Heavy Metals Removal on Dye – Modified Fly Ash Substrates

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ABSTRACT

The fly ash is a cheap waste materials which can be an efficient substrate in wastewater treatment for the immobilization of heavy metals, mainly Cd$^{2+}$, Pb$^{2+}$, Ni$^{2+}$, Zn$^{2+}$, Cu$^{2+}$, and for dyes removal.

The use of FA for heavy metals removal, from wastewaters resulted in the dye finishing industry, faces a supplementary problem, related to the dyes affinity for oxide surfaces. Working with industrial wastewaters proved that there is a competitive adsorption process involving heavy metal cations and dyes. Still, some dyes fixed on the FA surface can act as complexion agents, increasing the adsorption efficiency of the heavy metals.

The paper presents a comparative study of the efficiency obtained when modifying fly ash, by washing with ultrapure water followed by alkali treatment (NaOH 2N) and by dyes immobilization. The Pb$^{2+}$, Zn$^{2+}$ removal efficiency on fly ash with and without dyes is investigated.

The adsorption kinetic, the substrate capacities and the mechanisms are discussed correlated with the surface structure (XRD) and morphology (AFM). The results show that, fly ash with controlled surface properties allows the simultaneous removal of heavy metals and dyes, resulting waters that respect the discharge regulations.

INTRODUCTION

The degree of pollutants persistence in the environment varies from a few days up to several years and can affected the humans and the biota. Heavy metals, like Cd$^{2+}$, Pb$^{2+}$, Ni$^{2+}$, Zn$^{2+}$, Cu$^{2+}$, Cr$^{3+}$ are among the most toxic pollutants, event hazardous, and can be found in waste waters, as resulting from mining, metallurgy, metal plaiting, smelting flux electrolysis, battery manufactories, petroleum refineries, paint manufacture, printing and photographic industries, etc.

Most of industrial undertakings have developed small waste water treatment plants and are interested to develop various technologies targeting heavy metal removal from the wastewaters.
If combined with dyes, the wastewater containing heavy metals becomes even more difficult to treat, because stable and toxic compounds can develop between the dye and the cation. Undesired in solutions, this property can be exploited if fixing the dye on a substrate and activating it for cation adsorption.

The conventional techniques used for heavy metal and dyes removal are expensive and with average efficiency and are running in sequential steps. The most commonly used methods for removal of heavy metal ions can be: chemical precipitation, solvent extraction, oxidation, reduction, dialysis/electro-dialysis, electrolytic extraction, reverse osmosis, ion-exchange, cementation, dilution, flotation, flocculation, sedimentation, soil flushing/washing chelating, etc. For example, at industrial scale the ion-exchangers and activated carbon are used but there are certain disadvantages. The activated carbon is a great adsorbent for dyes but the efficiency in heavy metals removal is average and desorption and regeneration is difficult under common conditions, thus the overall process becomes expensive. Ion-exchange is an efficient method, with moderate selectivity since it can not only remove the heavy metal ions but exchange the $\text{Ca}^{2+}$, $\text{Mg}^{2+}$ ions. Supplementary, the ion exchangers can load with dyes, thus modifying the surface and decreasing the process reversibility. These adsorbents are efficient but do not represent a sustainable solution.

Still, adsorption is an efficient process which can use various biological materials, mineral oxides, activated carbon, resins even waste materials. Many researches had investigated the adsorption capacity of less expensive materials such as red mud, natural zeolite, wood based biosorbents, scrap rubber, bituminous coal, peat, sugar beet pulp, marine alga Padina or bone char, etc. on heavy metals (cadmium, cooper, zinc, nickel, iron) and dyes removal.

Ash, resulting from coal or biomass burning, is a mixture of oxides with less unburned carbon and other minority inorganic compounds thus has a predominant negative surface charge and represents a promising adsorbent. Many applications in wastewater treatment are already reported, most of them at pilot scale.

Fly ash, the lightest fraction resulted in coal burning is also largely investigated for heavy metals and dyes adsorption, because the priority compounds from fly ash favour the heavy metals adsorption and are active sites in dyes’ immobilization.

