Reduction of Lead and Antimony Ions from the Crystal Glass Wastewaters Utilising Adsorption

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Abstract: The presented research examined five adsorbents, i.e., zeolite 4A, a mixture of three zeolites (4A, 13X, and ZSM-5), natural zeolite (tuff), activated carbon, and peat, and their potential capability for removal of exceeded ions of lead (Pb), antimony (Sb), sulphates (SO\textsubscript{4}\textsuperscript{2-}), and fluorides (F\textsuperscript{-}) from real wastewater generated in the crystal glass industry, which was previously treated in-situ by flocculation, with the aim to attain the statutory values for discharge into watercourses or possible recycling. The screening experiment evidenced that the tuff was the most suitable adsorbent for the reduction of Pb (93.8%) and F\textsuperscript{-} (98.1%). It also lowered wastewater’s pH sufficiently from 9.6 to 7.8, although it was less appropriate for the reduction of Sb (66.7%) as compared to activated carbon (96.7%) or peat (99.9%). By adjusting the pH of the initial wastewater to pH 5, its adsorption capacity even enlarged. Results from the tuff-filled column experiment revealed reduction of Pb up to 97%, Sb up to 80%, and F\textsuperscript{-} up to 96%, depending on the velocity flow, and thus it could be used for post-treatment (and recycling) of wastewaters from the crystal glass industry. Moreover, the system showed an explicit buffering capacity, but negligible reduction of the SO\textsubscript{4}\textsuperscript{2-}.

Keywords: crystal glass industry; wastewater treatment; adsorbents; antimony; lead

1. Introduction

Fast-growing industrial wastewaters, which originate from metallurgy plants, the textile industry, glass production, chemicals and pigments’ manufacturing, metal deposition facilities, mining activities, tanning, and petroleum refining, etc., in recent decades have represented severe environmental problems due to their variable and complex composition [1–3]. They contain numerous pollutants of different origin and properties, including mixtures of chemicals, organic matter, heavy metals, and coloured compounds with elevated organic parameters, i.e., chemical oxygen demand (COD); biochemical oxygen demand (BOD); total organic carbon (TOC); adsorbable organic halogens (AOX); and inorganic parameters, i.e., chlorides, sulphates, sulphides, fluorides, nitrates, etc.

Unlike organic compounds, heavy metal ions such as cadmium (Cd), zinc (Zn), copper (Cu), nickel (Ni), arsenic (As), chromium (Cr), mercury (Hg), antimony (Sb), and lead (Pb) are not biodegradable. On the other hand, they are highly soluble in water, and thus tend to bioaccumulate and biomagnify in living tissues, which could lead to the initiation of different diseases and disorders [4]. Moreover, many heavy metal ions are toxic or carcinogenic, depending on the route and duration of the metals’ exposure, as well as the absorbed dose [5]. Therefore, they need to be removed from the wastewaters prior to discharge into biological treatment plants and/or water ecosystems, by the selection of a proper treatment process depending on the composition and amount of effluent.

Several techniques are employed for the reduction of heavy metals in wastewaters, including coagulation, adsorption, membrane filtration, electrodialysis, oxidation, chemical precipitation, reverse osmosis, ion exchange, etc. [5–11]. Among those listed, adsorption is one of the most popular, since it is a simple, easy to operate, low-cost, and efficient purification method, used widely for diverse wastewaters [12,13]. It involves attracting
and retaining the adsorbate molecules over the surface of an adsorbent, either via physical interaction (physisorption) or by chemical forces (chemisorption) between the adsorbate and adsorbent. Thus, the adsorption efficiency depends on different parameters, such as the physical or chemical properties of the adsorbent, the surface area/unit weight of the adsorbent, and the nature of the particle being adhered on the surface of the adsorbent [14]. For these purposes, numerous low-cost adsorbents were studied, namely, clay minerals, natural biomass, zeolites, activated carbons, etc. [6,7]. Their sorption properties depend on the location where they are found [15].

The industry of glass manufacturing in the EU is very large and widespread, reaching a volume of 37.2 million tons in 2019 (Europe Glass Alliance Statistical Report 2019–2020). Five different sectors, i.e., container glass, building, automotive and solar-energy glass (flat glass), continuous-filament glass fibre, domestic glass, and special glass, include a variety of specific products and generate large quantities of highly hazardous wastewaters from different facilities, such as washing, cooling, cullet separation, grinding, and polishing [3,16]. They are composed of glass solids, heavy metals, oils, lubricants, soluble and insoluble silica particles, dissolved salts, etc. [3,17].

