



Research Article

REMOVAL OF Co(II) AND Se(VI) FROM RAW METAL AND GLASS INDUSTRY WASTEWATERS USING NANO-SiO₂ / ZrO₂-CALCIUM ALGINATE AEROGELS

Sevil AKÇAĞLAR*

Dokuz Eylül University, Dept. of Mechanical, Engineering, Buca-İZMİR; ORCID:0000-0002-5386-1862

Received: 16.11.2017 Revised: 17.12.2017 Accepted: 22.01.2018

ABSTRACT

By doping ZrO₂ to the SiO₂ with aerogel; the Co(II) and Se(VI) from metal and glass industry wastewaters can be removed due their large surface area and high pore volume. For maximum Se(VI) and Co(II) adsorptions (99% and 96%) the optimum Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel composite concentrations was found as 4 mg/l, at a pH of 6.0 at a temperature of 80 °C after 45 min contact time. Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel were reused with the percentages of 83 % and 87% for Co(II) and Se(VI), respectively after four sequential utilisation. This reduce the treatment cost by 38%.

Keywords: Co(II), Se(VI), Metal Industry Wastewater, Glass Industry Wastewater, Adsorption, Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel, Reuse, Cost.

1. INTRODUCTION

Se is found in the effluents in the form of selenate (SeO₄²⁻) and selenite (SeO₃²⁻) from oil refineries in addition to the industries of glass production, semiconductors [1]. Cobalt, a natural element present in certain ores of the Earth's crust, is essential to life in trace amounts. It exists in the form of various salts. Cobalt has both beneficial and harmful effects on health. Important natural sources of cobalt in the environment are soil, dust and sea water. Cobalt and its salts are used in nuclear medicine, in semiconductors, in painting on glass and porcelain and electroplating as a catalyst for organic chemical reactions. The permissible limits of cobalt in the irrigation water and livestock watering are 0.05 and 1.0 mg/dm³, respectively (Environmental Bureau of Investigation, Canadian Water Quality Guidelines).

Adsorption studies have been utilized to understand the mobility and bioavailability of selenium in diverse systems, e.g. aluminium oxide [2], manganese nodules [3], [4], activated carbon [5], [6] and magnetite [7]. Silica (SiO₂), one of the most common oxide materials, has excellent insulation, high chemical stability, low thermal-expansion coefficient and low thermal conductivity [8]. SiO₂ glass has no grains with brittle uniform microstructure. This characteristic prevents further application of SiO₂ for structural usage.

Zirconium dioxide (ZrO₂) has high thermal expansion coefficient and excellent corrosion resistance [9]. Owing to the large surface area of ZrO₂, controllable pore size, and easy

* Corresponding Author: e-mail: sevil.akcaglar@deu.edu.tr, tel: (232) 301 92 36 / 19236

functionalization [10], mesoporous materials have opened several new avenues. Hydrogels are also promising candidates for many other applications in which small pores, such as micropores (pore size < 2 nm) and mesopores (2 nm < pore size < 50 nm), result in a high porosity and surface area responsible for adsorption [11]. SiO₂ aerogels match these conditions because they are highly ordered mesopore structures, showing large surface area (360-860 m²/g) and pore volume (0.36e2.9 1 cm³/g) [12].

High surface area and high porosity are the major requisite features including catalysis [13], adsorption and environmental cleanup [14], energy storage devices [15], and water repellent coatings [16] to name only a few examples for ZrO₂ / SiO₂ nano composite. Owing to the above-mentioned properties, environmental remediation feature of aerogels is of those recent rapidly growing and high-performance applications in energy related fields. The environmental remediation of aerogels is quite a matured field and could be conferred to air cleaning such as CO₂ adsorption from atmospheric air, industrial and municipal effluents and adsorptive removal of volatile organic contaminants and, to the water treatment process for adsorption of oil and hazardous organic compounds and heavy metal ions. The above-mentioned contaminants are of major pollutions causing the serious environmental problems such as global warming and hazards for human health.

In the current study, the feasibility of adsorbing of Selenium (VI) and Cobalt (II) from glass and metal industry wastewaters by nano SiO₂ / ZrO₂-Calcium Alginate Aerogel composite produced under laboratory conditions was investigated for the first time. The physicochemical properties of Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel composite were investigated by SEM, BET and Nitrogen adsorption / desorption isotherms. The effects of increasing Calcium Alginate Aerogel Concentrations in the Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel composite (2, 4, 6 mg/L), effects of Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel composite concentrations (1, 2, 3, 4, 5, 6 and 7 mg/L), effects of contact time (30, 45, 60, 70 and 80 min) and effect of pH (2, 4, 6, 7 and 8) on the adsorption capacities of Se(VI) and Co(II) were investigated.

2. MATERIAL AND METHODS

2.1. Preparation of Nano-Composites

2.1.1. Preparation of Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogels

The preparation of SiO₂ / ZrO₂-Calcium Alginate Aerogels mainly includes three steps [17]:

1. Synthesis of SiO₂ sol: 5.30 g of Polyethylene glycol (PEG) was dissolved in 30 mL hydrochloric acid (0.02 M). Then, 15 mL of Tetraethoxysilane (TEOS) was added into the resulting solutions with rapid stirring for 45 min, and 20 mL of Propylene oxide (PO) was added into the mixture. This mixture was transferred to the oven at 40 °C.