The ashes composition and surface aspect strongly depend on the type of coal, on the burning process and on the equipment design. Raw ash contains soluble compounds, therefore washing before use is compulsory. Previous studies proved that further conditioning by alkali treatment can be needed for enhancing the adsorption efficiency of heavy metals, or multi-component systems of heavy metals and dyes, on fly ash.

It can be supposed that adsorbing a dye on the fly ash surface may result in an homogeneous, efficient adsorbent surface. The objective of the present study is to assess the ability of low cost fly ash in removing $\text{Pb}^{2+}$ and $\text{Zn}^{2+}$ from synthetic aqueous solutions. Fly ash was modified in two steps: (1) with NaOH 2N solution followed by (2) a treatment in methyl orange 0.2mM solution.
2. EXPERIMENTAL

2.1. THE SUBSTRATE

The fly ash (FA) used in the experiments was obtained from lignite coal burned in the CPH plant CET Brasov, Romania. The major constituents of this fly ash are presented in Table 1. According to the ASTM standards, the FA collected from the electro-filters of the plant is of F type (the sum of the major compounds, oxides SiO$_2$, Al$_2$O$_3$ and Fe$_2$O$_3$, is over 70%).

Table 1. Fly ash composition

<table>
<thead>
<tr>
<th>FA Composition [%]</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>K$_2$O</th>
<th>Na$_2$O</th>
<th>TiO$_2$</th>
<th>MnO</th>
<th>LOI*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>53.32</td>
<td>22.05</td>
<td>8.97</td>
<td>5.24</td>
<td>2.44</td>
<td>2.66</td>
<td>0.63</td>
<td>1.07</td>
<td>0.08</td>
<td>1.58</td>
</tr>
</tbody>
</table>

*LOI: loss of ignition

The pH value of the raw fly ash was evaluated by mixing 100 g of FA with 1000 mL ultra pure water, then stirring, at room temperature till constant pH and conductivity values (10.2, and respectively, 1.710 mS). The initial TDS value of the batch is 600 mg/L and after 24 h increases to 820 mg/L, being in the end (48 h) 850 mg/L. The soluble compounds: K$_2$O, Na$_2$O, MgO, CaO, were thus removed in solution and can be available by further separation and purification.

Raw and washed FA shows a limited adsorption affinity for heavy metals as result of a high heterogeneity in the surface charge. Previous studies proved that negative surface charges can be obtained by using NaOH 2N solution as modifier. The FA, washed in ultra pure water, was further stirred 48 hours at room temperature with NaOH 2N alkaline solution (FA-NaOH) followed by filtration, washing and drying, at 105-120°C, till constant mass. The dried FA-NaOH was sieved and the 40 -100 µm fractions were selected for adsorption experiments.

One half was used for Zn$^{2+}$ and Pb$^{2+}$ adsorption and other half was used to obtain a new substrate by mixing FA-NaOH with a Methyl orange MO (Merck) aqueous solution, for to 48 h, at room temperature, followed by filtration and flush with ultra pure water. Finally, the FA-NaOH-MO substrate was dried and used for the adsorption test of Zn$^{2+}$ and Pb$^{2+}$ cations.

Both substrates were characterized using XRD (Bruker D8 Discover Diffractometer) for FA crystalline structure and AFM images (Ntegra Spectra, NT-MDT model BL222RNTE) were used for morphology studies (roughness surface, pore size distribution).

2.2 ADSORPTION EXPERIMENTS

Kinetic and thermodynamic adsorption experiments were conducted in batch, at room temperature (20-25°C), under (a) magnetic stirring and (b) under vessel rotation.
The optimal contact time was evaluated on suspensions of 0.5 g of FA-NaOH or FA-NaOH-MO in 50mL solutions of Zn$^{2+}$ (350 mg/L) respectively Pb$^{2+}$ (1250 mg/L). Aliquots were taken each 10, 30, 45, 60, 90, 120, 180, 240 min. when stirring was interrupted and the substrate was removed by filtration. The residual metal concentration from the supernatant were analyzed by AAS (Analytic Jena, ZEEnit 700), at $\lambda_{\text{Zn}} = 213.9$ nm and $\lambda_{\text{Pb}} = 283.3$ nm, after calibration.