Especially, wastewaters from crystal glass production are rich with hazardous heavy metals, since typical crystal glass is composed of 54–65% of SiO$_2$, 25–30% of PbO, 13–15% of Na$_2$O or K$_2$O, and different additives. According to Besisa et al. [18], such wastewaters contain more than 30% of the toxic Pb compounds, which, if entering the system of drinking water, could cause digestive problems, neurological disorders, high blood pressure, reproductive health problems, kidney dysfunction, muscle and joint pain, as well as memory and concentration problems in adults [5]. PbO could be replaced partly with BaO, ZnO, and K$_2$O, but would result in lower density and brilliance as compared to PbO glass. In addition, some metallic ions based on Sb, As, Cu, Cr, Cd, Ni, Zn, etc., which are used as transparent pigments for the colouration of glass, are also toxic to human health in higher concentrations and longer exposure time, causing damage to the skin, eyes, lungs, stomach, liver, kidneys, heart, and nervous system [19,20].

Therefore, diverse approaches are used to treat effluents from the glass industry. Gholipour et al. [3] utilised a horizontal sub-surface flow constructed wetland (HFCW) system planted with Cortaderia Selloana, revealing high efficiency with removal rates of BOD$_5$ and COD up to 90%, total suspended solids (TSS) up to 99%, total nitrogen (TN) and total phosphorus (TP) of more than 90%. Kang and Choo [21] proposed a microfiltration/ultrafiltration (MF/UF) technique as an alternative for the existing coagulation and sand filtration processes for the separation of fine clay and glass particles, with the aim to reuse the treated water in the glass manufacturing process. In addition, the same authors [22] tested a pilot-scale MF system, combining two types of submerged membranes, for the reclamation and reuse of glass industry wastewater. Lee et al. [23] developed nanofiltration coupled with lime-precipitation for removal of scale-forming ions, such as calcium, sulphates and silicates, from crystal glass wastewaters, in order to obtain recycled water of high quality. Doma et al. [24] reported efficient reduction of hazardous Pb, organic pollutants, and suspended solids from crystal glass wastewaters by comparison of two low-cost treatment technologies, coagulation/flocculation (95%, 99%, and 99% of COD, TSS, and Pb removal), and plain sedimentation followed by rapid sand filtration (97%, 99% and 99% of COD, TSS and Pb removal), in order to reuse them as treated waters into the manufacturing processes, attaining zero discharge of wastewaters. Based on encouraging results, the second alternative was designed in the factory, composed of two settling tanks and four rapid sand filters, reducing water consumption by the range of 90% to 95%.

Studies dealing with the treatment of specific wastewaters from crystal glass production are rarely described in articles. The novelty of this study presents a three-phase study including: (i) A series of shake-flask trials for screening of five selected adsorbents, (ii) changing the pH and contact time in a batch adsorption experiment, and (iii) a laboratory-scale fixed-bed column system, using the findings from preliminary experiments. This kind of a system can be scaled-up and used for the post-treatment (and
recycling) of wastewaters onsite. There is no information in the literature concerning the use of the proposed five adsorbents (peat, two synthetic zeolites, tuff, and activated carbon) for the reduction of ions of Pb, Sb, SO$_4^{2−}$, and F$^−$ from the complex mixture of real wastewater generated in the crystal glass industry, a fact which confirms without a doubt the novelty of this work.

2. Materials and Methods

2.1. Wastewater Composition

The adsorption experiments were conducted on real wastewater generated in crystal glass production, which was a mixture of:

(i) Cooling water for abrasives from the grinding of crystal glass, contaminated with Pb, Sb, and abraded glass of size 0.001–0.07 mm,

(ii) Water from acid polishing of glass products, composed of residues of sulphuric acid (H$_2$SO$_4$), hydrofluoric acid (HF), hexafluorosilicic acid (H$_2$SiF$_6$) and their salts, neutralised in an industrial plant by Ca(OH)$_2$. It also contains Pb and Sb ions’ residues.

Twelve liters of cooling water were taken from the reservoir after treatment on an industrial flocculation plant and mixed with 8 L of neutralized water from acid polishing. The as-prepared wastewater sample was kept in a cool place and used further for the adsorption experiments.

Table 1 shows the minimal, maximal, and average values of the key quality parameters monitored monthly in both cooling and polishing wastewaters for a 2-year period.

|                            | Pb (mg/L) | Sb (mg/L) | pH     | Pb (mg/L) | Sb (mg/L) | pH   | SO$_4^{2−}$ (mg/L) |
|-----------------------------|-----------|-----------|--------|-----------|-----------|------|--------------------|
| **Minimal**                 | 0.2       | <DL *     | 8.32   | 0.1       | <DL *     | 7.3  | 1500               |
| **Maximal**                 | 4         | 1.8       | 10.44  | 2         | 0.4       | 9.1  | 3300               |
| **Average**                 | 1.08      | 0.45      | 9.18   | 0.6       | 0.2       | 7.8  | 2150               |
| **Limit value** **          | 0.5       | 0.3       | 6.5–9.5| 0.5       | 0.3       | 6.5–9.5| 1000               |

* below detection limit, ** UL RS 2007, no. 45, pp. 6206, Council Directive 2006/11/ES and Council Directive 96/61/ES.

