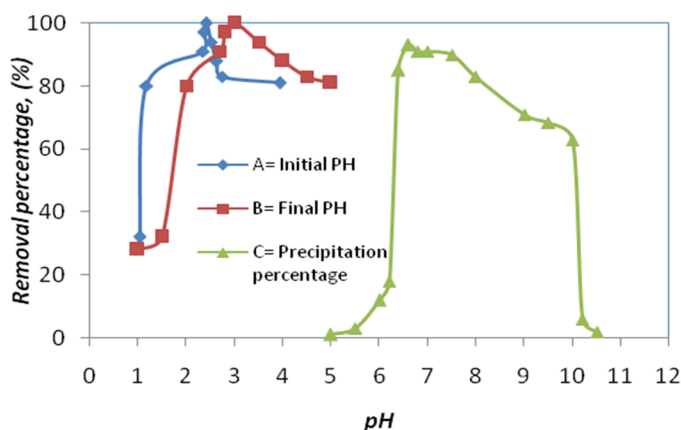


Figure.1: Effect of pH on removal percentage of Cr(III), (Initial concentration 500 ppm, BCKD dose =0.5 g/200 ml, particle diameter 20  $\mu\text{m}$ , agitation rate 200 rpm at  $25\pm 2^\circ\text{C}$ )

A= Adsorption percentage vs. Initial pH; B= Adsorption percentage vs. Final pH; and C= Precipitation percentage vs. pH (by precipitation of Cr(III) as  $\text{Cr}(\text{OH})_3$  in the absence of BCKD).

### 3.2 Equilibrium isotherms and Thermodynamic parameters

#### 3.2.1 Equilibrium isotherms

Figure (2) shows the equilibrium adsorption of Cr(III) ( $q_e$  vs.  $C_e$ ) using BCKD. The isotherm rises sharply in the initial stages for low  $C_e$  values. This indicates that there are plenty of radially accessible sites. Eventually a plateau is reached, indicating that the adsorbent is saturated at this level. The decrease in the curvature of the isotherm, considerably increasing the  $C_e$  values for a small increase in  $q_e$ , is possibly due to less active sites being available at the end of the adsorption process and/or the difficulty of the edge molecules in penetrating the adsorbent due to Cr(III) molecules partially covering the surface sites.

Langmuir isotherm is plotted in Figure (2) together with the experimental data points. The mean total error ( $\epsilon$  %) between this model with the experimental data was 33.47 %. Observed that the monolayer saturation capacity ( $Q_o$ ) is 142.756 mg/g as shown in Table (2).

Freundlich constants with the correlation coefficient are presented in Table (2) and theoretical data of Freundlich equation is shown in Figure (2). The value of  $n$  of this model falling in the range 1-10 indicates favourable adsorption. Value of ( $\epsilon$  %) is much lower than value of Langmuir isotherm model, which is reach up to 2.546%. This trend is due to the high surface area of the adsorbent, and multilayer of adsorption on the BCKD.

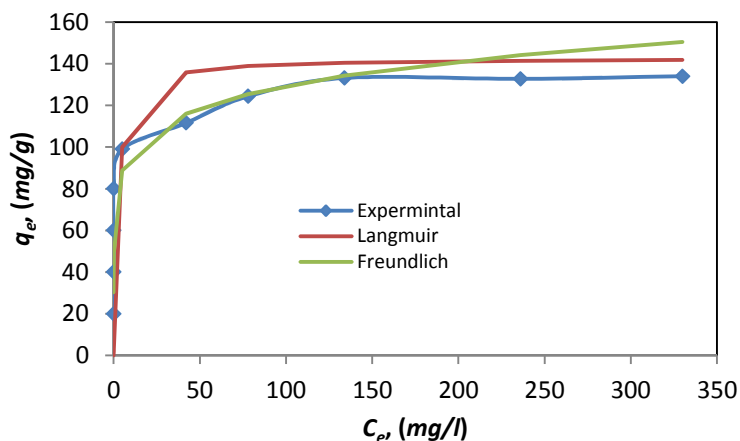


Figure.2 Equilibrium isotherms of Cr(III) on BCKD, Conditions (0.5g/ 100 ml, particle diameter =20  $\mu\text{m}$ , agitation rate 200 rpm, initial pH= 2.5 at  $25\pm 2^\circ\text{C}$ )

