Adsorption of Al, Cr and Zn from a wastewater effluent using basic oxygen furnace slag

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Abstract. Adsorption of Cr, Al and Zn from a powder coating aluminium process wastewater was achieved using Basic oxygen furnace slag (BOFS) as an adsorbent. Batch adsorption studies were used to investigate the effects of solid-loading effect, temperature and contact time on adsorption. Highest metal removal was obtained at a solid-loading of 4% m/v. The adsorption equilibrium time was 60, 80 and 100 mins for Zn, Cr and Al respectively. The adsorption of these metals onto BOFS was satisfactorily modelled using pseudo second order kinetics and Langmuir isotherm. The metal loaded BOFS could successfully be re-used three times before regeneration. The removal rate was 98.4%, 85.5% and 90.2% for Zn, Al and Cr respectively. BOFS can successfully be used to remove metal contaminants in effluent water as the residual metal concentration after 120 min agitation at 4% m/v solid loading was Zn 0.7%, Al 2.67% and Cr 3.4%.

1. Introduction
Industrial pollution of water resources is of major concern due to the reduction in precipitation especially in Southern Africa. One of the processes in the Aluminium industry is powder coating. Powder coating is one of the finishing stages in aluminium processing where a protective and a decorative finish are applied to the mill. The process results in the generation of waste water rich in Al, Zn and Cr.

The various methods that have been commonly used to remove metals from waste water are chemical precipitation, ion exchange, reverse osmosis and electrochemical methods [1-4]. Though these methods are effective, their disadvantage is the production of voluminous sludge and set up costs [5]. Adsorption is an alternative technique that can be used for waste water treatment. Adsorption is the enrichment of chemical species from a liquid phase on the surface of a liquid or a solid [6]. Adsorption is the most effective and broadly used method for treating wastewater due to its easiness, economic feasibility, technical viability and social recognition [6]. There are a variety of adsorbents that have been successfully used and these include clays, activated carbon, chitosan among others [7,8].

Basic oxygen furnace slag (BOFS) is an undesirable product formed in the steel industrial processes. BOFS is a multi-component material, where silicates are the major component [9]. Adsorption studies using BOFS have shown that it is a good adsorbent for vanadium and phosphorus, from the effluent reaching retention level of 2.0 g P/kg [10,11].
The objectives of this investigation were to determine the feasibility to use BOFS as an adsorbent for Cr, Al and Zn from aluminium powder coating effluent, to determine the mechanism of removal and test the reusability of the metal loaded BOFS. The research therefore seeks to turn a waste material into a useful adsorbent and therefore satisfy the requirements of a circular economy.

2. Materials and methods
Effluent from a South African company specialising in aluminium powder coating pre-treatment was collected in a 5 L polyethylene bottle. 1000 ppm standards of Zn, Cr and Al were used for the preparation of elemental calibration standards for AAS analysis. The effluent contained 45.24 ppm Zn, 18.4 ppm Al and 35 ppm Cr. Metal analysis was achieved through the use of the EPA 7000b method.

2.1. Equipment
Atomic Absorption spectrometer (AAS) (Thermo scientific ICE 3000 Series) was used to assay the metals. A thermostatic shaker (Labotec OrbiShaker 14254) was used to conduct the adsorption experiments.

2.2. Methodology
2.2.1. Adsorption experiments. Adsorption was conducted by making use of a thermostatic shaker to effectively mix the slurries. Filter papers (0.45 µm) were used to separate the slurry into the filtrate and residue, with subsequent metals analysis of the filtrate.

2.2.2. Effect of solid-loading ratio (m/v). The solid loading of BOFS was varied from 2 to 10% m/v. The slurries obtained were agitated in a Thermoshaker at 25ºC for 120 min at 200 rpm. After the agitation step, the slurries were filtered after which the filtrate was analysed to determine the residual concentrations of Zn, Cr and Al. The solid loading which gave the highest metal removal was then used for subsequent experiments.

2.2.3. Residence time and Temperature effect on adsorption. The waste effluent was mixed with BOFS at 4% m/v solid loading and agitated at 200 rpm and 25ºC at various time intervals (30, 60, 90 and 120 minutes) to determine the effect of time on adsorption. After each pre-determined time interval, agitation was stopped and the slurry was filtered and the filtrate was assayed for metals. The above experiment was repeated at 35 and 45ºC to determine the effect of temperature on the adsorption of metals. The amount of metal adsorbed per unit mass of adsorbent at equilibrium $q_e$ was determined using equation (1).

$$ q_e = \left( C_o - C_e \right) \times \frac{V}{M} $$

Where $q_e$ (mg/g) is the amount of metal adsorbed at equilibrium per unit mass of adsorbent, $C_o$ (mg/L) is the initial metal concentration in solution, $C_e$ (mg/g) is the equilibrium metal concentration in solution, $V$ (L) is the volume of the solution and $m$ (g) is the mass of adsorbent.