2.2. Adsorbents

Five different commercially available adsorbents were employed in the presented study. Two types of synthetic zeolites, zeolite 4A and a mixture of three zeolites: 4A, 13X, and ZSM-5 in a ratio of 60:30:10 (mix), both in the form of granules of 2–5 mm in size, were synthesised industrially and supplied by Silke Zeolites Production, Inc. (Kidričev, Slovenia). Natural zeolitic tuff was received from a quarry at Zaloška Gorica, Slovenia, with particles’ sizes of 3–10 mm. Based on the supplier’s information, it was extremely rich with natural zeolites (more than 50%) and other minerals such as quartz, plagioclase, montmorillonite, and amorphous glassy compounds. Peat was purchased from Humko (Bled, Slovenia), and granular activated carbon (AC) with particle sizes of 2–5 mm from Riedel de Haen.

Before the experiments started, all adsorbents were washed with deionised water and dried; zeolites, tuff, and AC at a temperature of 105 °C and peat at 85 °C for 3 h. Additionally, adsorbents were kept at a constant temperature for 24 h.

2.3. Adsorption Trials

The ability of the selected adsorbents to reduce heavy metals, fluorides, and sulphates from crystal glass wastewater was evaluated in three phases:

(1) A preliminary screening trial, where five adsorbents, i.e., mix, 4A, tuff, AC, and peat, were employed in the batch adsorption experiments;

(2) A batch adsorption experiment with the most efficient adsorbent, namely tuff, selected in the preliminary phase; herein, pH and adsorption time were changed,
(3) A laboratory-scale column experiment with tuff; herein, wastewater flow was changed. All experiments were performed in triplicate at an ambient temperature of 22 ± 2 °C. Prior to analysis of the selected parameters, the treated wastewaters were centrifuged for 15 min at 3000 rpm.

In the screening adsorption experiment, a pre-optimised quantity of an individual adsorbent (30 mg) was added in a 500 mL conical flask, together with 200 mL of wastewater. All flasks were sealed and shaken on an orbital shaker at 160 rpm for 24 h. Afterwards, the parameters Pb, Sb, TOC, SO$_4^{2−}$, F$^{−}$, and pH were determined in a supernatant and the percentage of their reduction calculated.

Based on those results, tuff was selected as the most efficient adsorbent and was, therefore, used in further experiments. In the case of the batch trial, the same quantity of tuff (30 mg) was shaken in a 500 mL conical flask at 160 rpm, together with 200 mL of wastewater for different time intervals (6, 18, or 24 h). pH was adjusted to pH 4 by 50 mM citrate buffer, pH 5 by 0.1 M acetate buffer, pH 6 by 0.1 citrate buffer or pH 8 by sodium phosphate buffer. After completion of the adsorption trials, Pb, Sb, SO$_4^{2−}$, and F$^{−}$ were analysed in the supernatant, and the percentage of reduction and the amount of adsorbed pollutant were calculated, depending on the pH and contact time.

Finally, the laboratory-scale column experiment was accomplished, with the aim to compare treatment abilities of the two proposed techniques. The laboratory set-up was composed of a polypropylene column with a diameter of 6 cm and a length of 36 cm (1 L volume), with inlet and outlet pipes, a plastic reservoir for the wastewater storage equipped with a stirrer for constant mixing, and a pump to attain a continuous wastewater flow through the filled column. The columns were fortified with a PP net and packed with 458 g of tuff with a bed volume of 0.6 L. Nine litres of wastewater was pumped through the column with the flow rate of 10 mL/h, 30 mL/h or 90 mL/h. Water samples for the analysis were collected from the outflow and analysed afterwards.