2. The preparation of ZrO₂ started with mixing of 0.17 Polyoxyethylene (PEO), 1.80 g ZrOCl₂·8H₂O, 2.6 mL deionized water and 2.8 mL ethanol during 160 min. Then 0.48 mL of PO was slowly added in the mixture. The resulting mixture was stirred for 7 min and transferred to the incubator at 80 °C.

3. ZrO₂ was added to SiO₂ by stirring to form homogeneously distributed Nano-SiO₂ / ZrO₂ composite. Then, three different calcium alginate concentrations (2.0g, 4.0 g and 6.0 g) were incorporated into the Nano SiO₂ / ZrO₂ composite by stirring for 20 min. This Nano composite was incubated in an incubator at 40 °C. After production of an aerogel, the liquid solvents were removed by solvent exchange at 40 °C. The produced Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel were dried at 40 °C [17].

2.1.2. Characterization of Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogels

The micrograph was recorded by the scanning electron microscopy (SEM) (SU-70) with an accelerating voltage of 3.0 kV. The surface area, average pore diameter and pore volume of the products were studied by nitrogen adsorption and desorption analysis (AUTO SORB-1-C). An UV Visible Spectrophotometer (DU800) was used for obtaining the absorption spectra from 200 to 500 nm. Ultraviolet and Visible Spectrophotometry (UV Vis) is used the samples for testing. The phases of waste forms were characterized by X-ray diffraction (X'pert PRO) method through determining the existence of different characteristic peaks. The diffraction data were collected over the angle range 10⁰-90⁰ with a step size of 0.02⁰. The back-scattered scanning electron microscopy (Hitachi S-3700N) was coupled with Energy Dispersive Spectroscopy (EDS) to investigate distribution of elements and microstructure of the waste forms [17].

2.2. Analytical Procedure

2.2.1. Se(VI) Measurement Method

A volume of 1 mL of was digested with 5 mL HNO₃ and H₂O₂ using glass industry and metal industry, separately as follows: 20 min up to 250°C and 15min at 250°C. After cooling down the digests were diluted with 1% HNO₃ and analyzed by ICP-MS. Quantitation was achieved by 5 point external calibration (standards from 0.1 mg/L to 4 mg/L, correlation coefficient R² = 0.9998, limit of linearity 105 mg/L) and validated by the analysis of Se(VI) reference material. The limit of detection for Se(VI) was 0.39 × 10⁻³ mg/L. Mobile phases for anion exchange liquid chromatography (HPLC-ICP-MS analysis) were prepared by dissolving an appropriate amount of ammonium acetate in deionized water to obtain the required concentrations at pH = 4.7: i) 5 mmol/L (solvent A) and ii) 150 mmol/L (solvent B). The mobile phase flow rate was 1 mL/min at 22 °C. The solutions were filtered and degassed before the use. The injection volume was 100 µL. Compounds were eluted with the increasing linear gradient from 0%–100% of solvent B within 21 min. The chromatograms were obtained with Se(VI) detection. In order to perform identification by ESI-MS/MS eluates were collected to vials at times corresponding to the retention times of previously registered selenium signals. The volumes of collected fractions were various depending on the selenium registered peak width.

2.2.2. Co(II) Measurement Method

A PG-990 (PG instrument Ltd., United Kingdom) atomic absorption spectrometer equipped with deuterium background correction and cobalt hollow cathode lamp was used for the determination of cobalt at a wavelength of 240.7 nm. A Hettich centrifuge (Model Universal 320R, Germany) was used for centrifuging. The pH values were measured with a pH-meter supplied with a glass-combination electrode. 50 mL sample or standard solution containing Co(II) in the concentration range of 0.1–5 mg/L and 2.0 × 10⁻³ mol/L HCl was adjusted to pH 3.0 (±0.2) and was poured in a screw cap conical-bottom glass centrifuge tube. 0.5 mL of 2-Methylimidazole (H_{mim}), Tetrafluoroborate (BF₄) was added into the sample solution and the tube was manually stirred to ensure complete homogenization of the aqueous sample. Then, 4.0 mL of isoelectronic with sulfur hexafluoride, SF₆ and the Sodium hexafluorophosphate (NaPF₆) solution (0.5 mol/L) was quickly added, followed by the formation of a turbid solution. In order to accelerate phase separation, the cloudy solution was centrifuged for 10 min at 3000 rpm. As a result, the phase settled at the bottom of the centrifuge tube. The aqueous phase was then separated completely by a syringe. In order to reduce the viscosity of the extract in the tube was made up to 1.0 mL by adding ethanol. The resultant solution was introduced into the flame by conventional aspiration [18].