2.2.4. Analysis of results. Statistical analysis of variance (ANOVA) was achieved using Excel data analysis tool pack.

3. Results and discussions
3.1. Effect of varying solid-loading
There was an increase in metal removal (figure 1) with an increase solid loading due to an increase in available adsorption site. There was no statistical difference in the removal of metals from 4 to 10% m/v solid loading ($p=1.1\times10^{-4}$, $1.4\times10^{-6}$ and $6.7\times10^{-8}$ for Cr, Al and Zn respectively) attributed to the occupied sites being unavailable for excess ions after solid loading of 4 % m/v. Therefore, the 4%
solid loading was taken as the optimum.

**Figure 1.** Effect of solid loading on metal removal (Time 120 mins, Temperature 25°C).

### 3.2. Effects of adsorption time and temperature

Metal removal efficiency increased with residence time due to the increased interactions between the adsorbent and the effluent. Optimum contact time for slag adsorbent was found to be 100, 80, 60 min for Cr, Al and Zn respectively. Figure 2 shows that metal ions removal increased with increase in residence time before equilibrium was reached.

**Figure 2.** Effect of residence time on metal removal (Time 120 mins, Temperature 25°C, and Solid loading 4% m/v).

Metal removal per mass of adsorbent increased with an increase in temperature due to an increase in energy given to molecules (table 1). Above the optimum temperature, the adsorption capacity slightly decreased with increasing temperature. This may be attributed to the increase in mobility of the metal ions with increasing the temperature, which may responsible for the decrease of adsorption
capacity of slag.

### Table 1. Variation of $q_e$ with temperature.

| Temperature (ºC) | Zn $q_e$ (mg/g) | Al $q_e$ (mg/g) | Cr $q_e$ (mg/g) |
|------------------|----------------|----------------|----------------|
| 25                | 1.11           | 0.40           | 0.79           |
| 35                | 1.14           | 0.42           | 0.83           |
| 45                | 1.17           | 0.45           | 0.85           |

#### 3.3. Adsorption kinetics

The removal of Cr, Al and Zn from the effluent was modelled using the two most common adsorption isotherm models namely Freundlich and Langmuir isotherm [11,12]. The criterion for selection of the best model was based on the correlation coefficient of the isotherm plots. The linearised equations for the Langmuir and Freundlich isotherm are shown in equations (2) and (3) respectively.

\[
\frac{C_e}{q_e} = \frac{1}{q_m} + \frac{m}{q_m C_e} \\
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

Where $q_m$ (mg/g) is the maximum adsorption capacity, $b$ (L/g) is a constant related to enthalpy of adsorption, $K_F$ ((mol·kg\(^{-1}\))/(mol·L\(^{-1}\)) and $n$ are equilibrium constants indicative of the adsorption capacity and adsorption intensity. The Langmuir isotherm plot is shown in figure 3. The plot for Freundlich isotherm is not shown as the correlation coefficient was less than 0.96 [5].

![Langmuir plots for Zn, Cr and Al.](image)

The kinetic parameters of the adsorption process are shown in table 2. The pseudo second order model fit the adsorption of Cr, Al and Zn from the effluent. The adsorption of Al fitted both the pseudo first order and second order kinetic models. The pseudo second order kinetic model was chosen because the difference in calculated $q_e$ and experimental $q_e$ was small for pseudo second order model (0.14) as compared to 0.56 for pseudo first order [5].
Table 2. The adsorption parameters.

|                  | Pseudo First order |     | Pseudo second order |     |
|------------------|--------------------|-----|---------------------|-----|
|                  | $R^2$              | $\Delta q_e$ | $R^2$              | $\Delta q_e$ |
| Zn               | 0.84               | 12.11          | 0.98               | 0.28          |
| Al               | 0.96               | 0.56           | 0.96               | 0.14           |
| Cr               | 0.84               | 3.77           | 0.96               | 0.17           |

3.4. Reusability of metal loaded BOFS

The BOFS could be reused in three cycles without the need for regeneration (figure 4). At the fourth cycle there was a significant reduction in the removal of all metals possibly due to depletion of adsorbed sites which would have been occupied by adsorbed metals [5].

![Figure 4](image_url)

Figure 4. Effect of the number of adsorption cycles on metal removal.

4. Conclusion

BOFS can successfully be used as an adsorbent for Al, Cr and Zn. The removal follows Langmuir isotherm and pseudo second order kinetics model suggesting a chemisorption mechanism. BOFS has a high adsorption capacity as it can be reused twice before regeneration is required. The valorisation of BOFS allows the turning of a waste material into a useful adsorbent to be used for environmental engineering.

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