2.4. Analytical Procedure

2.4.1. Characterisation of Adsorbents

The surface morphologies of the selected adsorbents were characterised using Scanning Electron Microscopy (SEM). A small amount of an individual adsorbent in powder form was placed onto an adhesive carbon tape fixed to a brass holder and observed on a Gemini Supra 35 V P Scanning Electron Microscope (Carl Zeiss NTS GmbH, Oberkochen, Germany), with a maximum scan resolution of up to 1.5 nm at 20 kV. Fourier Transform Infra-Red (FTIR) spectroscopic measurements of adsorbents were carried out to determine the functional groups responsible for adsorbate uptakes, using an FTIR System Spectrum GX spectrophotometer (Perkin Elmer) with a Golden Gate ATR attachment and a diamond crystal. The transmittance spectra were obtained within the range of 4000−650 cm$^{-1}$, with 16 scans and a resolution of 4 cm$^{-1}$. The pH of individual adsorbents was determined in 0.01 M CaCl$_2$ solution, using an adsorbent: solution ratio 1:5, according to standard ISO 10390, using an MA 235 pH/ion analyser (Mettler Toledo). Nitrogen physisorption measurements of the selected adsorbents were performed on a Tristar 3000 adsorption analyser (Micromeritics) at 77 K. The samples were purged with nitrogen overnight at 200 °C prior to the measurements. The BET specific surface area was calculated using the adsorption branch of the isotherm in the relative pressure (p/p0) range between 0.01 and 0.1.

2.4.2. Analysis of Wastewaters

The pH of wastewaters before and after trials was measured according to the ISO 10523 standard, using an Orion Star™ A221 portable pH meter (Thermo Fisher Scientific, Waltham, MA, USA). The Total Organic Carbon (TOC) was determined by means of a Multi N/C 2100 S analyser (Analytik Jena, GmbH, Jena, Germany), in accordance with the ISO 8245 standard. Pb and Sb metal ions were determined using Flame Atomic Absorption Spectrometric (FAAS) analysis on a SpectrAA-30 (Varian) atomic absorption spectrometer.
with a hollow cathode lamp as the radiation source and a deuterium background corrector, at respective wavelengths or according to the electrical atomic absorption spectrophotometry (ETAAS) on a platform in the case of lower concentrations. Fluorides were determined potentiometrically with an ion-selective electrode, using WTW pMX 3000/Ion (Xylem Analytics, Nesttun, Norway) and sulphates spectrophotometrically at a definite wavelength of 450 nm, using a HACH-DR/2000 spectrophotometer (Danaher, Washington, DC, USA).

The percentage of pollutant reduction (R) was calculated according to Equation (1), and the amount of adsorbed pollutant (Q) according to Equation (2) [15]:

\[
R = \frac{C_0 - C}{C_0} \cdot 100
\]

\[
Q = (C_0 - C) \cdot \frac{V}{W}
\]

where \( C_0 \) is the initial concentration of pollutant (mg/L); \( C \) is the concentration of pollutant after treatment (mg/L); \( Q \) is the amount of adsorbed pollutant (mg/g); \( V \) is the initial volume of wastewater (L); and \( W \) is the weight of adsorbent (g).

3. Results and Discussion

3.1. Characterisation of Adsorbents

Five commercially available adsorbents, i.e., one natural and two synthetic zeolites, peat and activated carbon, were assessed for post-treatment of wastewaters from crystal glass production, with a special focus on heavy metals’ reduction. Tuff and peat were selected due to their low cost, AC due to its proven high efficiency and wide applicability for diverse pollutants, and both synthetic zeolites due to their specific structure, with the aim to compare their removal capacity with previously mentioned adsorbents. Several analytical techniques were employed in order to provide qualitative information about the chemical composition, surface morphology and pH of adsorbents that could impact on their adsorption and filtration abilities as well as ion exchange capacity. The adsorbents’ surfaces under SEM are shown in Figure 1.

![Figure 1. SEM of selected adsorbents: (a) Mix; (b) 4A; (c) tuff; (d) AC; and (e) peat.](image)

From Figure 1a a mixture of different zeolites can be perceived unequivocally, namely, cubic crystals of zeolite A (as in Figure 1b), octahedral crystals of zeolite X and pentasil building blocks of zeolite ZSM-5 with average size of 1–3 µm. Zeolitic tuff (Figure 1c) has a heterogenous, coarse-grained structure, similar to activated carbon (Figure 1d), with a high specific surface area and high ion exchange capacity, indicating good adsorption ability [6]. As compared to other adsorbents, peat has a highly porous structure shown in Figure 1e, which is an assemblage of decayed plant cellular structures interconnected with less decayed fibres [25].

Within the IR spectra in Figure 2a, the assignment of characteristic band positions can be a basis for the identification of materials and their chemical structures that could
influence the physical, or even chemical, attractions between pollutants and adsorbents in a system. On the other hand, the pH of the adsorbents themselves (Figure 2c) could affect (increase or decrease) the pH of treated wastewaters significantly, and thus, also the pollutant uptake.