2.3. Co(II) and Se(VI) Concentrations in the Raw Glass and Metal Industries

The Co(II) concentrations in the raw metal concentrations varied between 1, 1.5, 2.0 and 2.5 mg/L while the Se(VI) concentrations in glass industry wastewater were 0.4, 0.8, 1.2 and 2.5 mg/L, respectively.

2.5. Statistical Analysis

Regression analysis is used to understand which among the independent variables are related to the dependent variable, and to explore the forms of these relationships. Alpha (α) level is the significance of the Analysis of Variance (ANOVA) statistic. In the study α was accepted as 0.05. F value of the analysis was performed using MS Office 2010 Excell program.

3. RESULTS

3.1. Characterization of Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel Composite with SEM

The SEM morphologies of the Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel composite are shown in Fig. 1a and 1b for 2 mg/L and 4 mg/L Calcium Alginate Aerogel concentrations, respectively.

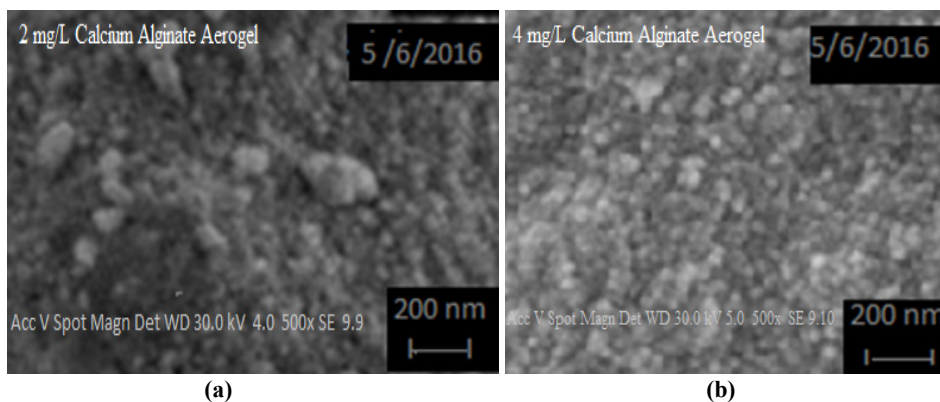


Figure 1. SEM images of 5 mg/L Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel composite with 2 mg/L (a) and 4 mg/L (b) Calcium Alginate Aerogel concentration

The SEM images showed that the silica aerogels possess spherical primary particles aggregates and porous structure. These characteristics enable the SiO₂ become a good skeleton for the composite aerogels. Fig. 1a and 1b show that the morphologies of 6 mg/L Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel composite with 2 mg/L Calcium Alginate Aerogel are different due to their not similar calcium alginate contents. The spherical primary particles in Fig 1a, the Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel composite are smaller than silica aerogels and the pore diameter is decreased with the increasing contents of calcium alginate (diameter data not shown). There are mainly two possible causes for this phenomenon: Firstly, the incorporation of ZrO₂ into the SiO₂ lattice produced new bonds in the aerogels [17]. Secondly, calcium alginate filled a part of the pores with the increasing contents [4], [9]. Calcium alginate filling the pores was explained by EDS analysis of Ca (Fig. 2). It was found that crystalline phases were constituted by the all components of the nano composite. SiO₂ was monitored in the background of the Fig.2. The grey, and semitransparent domains are Ca₂SiO₄ and ZrO₂ coated with SiO₂.The Calcium Alginate

Aerogels (a), Si (b), Ca (c) and Zr (d) are illustrated in Fig. 2. The EDS analysis results showed that ZrO_2 and SiO_2 were incorporated to Calcium alginate and this nanocomposite was stable.

