Removal of Selenium from FGD water streams by a non-conventional adsorbent by-product

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ABSTRACT
The use of FGD-gypsum as material for selenium removal from re-circulated waters at a coal-fired power plant equipped with a wet limestone flue gas desulphurisation (FGD) system with use of an Al-additive (to boost the desulphurisation efficiency), has been evaluated by adsorption studies. Potentiometric titration experiments for FGD-gypsum samples, based on the point zero of zero charge (pHpzc) and the potenciometric curves indicate that at pH lower than 7.5 the FGD-gypsum surface is positively charged. This points out that the adsorption of Se in the FGD gypsum is governed by the protonation of the FGD-gypsum surface. The protonation of the FGD-gypsum may be attributed to the use of the Al-additive.

1. INTRODUCTION

Even though most of selenium released during combustion is captured in cleaning systems by high-efficiency particulate collectors, some gaseous selenium existing as SeO_2 escapes and is dissolved in the aqueous phase of flue gas desulphurisation (FGD) gypsum slurries (FGD absorber slurry). Selenium and other elements of environmental concern, such as Al, F, Cl, B, U, and Hg form highly soluble salts favoring element enrichment and saturation in the re-circulated water streams of FGD scrubbers [1]. This causes the emission of such elements by entraining particles and droplets of gypsum slurry in the OUT-FGD gas, and/or their precipitation as solid species in the FGD-gypsum end-product.

Selenite (SeO_3^{2-}) generally is removed by conventional wastewater treatments such as coagulation-sedimentation whereas selenate (SeO_4^{2-}) requires a biological and/or chemical reduction processes to be removed by wastewater treatments [2-4]. The chemical reduction process has already been installed in some coal-fired power plants but it is not currently carried out owing to the expensive cost of maintenance and the discharges of large amount of sludge [5].

At coal-fired power plants the final fate of FGD-gypsum produced in the desulphurisation process is the disposal in landfills. With the advent of increasingly restrictive regulations on air, water, and soil quality and the growing concern about health effects of exposure to heavy metals even at trace levels, the employment of FGD gypsum for the selenium adsorption could established as prevention measure based on the management on solid (FGD gypsum) and water (aqueous phase of gypsum slurry) streams before their production and the subsequent disposal in landfills and/or in application scenarios. However, selenate and sulphate have similar structural and chemical properties (negative electrical charge) and they can play a similar geochemical role. The competition between both anions has been considered in different fields, e.g., sorption onto mineral surfaces [6], absorption in plants and bacteria [7-9], and substitution in crystal structures [10].

A recently study [11] at a coal-fired power plant has shown that the protonation of the FGD gypsum surface induced by the addition of $Al_2(SO_4)_3$ could contribute to the retention of Se in the FGD gypsum. Although the point of zero charge and variation of the gypsum surface charge with pH is barely known, to our knowledge, only one unpublished work by Shang et al [12] describes the variation of surface zeta potential with pH. In view of this, the aim of this work is twofold: evaluate the FGD-gypsum as possible material to be used for selenium removal in FGD waters from a coal-fired power plant that uses an Al-additive to boost the desulphurization efficiency, and describes the variation of surface zeta potential with pH of FGD-gypsum surface.

2. MATERIALS AND METHODS

2.1 Material
Sodium selenate (Na_2SeO_4) was used as source of Se for the adsorption experiments in order to assess the effectiveness treatment and management for the removal of selenium based on adsorption processes by FGD gypsum. Sodium selenate of analytical grade (>95%) was supplied by Sigma Aldrich and used in the experimental tests.

2.2 Adsorbent material
The specific surface area and the volume and distribution of pores of the FGD gypsum were measured using a gravimetric method based on the adsorption of N_2 and at constant temperature with Quantachrome Nova Wing 2.

The surface charge of the FGD gypsum was carried out by potenciometrical tritation in a N_2-rich atmosphere using 0.02N HCl and 0.02N NaOH. Three samples of 0.3g of FGD gypsum were placed in a vessel containing 100 mL of 1 and 0.01M KCl as background electrolyte. The titrations were carried out by adding 0.2 mL of the titrants by 20 minutes of reaction [13].

2.3 Adsorption studies

2.3.1 Kinetics
Selenium adsorption kinetics was conducted in 100 mL amber bottles previously treated with TOC water and HNO_3. Volumes of 40 mL of Na_2SeO_4 solution (C_o = 10 mg/L) was mixed with 0.5 g of FGD gypsum samples. The FGD gypsum/Na_2SeO_4 solutions at pH 7.6 were initially shaken for 5, 15, 30, 45 min; and subsequently for 1, 2, 4, 6, 8, 10, 12, 24, and 48h at a rate of 110-120 rpm at 30°C, and filtered through a filter of 0.45μm. The concentration of Na_2SeO_4 in the supernatant solution was measured by Atomic Absorption Spectroscopy coupled with hydrides generation (HGAAS) as a consequence of interferences, poor reproducibility, and poor detection limits produced by alternative methods.