Figure 2a,b depict the FTIR spectra of the selected adsorbents, with typical peak positions for zeolites, namely, the intensive transmittance peak in the area of low frequency at a wavenumber of ca. 966 cm\(^{-1}\) (both synthetic zeolites) and a broader peak at 997 cm\(^{-1}\) (tuff), which corresponds to the stretching vibrations of the Si(Al)-O functional groups [26]. In addition, smaller peaks within the range of 840–790 cm\(^{-1}\) are attributed to the Si-O-Si vibrations of internal oxygen bridges, and a small transmission band at ~1645 cm\(^{-1}\) to water molecules. The FTIR analysis of natural peat revealed stretching vibrations of free hydroxyl groups at 3450–3100 cm\(^{-1}\), stretching vibrations of C-H bonds at 2980–2840 cm\(^{-1}\), stretching vibrations of C=O bonds at 1750–1500 cm\(^{-1}\) and water molecules at ~1645 cm\(^{-1}\), and stretching vibrations of C-O bonds at 1100–1000 cm\(^{-1}\), as also interpreted fully by [15]. The presence of numerous functional groups on the peat’s surface, together with its highly porous structure, makes peat an attractive adsorbent for diverse pollutants and also heavy metals. On the other hand, FTIR analysis of AC does not indicate any functional group on its surface. As explained by Kołodynska et al. [27], the type of feedstock for the preparation of AC, as well as the operating conditions of the carbonisation and activation process, affect its surface and physicochemical properties, selectivity and capacity, and, thus, adsorption capability.

From Figure 2c it can be seen that both synthetic zeolites have high pH, on average 10.8 (mix) and 11.3 (4A), due to the mode of preparation, utilising the hydrothermal crystallisation of the amorphous sodium aluminosilicate gels containing a proper molar ratio of reactive sources of silicon dioxide (SiO\(_2\)), aluminium oxide (Al\(_2\)O\(_3\)), water (H\(_2\)O), and sodium oxide (Na\(_2\)O), as described in [26]. AC also has an alkaline pH (around pH 11), which, as explained above, depends on the type of feedstock and conditions during its
processing. On the other hand, peat has a highly acidic pH due to the content of fulvic and humic acids (high concentration of H⁺ ions), depending on the excavation site, i.e., humidity, temperature, maturity of the peat, organic matters, etc. [15, 28]. Tuff had pH 8, measured in a 0.01 M CaCl₂ solution. During the 1 h trial, some admixtures were leached out from the tuff (e.g., carbonates), increasing the pH value.

### 3.2. Batch Experiment

The screening of five adsorbents was carried out in the first stage of the proposed study (Figure 3). Therein, the presence of two metallic ions (Pb, Sb), TOC, SO₄²⁻, F⁻, and pH were determined in the initial crystal glass wastewater, and in the treated wastewater after 24 h of the shake-flask experiment. Moreover, the percentage of reduction was calculated for an individual pollution parameter according to Equation (1) and presented graphically on the secondary axis.

![Figure 3](image-url)

**Figure 3.** Screening of adsorbents. The amount of pollutants in wastewater was shown in columns on primary y axis and pollutant reduction as black dots on secondary y axis. Orange lines are limit values for discharge in watercourses (UL RS 2007, no. 45, pp. 6206, Council Directive 2006/11/ES and Council Directive 96/61/ES).

As can be seen from the initial values in Figure 3, the mixture of real wastewaters from crystal glass production (as described in Section 2.1) was highly contaminated with Pb, Sb, SO₄²⁻, and F⁻ ions, vastly exceeding the limit values for discharge in watercourses as stated in UL RS 2007, no. 45, pp. 6206, Council Directive 2006/11/ES and Council Directive 96/61/ES. The initial pH was slightly above the regulation, although these wastewaters sometimes reach high alkalinity (pH >10.5–Table 1), depending on the type of production facility (wastewater content) and the production extent. The increase or decrease of the wastewater’s pH during adsorption trials (Figure 3), and, consequently, the absorption capability, was caused by the intrinsic pH of individual adsorbents (Figure 2b). Adsorbents with highly alkaline pH (AC, 4A and mix) enlarged the wastewater pH (up to pH 12.1), and peat with acidic pH decreased the pH (down to 4.4), which can also influence the environment negatively. Bartczak et al. [15] provided an additional explanation for the combination of peat and metal ions in water based on the ion exchange principles—the more metal ions were adsorbed on the peat, the more hydrogen ions (H⁺) were released from peat into the water, decreasing its pH value.