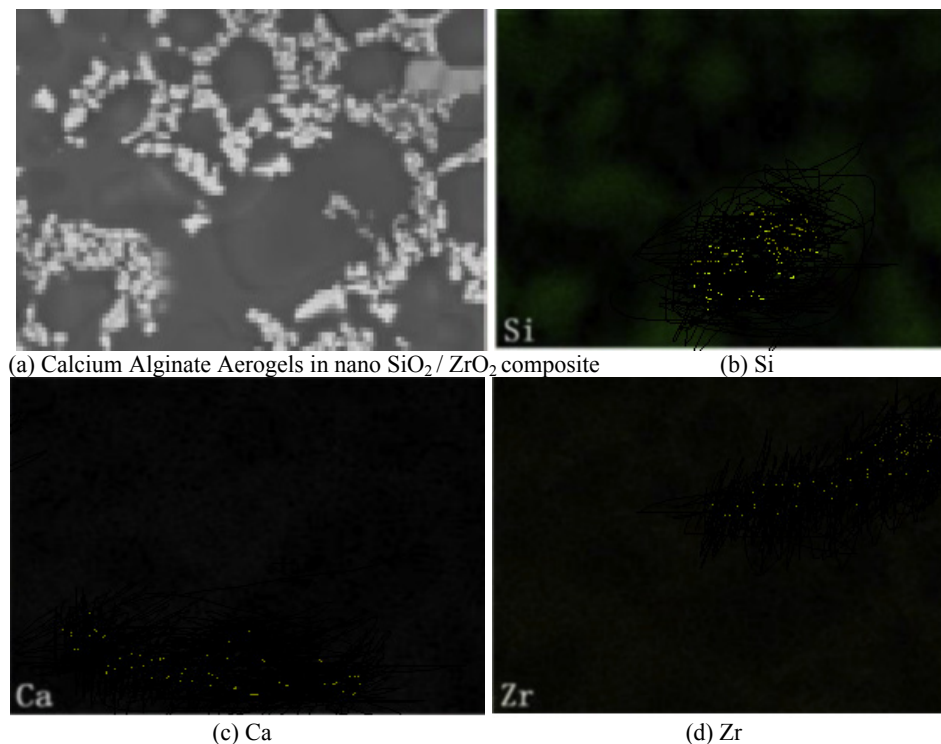


Figure 2. EDS analysis of Ca_2SiO_4 aerogel (a), Si (b) Ca (c) and Zr (d) in the SiO_2 - ZrO_2 -Calcium Alginate Aerogels

3.2. Nitrogen Adsorption / Desorption Isotherms of the SiO_2 - ZrO_2 -Calcium Alginate Aerogels for Co(II) and Se(VI)

The nitrogen adsorption / desorption isotherms of the SiO_2 / ZrO_2 -Calcium Alginate Aerogels are shown in Fig. 3a for Se(VI) and Co(II). The maximum volume adsorbed was found as 110 cc/g for Se(VI) while the maximum volume adsorbed was 85 cc/g for Co(II) at 1 P/P₀ value.

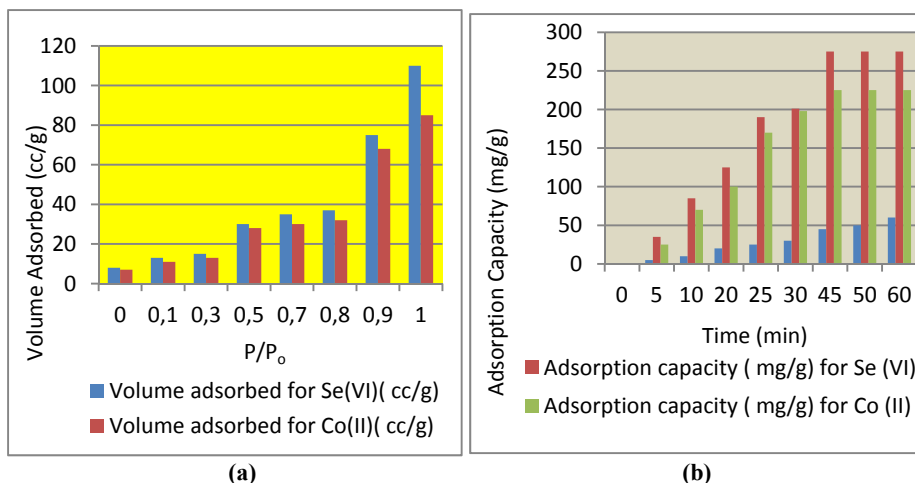


Figure 3. Nitrogen adsorption / desorption isotherms of the SiO₂-ZrO₂-Calcium Alginate Aerogels for Se(VI) and Co(II)(a); BET analysis of Se(VI) and Co(II)(b)

3.3. BET Analysis

The adsorption capacity of Se(VI) and Co(II) on SiO₂ / ZrO₂-Calcium Alginate Aerogel composite versus contact time is represented in Fig. 3b. The maximum adsorption capacity of Se(VI) reached 275 mg/g (with a maximum adsorption yield of 98) (data not shown) after 45 min adsorption time. The maximum adsorption capacity of Co(II) was 225 mg/g after 45 min. The adsorption capacity was low at the beginning of adsorption times (70 and 85 mg/g after 10 min for Co(II) and Se(VI) respectively). The adsorption capacity of two metals increased as the time elapsing, it increased quickly in the initial stages up to thirty minutes of hours, and then increased after 45 min at subsequent contact time. Then it remained constant. The faster initial adsorption rate due to the existence of a good deal of active sites is available for Se(VI) and Co(II) ions bindings. With the increase of contact time, the adsorption capacity did not change because of the vacant surface sites of Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel composite were occupied and formation of repulsive forces between the Se(VI) and Co(II) ions on the composite surface and in the liquid phase as reported by Caiping, 2010 [19]. BET analysis indicates that the products possess high surface areas with 462.10 m²/g for Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel composite with 2 mg/L Calcium Alginate Aerogel concentration in the adsorptions of Se(VI) and Co(II) (Table 1). The pore diameter is high in the nano composite containing 2 mg/L calcium alginate aerogel concentration compared to nano composite having 4 mg/L calcium alginate aerogel concentration. The pore diameter and the pore volume of nano composite having 2 mg/L calcium alginate aerogel concentration were 8.60 nm and 0.5 cm³/g pore volume. The nano composite with 4 mg/L Calcium Alginate Aerogel concentration has lower surface area and pore diameter.