In all cases, the working pH was the natural value of the solutions. Preliminary experiments proved that heavy metals losses due to adsorption to the container walls and to the filter paper were negligible.

3. RESULTS AND DISCUSSIONS

The XRD spectra, Fig. 1, show that the major components of fly ash are: carbon (graphite), carbon hexagonal (chaoite or white), SiO$_2$ in various structures (cubic, rhombohedra) combined with Al$_2$O$_3$ as rhombo $\gamma$, mullite (3Al$_2$O$_3$·2SiO$_6$), along with $\gamma$-Al$_2$O$_3$, hematite (Fe$_2$O$_3$), TiO$_2$ brookite, was also traced along with Cd, Cu, Zn (0.0742 mg/l), Pb (0.0094 mg/L) compounds. These components are characterizing the raw fly ash but are found also in the modified FA. The aluminium silicate, oxide components vary from one type of substrate to another, and the alkali treatment (FA-NaOH) can be responsible for partial dissolution processes.

![XRD spectra](image)

Fig. 1 XRD of (1). FA modified with NaOH 2N, (2). FA modified with NaOH 2N and MO 0.02 mM.

Heavy metals and dyes removal on FA are pH depended. Previous studies showed that the lowest heavy metals adsorption efficiency occurred when the FA was treated with HCl 2N$^{23}$, this effect is caused by a positive surface charge leading to repulsions between the surface (≡ SiOH$^+$) and metal ions$^{21}$. Supplementary, silica and alumina are forming alumino-silicates with pH-dependent structures. On the FA, during alkali conditioning with NaOH 2N solution for 48 h, several interactions are expected, according to the following reaction$^{16}$:

$$16...$$
NaOH$_{aq}$ + FA$_s$ $\rightarrow$ Na$_a$(AlO$_2$)$_b$(SiO$_2$)$_c$·NaOH ·H$_2$O \hspace{1cm} (1)

when on the FA surface can developed new active site (≡ SiO\(^{\cdot}\)) and (≡ AlO\(^{\cdot}\)) which allows metals to form complexes at the surface (eq. 2, 3)\(^{3,18}\): 

\[
2(≡ SiO^{\cdot}) + M^{2+} \rightarrow (≡ SiO)^2M \\
2(≡ AlO^{\cdot}) + M^{2+} \rightarrow (≡ AlO)^2M
\]

The planar structure of Methyl orange molecule, with two aromatic rings can act as an electron donor in the interaction with the heavy metals cations, Fig. 2:

![Fig 2. Chemical structure of Methyl orange in alkali solution](image)

Fig 2. Chemical structure of Methyl orange in alkali solution

Therefore, the alkali form of MO may act as a supplementary complexion agent, which, adsorbed on the FA surface can increase the affinity for heavy metals by terminal group (−SO$_3^-$) and/or to decrease the pore size on the surface, Fig. 2.

![Fig.3. The pores distribution on FA surface](image)

These chemical and structural changes are mirrored in morphology modifications, Fig 4 (a) and (b), resulting in large differences in the substrates’ affinity for heavy metals.

The various roughness values appear due to a complex of factors, involving alkaline oxides leaching, methyl orange treatment, and the formation new structures with important role in the heavy metals adsorption.
3.1 UPTAKE KINETICS OF THE HEAVY METALS

For the metal removal kinetic studies, the metal uptake \( q_e \) (mg/g) was evaluated using the initial and current, \( t \), heavy metal concentrations (\( c_{cation}^i \) and \( c_{cation}^c \)), in a given solution volume, \( V \), for a given amount of FA substrate, \( m_s \) (eq. 4):

\[
q_e = \frac{(c_{cation}^i - c_{cation}^c) \times V}{m_s}
\]  

(4)

The kinetics of the heavy metals adsorption was modelled by the following equations:

- The pseudo first-order, Lagergren equation\(^{11}\):

\[
\log (q_e - q_t) = \log (q_e) - \frac{K_L}{2,303}t
\]

(5)

where \( K_L \) is the Lagergren constant, \( q_0 \) is the initial uptake value and \( q_t \) the current metal uptake.