2.3.2 Adsorption isotherms
Aliquots of 50 mL of five initial solutions (1.5, 2.5, 3.5, and 6.0 mg/L) of Na_2SeO_4 were added to 1g of FGD gypsum samples. The Na_2SeO_4/FGD gypsum suspensions were shaken for 60 min at 30°C. The experiments were carried out at the natural pH values of each suspension 7.4-7.6. The concentration of Na_2SeO_4 in the supernatant solutions was measured by HGAAS.

3. RESULTS AND DISCUSSION

3.1 FGD gypsum characterization

FGD gypsum presents a relatively small specific surface area (9.548 m^2/g) in comparison with conventional adsorbents materials such as alumina, bauxite, and activated carbon, which usually present superficial surface areas higher than 200 m^2/g. Physical and chemical properties of FGD gypsum is depicted in Table 1.

Table 1. Physical and chemical properties of FGD gypsum

	FGD gypsum
Specific surface area	9.548 m^2/g
Pore diameter	0.004 µm
Pore volume	0.024 cc/g
pH (H_2O)	7.6

3.2 Adsorption kinetics

In selenium adsorption kinetics on FGD gypsum three phases can be observed (Figure 1). A dynamic and progressive phase of adsorption up to the first ten minutes with a maximum adsorption attained close to the first eight minutes of the kinetic process. The second phase is characterised by desorption stage from 10 to 30 minutes with a second adsorption sequence from 30 to 55 minutes of the kinetic process. The final phase of the kinetic process (60-120 minutes) is predominated by the equilibrium. These three phases could be associated to the changes of pH observed during the kinetic process (Figure 2).
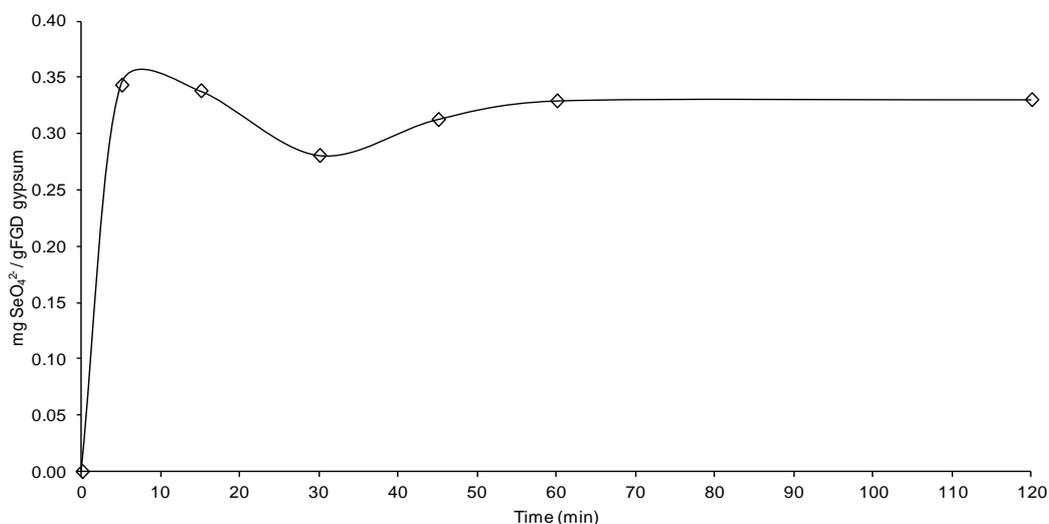
Figure 1. Selenium adsorption kinetics on FGD-gypsum.

In the figure 2 can be observed a fast drop of pH during the first five minutes followed by a slight increase from 10 to the next 5 minutes. This suggests that the adsorption may initially be linked to the decrease of pH of the solution. However, at the 15 minutes of the kinetic process, the pH of the solution decreases slightly and reaches the lower pH value in the desorption stage (45 minutes). This reveals that is not possible to determine an association between the adsorption process and the changes of pH during the kinetic process.