Table 1. Surface physical parameters of SiO₂/ZrO₂-Calcium Alginate Aerogel with 2 mg/L, 4 mg/L and 6 mg/L Calcium Alginate Aerogel concentration

Samples	Surface area (m ² /g)	Average pore diameter (nm)	Pore volume (cm ³ /g)
2 mg/L*	462.10	8.60	0.50
4 mg/L*	420.80	2.26	0.50
6 mg/L*	233.44	1.76	1.26

* Calcium Alginate Aerogel concentration

3.4. Effects of increasing Calcium Alginate Aerogel Concentrations in the Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel Composite on the Removals of Co(II) and Se(VI)

As the Calcium Alginate Aerogel Concentrations were increased from 2 mg/L up to 6 mg/L and equilibrated for 6 hours, both Co(II) and Se(VI) adsorption yields decreased(Figure 4a). The maximum Co(II) and Se(VI) adsorption removals were obtained at a Calcium Alginate Aerogel Concentration of 2 mg/L. The maximum adsorption yields for Se(VI) is higher than Co(II). This shows that the removal of Co(II) as a function of the Calcium Alginate Aerogel concentration.

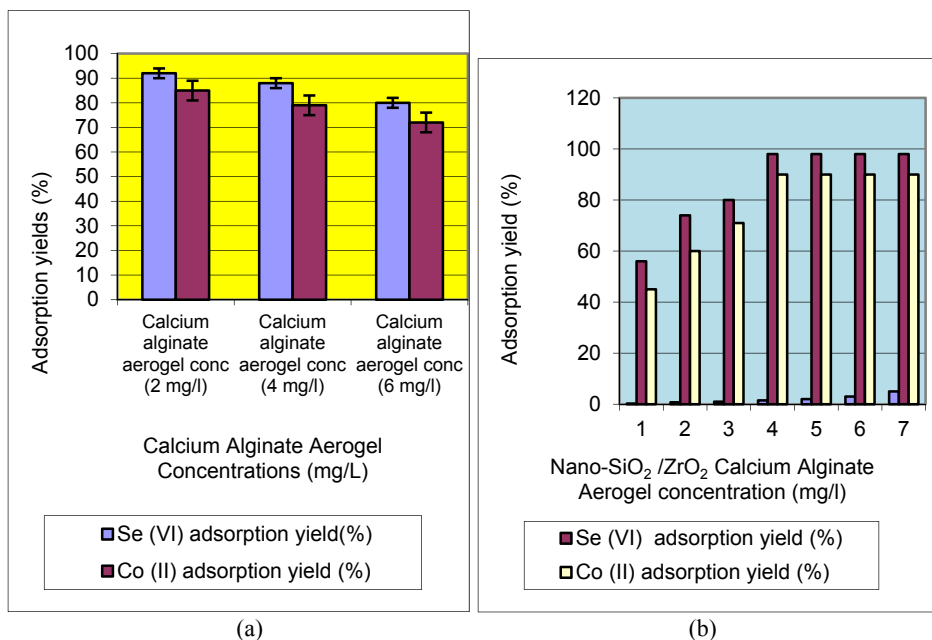


Figure 4. Effects of increasing Calcium Alginate Aerogel concentrations in the Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel composite on the removals of Co(II) and Se (VI)(a) Effects of Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel Composite Concentrations on the Removals of Co(II) and Se(VI) at 2 mg/L Calcium Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel Composite Alginat Aerogel concentration(b)

A multiple linear relationship between maximum adsorption yields of Se(VI) and Co(II) and Calcium Alginate Aerogel concentrations (from 2 mg/L to 4 mg/L and 6 mg/L) was obtained (R=0.89) and this regression was significant (ANOVA p=0.0009< α (0.05) and F=1.10).

3.5. Effects of Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel Composite Concentrations on the Removals of Co(II) and Se(VI)

The studies were performed at a 2 mg/L Calcium Alginate Aerogel concentration since in the previous study the maximum adsorption yields of Se(VI) and Co(II) were obtained with this adsorbent concentration. As the Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel composite concentrations were elevated from 1 mg/L up to 4 mg/L; the the adsorption yields of Se(VI) increased from 57% up to 98% (4b). Further increase of composite concentration to 5, 6 and 7 mg/L did not affect the Se(VI) adsorption yields. The adsorption yields remained as in 4 mg/L.

Similar results was found for Co(II). The maximum adsorption yields for Co(II) was obtained at 4 mg/L Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel composite concentration. Increasing of the composite concentration did not affect the adsorption yield of Co(II). These results showed that the adsorption yields of both metals depends to the nano-composite concentration up to 5 mg/L. This may be due to the high ion exchange capacity of the Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogels [4], [9]. The experimental results revealed that Co(II) and Se(VI) adsorption yields increases up to the optimum dosage beyond which the removal efficiency has no change with the Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogels dosage as reported by Somiya et al., (1988) and Matias et al., (2015) [20], [21]. As expected, the equilibrium concentration decreases with increasing composite doses for a given initial composite concentration, because for a fixed initial concentration, increasing composite doses provide greater surface area or adsorption site up to a optimum concentration as reported by Somiya et al., (1988) and . Matias et al., (2015) [20], [21].