- The pseudo-second order kinetic equation, developed by Ho and McKay\(^8\):

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

(6)

where \( k_2 \) is the equilibrium rate constant for the pseudo second-order adsorption (g mg\(^{-1}\) min\(^{-1}\)) and can be evaluated from the slope of the plot. This model is based on
the assumption that the rate limiting step may be a chemical adsorption involving the valence forces through sharing or exchange of electrons between the adsorbent and the adsorbate. The model is mentioned in literature for Cu$^{2+}$, Co$^{2+}$, Zn$^{2+}$, Mn$^{2+}$ adsorption on zeolites, and of Pb$^{2+}$ and Cu$^{2+}$ on humic acid.

Other possible kinetic model which can be applied in adsorption processes on porous materials is the interparticle diffusion model. In this case, the amount of heavy metals ions adsorbed can be calculated with the equation:

$$q = k_{id} t^{1/2} + C$$

(7)

This model can be fitted well for, Pb$^{2+}$ for adsorption, on both types of substrates. The linearization proved that the pseudo-second order kinetic describes well the adsorption mechanism both for Zn$^{2+}$ and Pb$^{2+}$, while the pseudo-first order kinetic, can describe only the adsorption processes of Zn$^{2+}$ ions on FA-NaOH and the adsorption processes of Pb$^{2+}$ ions on FA-NaOH-MO. The kinetic parameters are presented in Table 2.

<table>
<thead>
<tr>
<th>Type of FA</th>
<th>$n = 1$</th>
<th>$n = 2$</th>
<th>Interparticle Diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_c$ [min$^{-1}$]</td>
<td>$R^2$</td>
<td>$k_2$ [g mg$^{-1}$ min$^{-1}$]</td>
</tr>
<tr>
<td>Lead (Pb$^{2+}$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FA-NaOH</td>
<td>0.03</td>
<td>0.868</td>
<td>0.064</td>
</tr>
<tr>
<td>FA NaOH-MO</td>
<td>0.02</td>
<td>0.920</td>
<td>0.304</td>
</tr>
</tbody>
</table>

| Zinc (Zn$^{2+}$) | | | | | | | |
| FA-NaOH | 0.03 | 0.989 | 0.091 | 18.87 | 0.997 | 0.88 | 11.14 | 0.883 |
| FA NaOH-MO | - | 0.758 | 0.507 | 8.49 | 0.976 | 0.37 | 4.53 | 0.845 |

The Pb$^{2+}$ adsorption capacity on both substrates was 94.339 mg-Pb$^{2+}$/g and 42.194 mg Pb$^{2+}$/g, showing a possible chemical adsorption, involving valence forces (through electrons sharing) between the adsorbent and the adsorbate.

The lead in aqueous solution may suffer solvation, hydrolysis or polymerization. It has been reported that lead can form many polynuclear species such as: Pb$_2$(OH)$_3^+$, Pb$_3$(OH)$_4^+$ which can be adsorption etc. The Raman spectrum show that in aqueous solution the zinc cations are hexahidrated [Zn(H$_2$O)$_6^{2+}$].

The Zn$^{2+}$ cation can interact with the MO molecules, forming stable complexes on the FA surface. Adsorption studies carried out to estimate heavy metal removal from wastewater, using fly ash, showed that the efficiency follow the order: Pb$^2+$ > Zn$^{2+}$ > Cu$^{2+}$ > Cd$^{2+}$ > Ni$^{2+}$.

3.2. OPTIMIZING THE ADSORPTION ON FA
The $\text{Pb}^{2+}$ and $\text{Zn}^{2+}$ adsorption efficiency, $\eta$, on modify FA was evaluated to optimize the contact time and the amount of FA and was calculated with equation (8):

$$\eta = \frac{(c_{\text{cation}}^i - c_{\text{cation}}^e)}{c_{\text{cation}}^i} \times 100$$

(8)

where $c_{\text{cation}}^i$ and $c_{\text{cation}}^e$ are the initial and equilibrated cations concentrations (mg/L).

The dynamic adsorption results are presented in Fig. 5a and 5b for the lead and zinc adsorption on FA-NaOH, compared with the results obtained using FA-NaOH - MO as adsorbents.