It is also important to point out that this kinetic process of the removal of selenium can be governed by a combination of adsorption and precipitation processes.
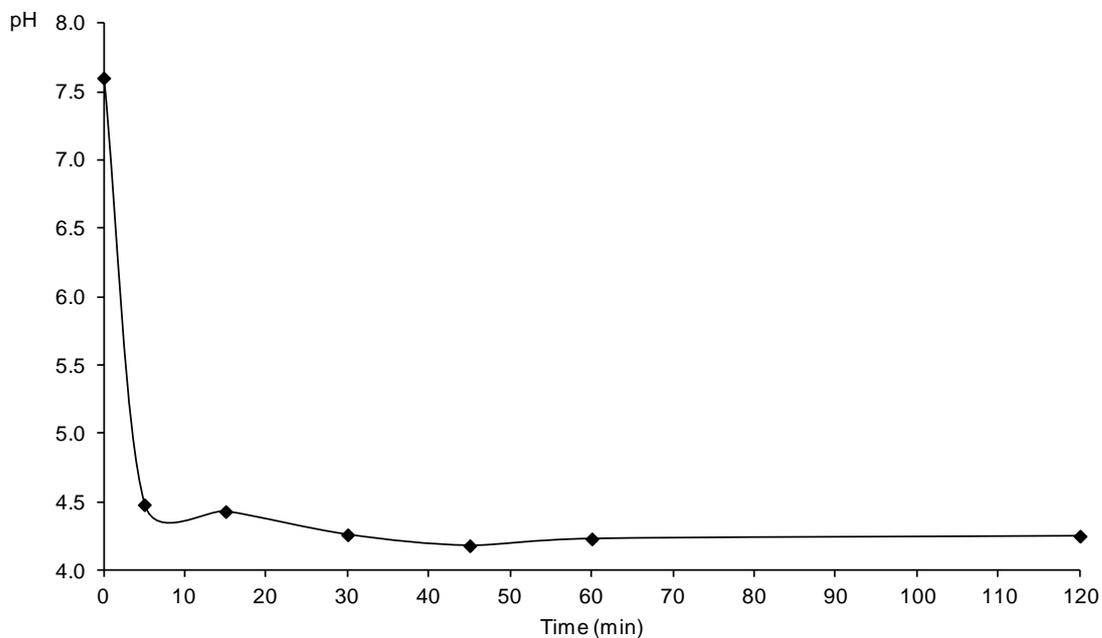
Figure 2. Variation of the pH in the kinetic process

3.3 Adsorption isotherms
3.2.2 Adsorption mechanism
Figure 3 shows the plots for the adsorption of Se on FGD-gypsum and Freundlich constants derived from these plots are presented in Table 2.The experimental data correlates with the lineal Freundlich isotherm of Se (r^2= 0.9213).
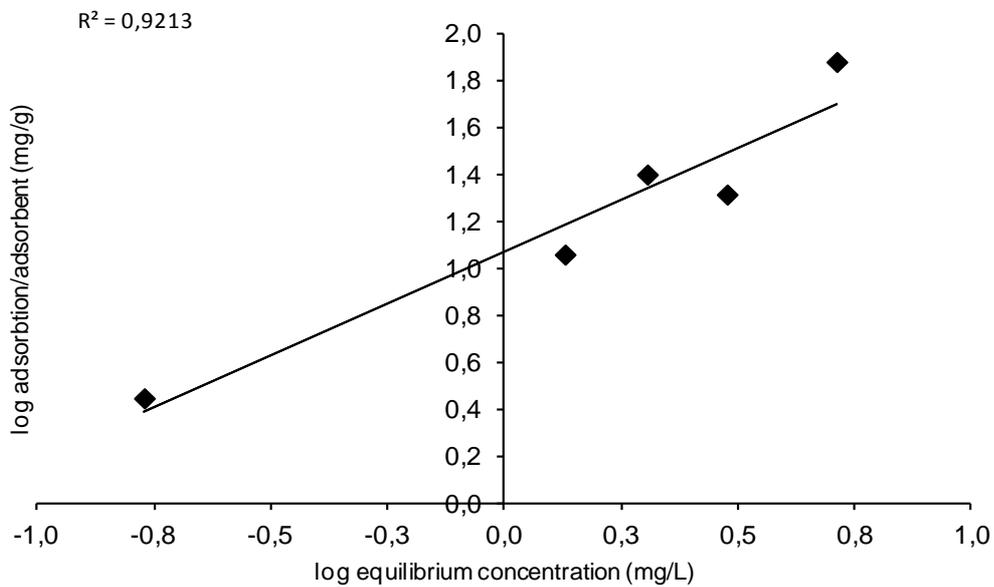
Figure 3. Freundlich lineal equation of Se adsorption

Table 2. Freundlich constants of Se adsorption on FGD-gysum

Freundlich constants	Laboratory temperature (25ºC)
n	0.887
K_F	0.1327

The successive steps involved in the adsorption of an organic/inorganic compound by an adsorbent are (Mittal et al., 2006):

i) transport of the ingoing ions (adsorbate) to the external surface of the adsorbent (film diffusion);

ii) transport of the adsorbates within the pores of the adsorbent except for a small amount of adsorption, which occurs on the external surface (particle diffusion);

iii) adsorption of the ingoing ion (adsorbate) on the interior surface of the adsorbent.