Figure 3 also indicates that the best adsorbents for reduction of Pb ions were tuff (93.9%), peat (93.9%), and the zeolite mix (83.1%), although all the studied adsorbents lowered Pb significantly below the maximal permissible value. These results are in accordance...
with the results obtained by different authors. Bartzak et al. [15] reported removal efficiency of Pb ions using natural peat from 63.1% (at pH1) up to 100% (at pH5). Malik et al. [4] summarised different studies, where Pb removal efficiency varied from 80.6% up to 100% using AC of different sources, and from 55% up to 99% using different natural zeolites. Similar was summarised by [6], revealing that natural zeolite of clinoptilolite type absorb up to 99% of Pb ions. The three-dimensional crystal structure of tuff with interior channels allows penetration of inorganic and organic ions into the structure, and thus, is recognised as a low-cost and very effective adsorbent for metallic and inorganic ions, as well as organic contaminants (TOC) [29]. Moreover, the selected tuff is composed of various minerals such as quartz, plagioclase, montmorillonite, and amorphous glassy compounds, which have an important impact on its ion exchange and adsorption ability, besides a high specific surface area. Additionally, the best adsorbents for Sb ions were peat (99.9%) and AC (86.7%), reaching acceptable values for release in watercourses. The AC had the highest BET surface area (840 m$^2$/g), followed by tuff (480 m$^2$/g), mix (204 m$^2$/g), and 4A (120 m$^2$/g). The specific surface area of peat as a natural adsorbent is small, i.e., 12 m$^2$/g, in spite of its good sorption properties. This could be attributed to the large total pore volume and pore size of peat, as could be observed from the SEM micrograph (Figure 1e). Peat also has a lot of functional groups, such as carboxyl, phenolic, hydroxyl, etc. (Figure 2a), which contributed significantly to the interactions with the positively charged heavy metal ions, and, consecutively, to its high adsorption capability [15,25,30]. Thus, the removal mechanism of peat is based upon metal biosorption, including chemisorption, complexation, adsorption on the surface, diffusion through pores, and ion exchange. On the other hand, peat increased TOC (from 4.82 mg/L up to 9.15 mg/L), due to the releasing of the organic compounds from which peat is composed, into the solution, including organic acids, cellulose, lignin, and proteins [15].

All the selected adsorbents were less efficient for the removal of SO$_4^{2-}$, due to their low affinity for anions. Despite the 38.7% and 35.5% reductions reached by tuff and AC, respectively, SO$_4^{2-}$ remained significantly above the tolerated values for discharge in watercourses, which would cause an imbalance in the natural sulphur cycle. A similar result was published by Runtti et al. [31], where barium-modified zeolite lowered SO$_4^{2-}$ ions in synthetically prepared wastewater up to 32% at initial concentration of 5 g/L, depending on pH. Furthermore, the reduction of F$^-$ ions in our study ranged from 49% (mix) up to 98% (tuff), which was higher compared to SO$_4^{2-}$, although only tuff reduced the vast amount of F$^-$ ions in initial wastewater (882 mg/L) sufficiently below the limit value (25 mg/L). Waghmare et al. [32] noticed that the H ions present in the solution reacted with the F$^-$ ions in pH 4 to 8, leading to the weak ionised H-F formation, and thus, to higher adsorption. On the other hand, the removal capacity of fluoride decreased in a pH above 8, when both zeolites and AC were employed, due to the negatively charged adsorbent surface, and, consequently, higher concentration of OH ions in the solution that compete with the F$^-$ ions for adsorption. The same authors also found that SO$_4^{2-}$-coexisting ions had a negligible effect on F$^-$ removal, although the presence of positively charged heavy metal ions in the presented study, as well as the high concentration of SO$_4^{2-}$, could, mutually, influence the adsorption ability of individual adsorbents.

The efficient adsorption of heavy metals is highly dependent on the initial wastewater’s pH, which determines the surface charge of the adsorbent, the concentration of ions on the functional groups of the adsorbent, and the degree of ionisation of the adsorbate [33,34]. Moreover, as the adsorption depends also on the contact time, thus, the best adsorbent obtained from the screening experiment (in our case zeolitic tuff) was used further in the pH- and time-dependent study, adjusting the pH to 4, 5, 6, or 8, and the adsorption time to 6, 16, and 24 h. The results of the reduction of an individual pollution parameter in wastewater calculated according to Equation (1) and the adsorption capacity of tuff calculated according to Equation (2), were depicted in Figure 4.
further in the pH- and time-dependent study, adjusting the pH to 4, 5, 6, or 8, and the adsorption time to 6, 16, and 24 h. The results of the reduction of an individual pollution parameter in wastewater calculated according to Equation (1) and the adsorption capacity of tuff calculated according to Equation (2), were depicted in Figure 4.

Figure 4. Reduction percentage (left) and amount of pollutant per weight of adsorbent (right): (a) Pb; (b) Sb; (c) SO\(_{4}^{2-}\); and (d) F\(^{-}\).