A multiple linear relationship between maximum adsorption yields of Se(VI) and Co(II) and Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel Composite concentrations up to 5 mg/L Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel Composite was obtained (R=0.86) and this regression was significant (ANOVA p=0.007< α (0.05) and F=1.30). Further increase of Nano-SiO₂ / ZrO₂ Calcium Alginate Aerogel Composite concentration did not affect both Co(II) and Se(VI) adsorptions.

3.6. Effects of Contact Time on the Adsorption Capacities of Co(II) and Se(VI)

The studies were performed at 2 mg/L Calcium Alginate Aerogel Concentration at 5 mg/L Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel composite to determine the effects of adsorption time on the adsorption yields of Se(VI) and Co(II). Fig. 5a shows the effect of contact time on the adsorption capacities of Se(VI) and Co(II) by 5 mg/L Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel.

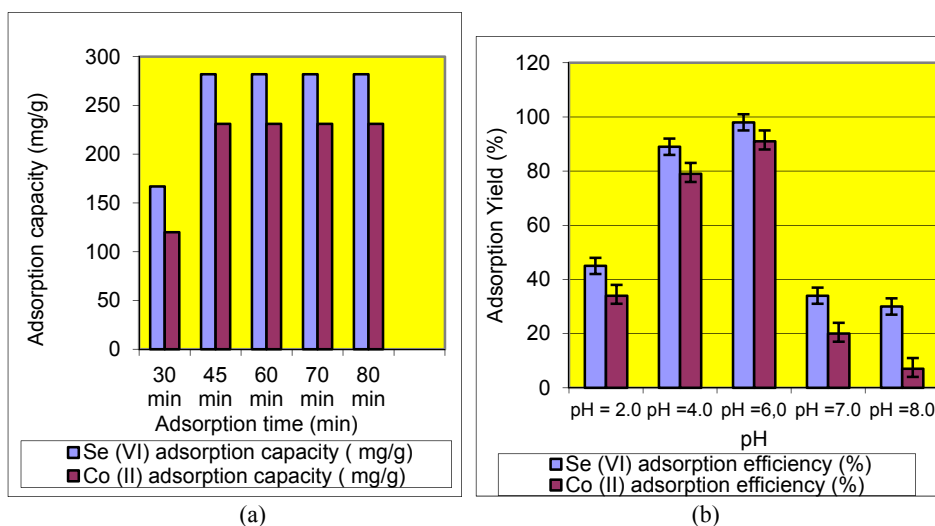


Figure 5. Effects of Contacting Time on the Adsorption Capacities of Co(II) and Se(VI)(a), Effect of pH on the adsorption efficiency of Se(VI) and Co(II) at 5 mg/L Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel composite after 45 min adsorption time at pH=6.1(b)

The adsorption capacities of Nano SiO₂ / ZrO₂-Calcium Alginate Aerogel composite; increases with time and attains equilibrium within 45 min for both metals. The equilibrium time was dependent up to 45 min adsorption. Then, the increase of contacting time did not affect the adsorption capacities of both metals. It was found that Se(VI) adsorption capacity (275 mg/g) was higher than Co(II) adsorption capacity (225 mg/g) after 45 min adsorption time at 5 mg/L composite and 2 mg/L Calcium Alginate Aerogel concentration. The metal uptake versus time curves are monotonously increasing to saturation, suggesting the possible monolayer coverage of metal ions on the surface of the adsorbent up to a contacting time of 60 min.

A multiple linear relationship between maximum adsorption yields of Se(VI) and Co(II) and adsorption times up to 45 min was obtained (R=0.89) and this regression was significant (ANOVA p=0.005< α (0.05) and F=1.09). Further increase of contacting time did not affect both Co(II) and Se(VI) adsorption yields.

3.7. Effect of pH on the Adsorption Yields of Co(II) and Se(VI)

The effect of pH on the Co(II) and Se(VI) adsorption on the nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel composite at a pH between 2.0 and 8 is presented in Fig. 5b. It can be found that the adsorption yields, increased with pH for both metals. The uptake of Co(II) and Se(VI) by Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel composite increased as the pH increased from 2.0 to 6.1. At higher pH values (7.0 and 8.0) the adsorption efficiency decreased for both metals. Although a maximum uptake was noted at a pH of 7.1, as the pH of the solution increased to >6.1 Co(II) started to precipitate out from the solution. Therefore, the increased capacity of adsorption at pH = 6.1 may be a combination of both adsorption and precipitation on the surface of the Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel composite. It is considered that Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel composite had a maximum adsorption capacity at a pH of 6.1, if the precipitated amount is not considered in the calculation. Therefore, the optimum pH for Co(II) and Se(VI) adsorption is 6.1. Similarly, Se(VI) adsorption on the Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel composites tends to increase with the pH. This is likely attributed to the fact that a lower pH value causes the surface to carry more positively charges and thus would more significantly repulse the positively charged species in solution. Therefore, the adsorption of Se(VI) at lower pH values resulted from an increased repulsion between the more positively charged Co²⁺ species and positively charged surface sites. Furthermore, at lower pH, H⁺ ions compete with Se(VI) ions to the surface binding-sites of the adsorbent [19]. The adsorption efficiencies of Se(VI) and Co(II) increased from 43% to 87% and up to 98% as the pH were increased from 2 to 4 and up to 6. In our study adsorption was directly dependent to the pH. For the Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel composite, the adsorption at pH above 6.0 shows a decreasing trend because of the formation of hydroxyl complexes of cobalt, Co(OH)₂ [22] and selenium, Se(OH)₂.