Of these, the second process can be considered the main mechanism of the Se adsorption on FGD-gypsum. However, in this adsorption process a desorption stage has to be considered. This could be related with the increase of the pH observed in the kinetic process and/or saturation of the FGD-gypsum surface by Se ions as a consequence of the non-homogeneous and impurities retain on FGD-gypsum surface.

3.4 Potentiometric titration

The point of zero charge (pzc) of the 2007 FGD-gypsum is 7.5 (Figure 4). The shape of the potentiometric curves point out that at pH lower than 7.5 the FGD gypsum surface is positively charged (Figure 3). When the pH is lower than the pzc value, acidic water donates more H^+ than OH^-, and therefore the adsorbent surface is positively charged (attracting anions). Conversely, above pzc the surface is negatively charged (attracting cations/repelling anions). Therefore, the acidic conditions of gypsum slurry in 2007 (pH 5.1) and in 2008 (pH 4.6) caused by the addition of $Al_2(SO_4)_3$, probably gave rise to the protonation of the surface of the FGD-gypsum. The protonation of the FGD-gypsum surface is probably the cause of the adsorption of Se on the FGD-gypsum surface.
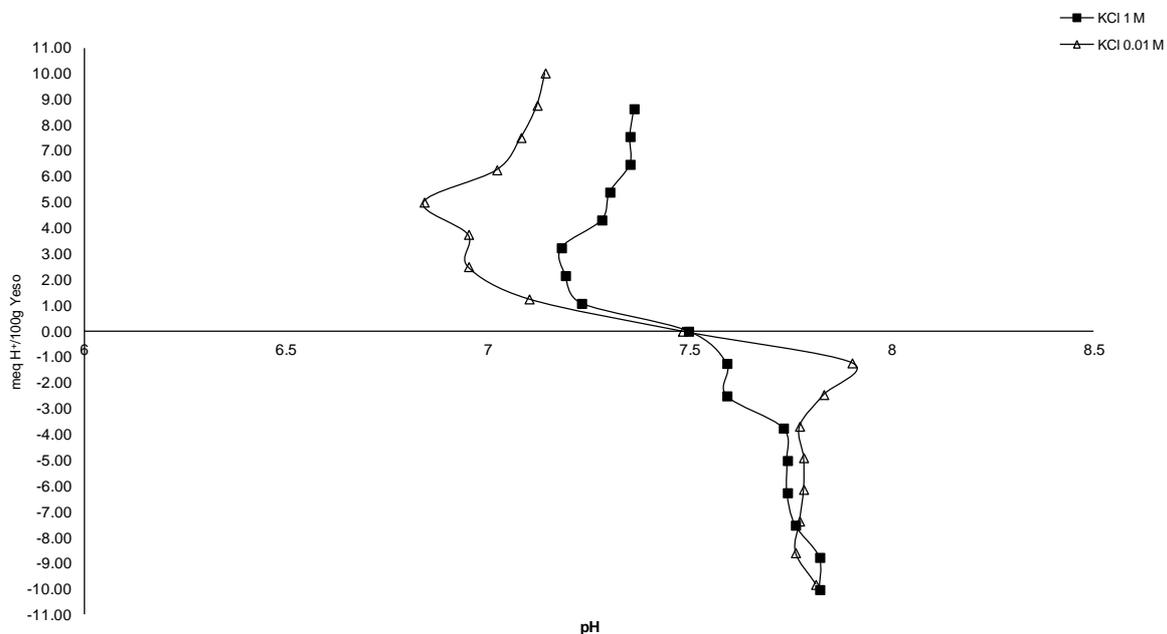
Figure 4. Potentiometric titration of FGD-gypsum

4. CONCLUSIONS

The report predicted from the current paper clearly suggest that use of FGD-gypsum as adsorbent is much economical, effectual and more viable than others to remove Se enriched in FGD waters. The different operational parameters observed during the process of investigations reveal that the pH, temperature, contact time, adsorbent dose and concentrations of the adsorbate govern the overall process of adsorption. The results obtained are well fitted in the linear forms of Freundlich isotherm.

The removal of Se from FGD waters by the employment of FGD gypsum is significant as prevention measure based on the management on solid (FGD gypsum) and water

(aqueous phase of gypsum slurry) streams before their production and the subsequent disposal in landfills and/or in application scenarios.

5. REFERENCES

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