Table 2 Langmuir and Freundlich isotherm constants

| <i>Langmuir Isotherm</i> |       |        |       |            | <i>Freundlich Isotherm</i> |      |       |            |
|--------------------------|-------|--------|-------|------------|----------------------------|------|-------|------------|
| $K_L$                    | $a_L$ | $Q_o$  | $r^2$ | $\epsilon$ | $K_F$                      | $n$  | $r^2$ | $\epsilon$ |
| l/g                      | l/mg  | mg/g   | -     | %          | l/g                        | -    | -     | %          |
| 66.67                    | 0.467 | 142.76 | 0.99  | 33.47      | 72.443                     | 7.94 | 0.856 | 2.55       |

### 3.2.2 Thermodynamic parameters

Thermodynamic parameters of the adsorption process such as change in standard free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ), and entropy ( $\Delta S^\circ$ ) were obtained from experiments at various temperatures ranged from 25 to 90 °C to predict nature of adsorption process using the equations given by Wang & Li, (2005).

These constants using to apply *Van't Hoff* plot to carry out the computation of the thermodynamic parameters. The Langmuir constants at varies temperatures show a comparatively linear variation with temperature and hence used to calculate the thermodynamic parameters.

The negative values of the Gibbs free energy change (-25017.5, -25793.8, -27947.4, -30585.8 and -32306.5 J/mol at 25, 30, 50, 70 and 90°C, respectively) indicate that the adsorption process is spontaneous nature for all five temperatures studied; the positive enthalpy (8779.584 J/mol) reveals that energy is absorbed as adsorption proceeds, and the extent of the endothermic reaction will increase at higher temperatures. The positive entropy change (113.86 J/mol.K) may be due to the release of water molecules and the sulfate anions which are present on the surface or in the interlayer spaces of *BCKD* after the ion exchange reaction with the *Cr(III)* adsorbate.

### 3.3 *Cr(III)* desorption and regeneration studies

Regeneration of spent *BCKD* and recovery of *Cr(III)* would make the treatment process economical. Also desorption studies help elucidate the mechanism of adsorption. The effect of various reagents used for desorption studies (*DDW*, sulfuric acid and acetic acid) indicate that, sulfuric acid is a better reagent for desorption, because get more 96% removal of adsorbed chromium ions.

The percent desorption decreased from 97.767% to 20.66% when the pH was increased from 0.25 to 2 for initial concentration 200 ppm; and decreased from 92.96% to 8.23% when the pH was increased from 0.25 to 2 for initial concentration 1000 ppm. Only the *Cr(III)* ions that were adsorbed by ion exchange, not the chemisorbed species, might be desorbed from the adsorbent surface at acidic pH. Both desorption and thermodynamic studies suggest that the physisorption might be the major mode of removal of *Cr(III)* by adsorption on *BCKD*.

### 3.4 Tests with tannery wastewater

A complete removal of *Cr(III)* was obtained at a *BCKD* concentration of 5.5 g/250 ml (about 22 mg/l) for both effluent samples. Increase of adsorbent dose required to removal of *Cr(III)* in the real wastewater compared to synthetic wastewater due to increase the amount of initial concentrations of *Cr(III)* ions and due to the presence of other constituents present in the tannery wastewater, which compete with *Cr(III)* ions for adsorption.

## 4. Conclusions

The obtained results showed that pH, adsorbent dose, initial metal concentration uptake time and solution temperature highly affected the *Cr(III)* ions removal by *BCKD*.

Adsorption followed Freundlich isotherm and the monolayer saturation capacity ( $Q_o$ ) is 142.756 mg/g at pH 2.5. The calculated thermodynamic parameters showed that reactions were endothermic and spontaneous in nature that proceeds. Desorption data obtained reveal to that, the adsorption process of *Cr(III)* onto *BCKD* are physical-sorption in nature. Application of *BCKD* for the removal of *Cr(III)* from tannery wastewater has been demonstrated. The data may be helpful for designing and fabricating tannery wastewater treatment plants for the removal of *Cr(III)*. All these facts confirmed that *BCKD* can be used as low cost adsorbent to removal *Cr(III)* ions.

## References

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