3.8. Recoveries of Se(VI) and Co(II)

The adsorption efficiencies in both metals were not reduced significantly after four sequential utilization of Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel composite (Table 2). In this study the adsorption yields of Se(VI) and Co(II) were 99% and 96% in the first utilization. After four sequential utilization of the same Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel composite the adsorption yields of Se(VI) and Co(II) decreased to 87 and to 83 %, respectively.

Table 2. Sequential treatment of Se(VI) and Co(II) with 4 mg/L Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel composite concentration, after 45 min adsorption time at pH 6.0, at a temperature of 80 °C and ionic strength 0.009 M

Parameters	Sequential cycles and adsorption yields (%)			
	First	Second	Third	Fourth
For Se(VI)	99	98	96	87
For Co(II)	96	94	90	83

4. COST ANALYSIS

A cost analysis was carried out for the adsorptions of Se(VI) and Co(II) from 1 m³ glass and metal industry wastewaters at optimum experimental conditions. The total cost of the adsorptions of Se(VI) and Co(II) from 1 m³ glass and metal industry wastewaters were found as 1,62 € and 1,99 €, respectively, at the optimum experimental conditions with Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel composite (Table 3). 1,10 € and 1,47 € were spent as electricity costs for glass and metal industries for adsorptions Se(VI) and Co(II), while the chemical cost of synthesizing Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel composite was 0.64 € (Table 3). In this study, the main part of the cost consisted of the electricity. Since the composite namely Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel composite produced under laboratory conditions can be used four times for adsorptions of Se(VI) and Co(II) with yields as high as 87% and 83% the cost is equal only to electricity consumptions. This reduce the adsorption costs to 0,98 € and 1.35 € for Se(VI) and Co(II).The total adsorption cost reduced by % 38.

Table 3. Cost analysis for the treatment of Se(VI) and Co(II) with adsorption

Cost Analysis	Treatment of glass and metal industry wastewaters with adsorption process
Electricity consumption	Electricity cost for rapid stirring in a mixer for 45 min= 0,20 €, Electricity cost for rapid stirring in a mixer for 45 min= 0,37 €, Electricity cost for incubation at an oven at 4 °C =0,40 €, Electricity cost for incubation at an incubator at 80 °C=0,5 €.
Chemicals	<u>For preparation of nano-SiO₂ sol:</u> 5.30 g of Polyethylene glycol (PEG) = 0,34 € , 30 mL hydrochloric acid (0.02 M)= 0,02 €. 15 mL of Tetraethoxysilane (TEOS)= 0,05 €, 20 mL of Propylene oxide (PO) = 0,06 € <u>For preparation of nano-ZrO₂:</u> 0.17 g Polyoxyethylene (PEO)= 0,03 € , 2.8 mL ethanol g ZrOCl ₂ -8H ₂ O= 0,06 € 0.48 mL of PO = 0,05 €. <u>For preparation of Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel composite</u> Calcium alginate 4.0 g = 0,03 €
Total cost for treatment of Se(VI) from 1m ³ glass industry wastewater	1.62 €
Total cost for treatment of Co(II) from 1m ³ metal industry wastewater	1,99 €

5. CONCLUSIONS

The results of this study showed that Se(VI) and Co(II) from glass and raw metal industry wastewaters can be effectively removed with adsorption process. The nano composite namely Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel was prepared under laboratory conditions. For maximum Se(VI) (99%) and Co(II) yields (96%) the optimum operational conditions were as follows: Calcium Alginate Aerogel, Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel composite concentrations, temperature, pH and adsorption time were 2 mg/L, 4 mg/L, 80 °C, 6.0, and 45 min, respectively. It was found that Se(VI) was adsorbed with high yields compared Co(II). The same Nano-SiO₂ / ZrO₂-Calcium Alginate Aerogel composite can be sequentially utilized for four times with yields as high as 87% and 83%. Therefore the adsorption costs reduced from 1.62 € to 0.98 € and from 1.99 € to 1.35 €.