The low adsorption efficiency of $\text{Pb}^{2+}$ and $\text{Zn}^{2+}$ cations on FACNaOHCMO compare with the efficiencies on FACNaOH show that a share of pores are occupied with
methyl orange molecules, as also supported by the AFM pictures and the average roughness values. Further, it may be concluded that in complex systems containing both the cation(s) and the dye, there are expected only average adsorption efficiencies.

The effect of the amount of adsorbent on the uptake of Pb\(^{2+}\), Zn\(^{2+}\) cations is presented in Fig. 6a and 6b.

Increasing the amount of adsorbent from 0.5 g up to 3 g for 50 mL solution the initial pH increases up to 8 (below the precipitation value) while the adsorption efficiency of the heavy metals increase because exist more active centres in the system.

The optimal adsorbant amount is found to be 1.5 g for Pb\(^{2+}\) cation removal respectively 1.25 g for Zn\(^{2+}\).

So the optimal parameters to remove the metals ions (Pb\(^{2+}\), Zn\(^{2+}\)) are:

- Contact time, \(t_{optimal}\): 60 min
- Amount of substrate in 100 mL of solution, \(m_s\): 1.25 – 1.5 g.

### Table 3. Parameters of the adsorption isotherms

<table>
<thead>
<tr>
<th>Type of FA</th>
<th>Langmuir Isotherm</th>
<th>Freundlich Isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(q_{\text{max}}) [mg/g]</td>
<td>(a) [L/mg]</td>
</tr>
<tr>
<td>Lead (Pb(^{2+}))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FA-NaOH</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>FA-NaOH-MO</td>
<td>31.646</td>
<td>0.006</td>
</tr>
<tr>
<td>Zinc (Zn(^{2+}))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FA-NaOH</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>FA-NaOH-MO</td>
<td>6.269</td>
<td>0.031</td>
</tr>
</tbody>
</table>

The adsorption isotherm data were experimentally obtained and the absorption parameters were calculated considering the Langmuir and Freundlich equations, respectively, as given below:

The Langmuir isotherm - linearization:

\[
\frac{C_{eq}}{q_{eq}} = \frac{1}{q_{\text{max}} \cdot a} + \frac{C_{eq}}{q_{\text{max}}} \tag{9}
\]

Where \(q_{\text{max}}\) (mg/g) represents the monolayer adsorption capacity, \(a\) is a constant related to the free energy of adsorption, \(q_{eq}\) and \(C_{eq}\) show the amount of metal adsorbed on.
The Freundlich isotherm linearization:

\[
\ln q_{eq} = \ln k_F + \frac{1}{n} \ln C_{eq}
\]  

(10)

Where \( k_F \) is Freundlich adsorption constants, being indicators of adsorption capacity and \( \frac{1}{n} \) dimensionless parameter is a measure of the adsorption density.

Table 3 presents the adsorption parameters for the heavy metal ions (Pb\(^{2+}\), Zn\(^{2+}\)) calculated from the slope of the plots.

The Langmuir model could better describe the lead and zinc adsorption on FA-NaOH-MO as result of a highly homogeneous substrate resulted after the dyes adsorption. The Freundlich model could better describe the adsorption of lead and zinc on FA-NaOH, the heterogeneous substrate.

CONCLUSION

The fly ash is a waste which can be used for the removal of aqueous lead and zinc ions, with good efficiency. Treating FA with alkaline NaOH solutions 2N the surface is modified by dissolution and re-precipitation reactions. By dissolution of acid oxides, the specific surface area is enhanced and activated and the efficiency of heavy metals removal increases.

Adding dye to the FA surface results in a new surface, which is one more homogeneous but less negatively charged. The overall effect is a decrease in the affinity for heavy metals.

The heavy metals removal was studied and the adsorption conditions were optimized in terms of contact time (60 min) and adsorbent mass in 100 mL solution (1.25-1.5 g).

The pseudo-second order kinetics did well apply to the majority adsorption processes.

The experimental results show that this can be an up-scalable solution and represent a first step in investigating the process of complex treatment of wastewaters containing dyes and heavy metals.

ACKNOWLEDGEMENT

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