As can be observed from Figure 4, the reduction of all inspected pollutants in wastewater, and thus, the adsorption capacity of tuff, was the highest when the initial wastewater’s pH was adjusted to pH 5, i.e., up to 96% or 6.4 mg/g (Pb), up to 75% or 6.0 mg/g (Sb), up to 53% or 5.67 g/g (SO\(_{4}^{2-}\)), and 99.6% or 4.15 g/g (F\(^{-}\)). The same phenomenon was reported and explained for diverse ions and adsorbents by different authors [6,20,35,36].
Kobayashi et al. [35] described that the quantity of adsorbed Pb ions on K-type zeolite synthesised from coal fly ash increased as the pH raised from 3 to 5 (from 52 mg/g up to 230 mg/g) and decreased sharply above pH 5 to 100 mg/g (at pH 9). The pH of the wastewater has a significant impact on the characteristics of heavy metals; at low to neutral pH, they exist in their cationic state and tend to be more soluble and mobile [34]. At higher pH, the heavy metals form complexes with hydroxide ions, affecting the oxidation state of the heavy metal. Also, the metals could form solids that precipitate out of the water. On the other hand, tuff has a high cation exchange capacity, due to the presence of hydrated cations such as Ca²⁺, Na⁺, K⁺, etc. on the interlayer surfaces, which can be easily replaced with heavy metal ions. Moreover, as explained by [35], in an acidic pH medium, the zeolite surface is covered with protons (Al-OH²⁺ and Si-OH²⁺), with which the metallic ions Pb²⁺ and Sb³⁺ compete for the adsorption sites. Thus, at lower pHs (below pH 4), the concentration of H⁺ ions in the solution are higher, and the absorbed amount of metal ions decreases in tuff. As the pH increased above pH 7, the deprotonation of hydroxyl groups increased, which implies that electron repulsion occurred in the basic medium between the negatively charged Pb and Sb species, e.g., Pb(OH)₃⁻, Pb(OH)₄²⁻, Sb(OH)₆⁶⁻, and the negatively charged tuff surface, decreasing the tuff adsorption capacity for both metals.

Furthermore, the removal efficiency of SO₄²⁻ ions is better when the initial pH is lower than, or equal to 5. The most probable reason for better removal under acidic conditions is the highly protonated surface of tuff in an acidic medium, which tends to adsorb negative ions. In addition, the large amount of negatively charged OH⁻ ions compete with the SO₄²⁻ ions for unoccupied surface sites at a higher pH, decreasing the sorption of SO₄²⁻ [31]. The pH of a solution also has a significant impact on the adsorption of F⁻ ions, as already explained in the screening experiment. A high concentration of H⁺ ions present at pH 5 leads to higher adsorption, and conversely, the removal capacity of F⁻ decreases at pH 8, on account of the higher concentration of OH⁻ ions in the solution that compete with the F⁻ ions for adsorption. Waghmare et al. [32] proposed another possible removal mechanism of F⁻ when metallic ions are co-present in a solution; when Na⁺ or K⁺ in zeolite are exchanged with metallic ions, they become active sites for F⁻ adsorption. The properties such as small size, hard base nature, and high electro negativity, makes the F⁻ compatible with metal ions. Moreover, the co-existence of other ions in wastewater and their concentration could influence the removal efficiency of tuff, which is not a part of this study, but will be researched in detail in the future. As mentioned by Ciosek et al. [37], in multi-component systems such as industrial wastewaters, the exchange rate may vary for the various counter-ions in the solution, with the possibility that the concentration of the initial compound in either the adsorbent or solution can fluctuate prior to attaining its balanced state.

In addition, the higher the contact time was, the higher the percentage of reduction, irrespectively of the pollution parameter. In the first 6 h, adsorption increased rapidly, due to the availability of adsorption sites on the tuff, and, after that, slowed down, depending on the water pH and pollutant type. The same was noted by Kobayashi et al. [35]. Under the experimental conditions of their study, the adsorption equilibrium was reached within approximately 6 h. In the case of our study, there was not a big difference in the adsorption capacity of tuff to Pb, Sb, and F⁻ ions between 16 and 24 h, since the equilibrium was achieved. SO₄²⁻ ions needed more time to adsorb, probably due to their high concentration.

3.3. Laboratory-Scale Column Trial

The performance of the column packed with pre-optimised adsorbent from the screening experiments (tuff) was evaluated by monitoring the different pollutants, i.e., Pb, Sb, SO₄²⁻, F⁻, and pH in both the initial and treated wastewaters, and the obtained results are summarised in Table 2. The system was operated continuously without backwashing at three velocity flows, 10, 30, and 90 mL/h, with the aim to determine the optimal conditions for removal of exceeded pollutants from crystal glass wastewater. As compared to the batch adsorption trial, in the column study, the adsorbate is continuously in contact with
a given quantity of fresh adsorbent, thus providing the required concentration gradients between adsorbent and adsorbate for adsorption [38]. Moreover, the columns’ or fixed-bed reactors’ approach is more convenient for industrial plants, requiring less investment and operational costs as compared to its batch mode counterparts [37].