REFERENCES

- [1] S. Lawson, J.M.Macy, (1995) Bioremediation of selenite in oil refinery wastewater, *Appl. Microbiol. Biotechnol.* 43 (4) 762–765.
- [2] D. Peak, (2006) Adsorption mechanisms of selenium oxyanions at the aluminum oxide/water interface, *J. Colloid Interface Sci.* 303 337–345.
- [3] J. Das, D. Das, G.P. Dash, K.M. Parida, (2002) Studies on Mg/Fe hydrotalcite-like compound (HTlc). I. Removal of inorganic selenite (SeO₃²⁻) from aqueous medium, *J. Colloid Interface Sci.* 251 (1) 26–32.
- [4] M. Duc, G. Lefèvre, M. Fédoroff, (2006) Sorption of selenite ions on hematite, *J. Colloid Interface Sci.* 298 (2) 556–563.
- [5] A. Afkhami, (2002) Kinetic-spectrophotometric determination of selenium in natural water after preconcentration of elemental selenium on activated carbon, *Talanta* 58, 311–317. [http://doi.org/10.1016/S0039-9140\(02\)00246-1](http://doi.org/10.1016/S0039-9140(02)00246-1).
- [6] E.I. El-Shafey, (2007) Removal of Se(IV) from aqueous solution using sulphuric acid treated peanut shell, *J. Environ. Manage.* 84, 620–627.
- [7] M. Martínez, J. Giménez, J. de Pablo, M. Rovira, L. Duro, (2006) Sorption of selenium (IV) and selenium (VI) onto magnetite, *Appl. Surf. Sci.* 252 (10) 3767–3773.
- [8] T. Kokubo, (1991) Bioactive glass ceramics: properties and applications, *Biomaterials* 12 155–163.
- [9] W.H. Tuan, J.R. Chen, C.J. Ho, (2008) Critical zirconia amount to enhance the strength of alumina, *Ceram. Inter.* 34 2129e2133.
- [10] Y.Y. Lyu, S.H. Yi, J.K. Shon, (2004) Highly stable mesoporous metal oxides using nanoproping hybrid gemini surfactants, *J. Am. Chem. Soc.* 126 2310e2311.
- [11] Prabha Dubey, Shashi, Dhar Dwivedi, Amarendra, Kim, In-Chul, Sillanpaa, Mika, Kwon, Young-Nam, (2014) Synthesis of graphene-carbon sphere hybrid aerogel with silver nanoparticles and its catalytic and adsorption applications, *Chem. Eng. J.* 244, 160-167.
- [12] Qina, Guotong, Yao, Yuan, Wei, Zhang, Tao, (2013) Preparation of hydrophobic granular silica aerogels and adsorption of phenol from water. *Appl. Surf. Sci.* 280, 806-811.
- [13] S.Jr. Swann, E.G. Appel, S.S. Kistler, (1934) Thoria aerogel catalyst: aliphatic esters to ketones *Ind. Eng. Chem.* 26 (1934). 1014–1014.
- [14] M. Adebajo, R. Frost, J. Klopogge, O. Carmody, S. Kokot, (2003) Porous materials for oil spill cleanup: a review of synthesis and absorbing properties, *J. Porous Mater.* 10 159–170.
- [15] J.W. Long, A.E. Fischer, T.M. McEvoy, M.E. Bourg, J.C. Lytle, D. Rolison, (2008) Selflimiting electropolymerization en route to ultrathin, conformal polymer coatings for energy storage applications, *PMSE Prepr.* 99 772–773.

- [16] S.S. Latthe, Y.N. Digambar, A.V. Rao, (2009) TMOS based water repellent silica thin films by co-precursor method using TMES as a hydrophobic agent, *Appl. Surf. Sci.* 255 3600–3604.
- [17] Junchuan Zhao, Xingeng Ding, Cheng Meng, Chunrong Ren, Huiqin Fu, Hui Yang, Adsorption and immobilization of actinides using novel SiO₂eZrO₂-calcium alginate aerogels from high level liquid waste <http://dx.doi.org/10.1016/j.pnucene.2015.09.006>.
- [18] Mohammad Reza Jamali, Bahram Soleimani, Reyhaneh Rahnama, Seyed Hojjat Allah Rahimi, Development of an in situ solvent formation microextraction and preconcentration method based on ionic liquids for the determination of trace cobalt (II) in water samples by flame atomic absorption spectrometry, <http://dx.doi.org/10.1016/j.arabjc.2012.08.004>.
- [19] Y Caiping, Adsorption and desorption properties of D151 resin for Ce(III) (2010) *Journal of rare earths*, Vol. 28, Spec. Issue, Dec. 2010, p. 183 DOI: 10.1016/S1002-0721(10)60324-9.
- [20] S. Somiya, N. Yamamoto, H. Yanagina, (1988) *Science and Technology of Zirconia (III)*, vol. 24A and 24B, American Ceramic Society, Westerville.
- [21] T. Matias, J. Marques, M.J. Quina, L. Gando-Ferreira, A.J.M. Valente, A. Portugal, L. Durães, (2015) Silica-based aerogels as adsorbents for phenol-derivative compounds, *Colloids Surf. A* 480 (2015) 260–269.
- [22] Lu-hua Jiang, Yun-guo Liu, Guang-ming Zeng, Fang-yu Xiao, Xin-jiang Hu, Xi Hu, Wang Hui, Li Ting-ting, Zhou Lu, Tan, Removal of 17 β -estradiol by few-layered graphene oxide nanosheets from aqueous solutions: External influence and adsorption mechanism, Xiao-fei, *Chem. Eng. J.* 284 (2016) 93–102., <http://doi.org/10.1016/j.cej.2015.08.139>.