Table 2. The monitored parameters in both initial and treated wastewaters.

| Velocity flow | Pb (mg/L) | Sb (mg/L) | SO$_{4}^{2-}$ (mg/L) | F$^-$ (mg/L) | pH         |
|---------------|-----------|-----------|----------------------|--------------|------------|
| Initial       | 0.95 ± 0.05 | 0.9 ± 0.08 | 2750 ± 112           | 450 ± 15     | 9.92 ± 0.40 |
| 10 mL/h       | 0.029 ± 0.01 | 0.18 ± 0.02 | 2115 ± 23            | 17 ± 2.7     | 7.82 ± 0.08 |
| 30 mL/h       | 0.095 ± 0.01 | 0.29 ± 0.02 | 2270 ± 46            | 89 ± 3.5     | 7.95 ± 0.07 |
| 90 mL/h       | 0.11 ± 0.04  | 0.37 ± 0.06 | 2390 ± 72            | 109 ± 10.4   | 8.05 ± 0.20 |

It can be noticed from Table 2 that the values of metallic ions Pb and Sb in the initial wastewater were 0.95 and 0.9 mg/L, respectively, which were highly above the limiting values, similar as in previous batch trials. After the wastewater had percolated through the column, Pb was reduced from 88.4% up to 97.2% and Sb from 59.9% up to 80%, depending on the velocity flow. The higher the velocity was, the lower the retention time, and consequently, the lower was the percentage of reduction of all pollutants, although these values were not linear. Similar results were reported by Mokgehle et al. [38], who observed an increase of SO$_{4}^{2-}$ removal efficiency of zeolite synthesised from coal fly ash with a reduced flow rate. In the same study, the percentage removal of SO$_{4}^{2-}$ was 79.14% and 89.12% for the 10 mg/L and 1 mg/L of inlet solutions, respectively, employing a zeolite bed height of 4 cm and flow rate of 0.45 mL/min. In our experiment, the tuff-packed column was less efficient for removal of SO$_{4}^{2-}$ as compared to the mentioned study, although the experimental conditions were different. The reduction was from 2.2% (90 mL/h) up to 23.1% (10 mL/h), which is comparable with the results obtained in the 6 h shake-flask adsorption experiment (Figure 4c). Meanwhile, the initial wastewater’s pH was lowered significantly at the outflow, irrespective of the velocity flow. A sufficient removal efficiency could be observed for F$^-$ ions, i.e., from 75.8% up to 96.2%. The removal mechanism of both negatively charged ions from wastewaters was described in detail above. Furthermore, it is evident from Table 2 that the tuff-filled column had an explicit buffering capacity, as already expected from the reported study [39].

In general, the results gained from the column experiment could be compared with the batch experiments, while in some cases the removal efficiency was even better (Pb removal), revealing that such kind of fixed-bed system could be used successfully for post-treatment (and recycling) of cooling and polishing wastewaters from crystal glass production, especially when the quantity of pollutants are not extremely high.

4. Conclusions

The mixture of real wastewaters from crystal glass production, i.e., cooling water for abrasives from grinding of crystal glass (treated in-situ on an industrial flocculation plant) and water from acid polishing of glass products (previously neutralised), was post-treated by successfully utilising the adsorption approach. Herein, five adsorbents (zeolite 4A; a mixture of three zeolites: 4A, 13X, and ZSM-5; zeolitic tuff; AC; and peat) were qualitatively analysed and, after that, screened for potential reduction of exceeded Pb, Sb, SO$_{4}^{2-}$, and F$^-$ values, using batch adsorption experiments. Tuff, as the most promising candidate for the successful reduction of selected pollutants, was employed further in a fixed-bed column. The tuff-packed column reduced Pb up to 97%, Sb up to 80%, and F$^-$ up to 96%, depending on the velocity flow. The higher the velocity, the lower the retention time, and consequently, the lower the pollutants’ reduction, although this phenomena was not linear. Moreover, the system showed an explicit buffering capacity, but, on the other hand, negligible reduction of the SO$_{4}^{2-}$ content. The obtained results proved unequivocally that such kind of system could offer an optimal solution to meet the environmental legislation,
as well as the requirements for an effective and inexpensive post-treatment (or recycling) of crystal glass wastewaters, or other industrial wastewaters that contained heavy metal ions. Further work, combining different low-cost adsorbents, is needed to improve the wastewater’s treatment efficiency, alongside the increase of the velocity flow. In addition, the obtained results from the column experiment will be verified by the full-scale system onsite, which will enable recycling and reusing of the treated effluent from the crystal glass manufacturing processes, and thus, contribute to the freshwater resources conservation and to a reduction of the operation costs for the glass industry.

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