

Reuse of residues/wastes as a sustainable solution for landfill leachate contaminated groundwater

EMRE BURCU ÖZKARAOVA*, ELIFCAN GÜVEN ORAL

Department of Environmental Engineering, Ondokuz Mayıs University, Samsun, Turkey

*Corresponding author: ozkaraova@omu.edu.tr

Citation: Özkaraova E.B., Güven Oral E. (2022): Reuse of industrial residues/wastes as a sustainable solution for landfill leachate contaminated groundwater. Soil Water Res.

Abstract: In order to increase the reuse of wastes and residues, as required by the Waste Framework Directive, the potential use of waste, residue and natural minerals as low-cost permeable reactive barrier (PRB) materials was investigated. The performance of a kitchen waste compost, sepiolite and steel slag was compared with that of volcanic slag, pumice and activated carbon in removing specific contaminants from landfill leachate. The experiments represented that the activated carbon removed 27% of the ammonium (NH_4^+), 75% of the chemical oxygen demand (COD) and 100% of the phosphate (PO_4^{3-}), zinc (Zn^{2+}) and nickel (Ni^{2+}) from the landfill leachate. Volcanic slag exhibited removal efficiencies of 50% COD and 100% PO_4^{3-} and pumice exhibited removal efficiencies of 20% NH_4^+ , 27% Zn^{2+} , 65% COD and 100% PO_4^{3-} . The reactive materials were also checked for their potential in releasing unwanted constituents and represented different levels of the solute (e.g., PO_4^{3-} , SO_4^{2-} , NH_4^+) release. Among the reactives, sepiolite was found to be the reactive material reflecting a minor release (e.g., Zn^{2+} , Cd^{2+} and Ni^{2+}), but also delivering removal efficiencies of 40, 50, 65, 95, 97, 98, 98 and 100% for Ni^{2+} , COD, Zn^{2+} , SO_4^{2-} , Cl^- , F^- , NH_4^+ and PO_4^{3-} , respectively. The results show that the studied materials have the potential as reactives for PRB systems treating high strength contaminant plumes.

Keywords: groundwater remediation; permeable reactive barriers; potential reactives

Since the 1970 s, groundwater contamination has become an important environmental problem in the world. Based on the current reporting, comprising 27 European Union (EU) member countries, approximately 1 170 000 potential polluted sites have been determined in these countries to date (van Liedekerke et al. 2014). Approximately one-third of an estimated total of 342 000 sites in the 39 European Environment Agency member and cooperating countries (EEA-39) has already been determined and about 15% of the same estimated total has been remediated (van Liedekerke et al. 2014). Costs for remediation activities generally are in the range of €50 000 to €500 000 (van Liedekerke et al. 2014). These numbers have put emphasis on sustainable approaches to the remediation. Sustainable remediation is broadly described as a remedy or combination

of remedies, whose net benefit on human health and the environment is maximised through the judicious use of limited resources (Ellis & Hadley 2009). Within the perspective of sustainability, industry service providers have started to incorporate some sustainability metrics during the evaluation of alternatives for remedial projects, remedial implementations and remedial endpoints (Raymond et al. 2009). Thus, new low-cost, low energy use remediation projects and strategies have emerged for groundwater remediation as more practical and permanent solutions (Bardos et al. 2013).

Permeable reactive barriers (PRBs) are generally favoured due to the reduction in operation and maintenance costs of the system (Interstate Technology and Regulatory Council 2005; European Commission Directorate General 2019; Maitra 2019). PRBs rely

on the natural flow of contaminated groundwater through a reactive zone. PRBs have been constructed as continuous, funnel-and-gate and more site specific PRB configurations (Özkaraova 2020). The treatment zones of PRB systems are made up from reactive materials capable of converting pollutants in a plume into less dangerous or immobile compounds. The processes involved during the treatment depend on the characteristics of the reactive material and their interaction with the pollutant. Sorption, complexation, oxidation/reduction and biological enhancement are basic processes prevailing in the reactive zone. Full-scale PRB systems have been installed as continuous 'hanging' wall, slurry or conventional trench construction methods for the treatment of acid mine drainage, chlorinated solvent and landfill leachate contaminated groundwater (Bekele et al. 2019; Grau-Martinez et al. 2019; Siggins et al. 2021). Alternative reactive materials like bone char, lignite, fly ash, steel mill waste and sugar industry waste have been studied for their potential use as reactive materials for the treatment of heavy metals and acid mine drainage (Torregrosa et al. 2019) in PRBs. In the present study, we tested volcanic slag, sepiolite, pumice, steel slag, kitchen waste compost and activated carbon for their suitability to remove specific contaminants from the landfill leachate. A landfill leachate has been selected due to the serious groundwater pollution that often occurs as a result of the absence of a proper liner or leachate collection systems at older landfills (Samadder et al. 2017; Shu et al. 2018). Landfill leachate is well known for its variability and complexity in chemical composition mainly depending on the waste composition, landfill age and climate conditions (Adhikari & Khanal 2015). Highly polluted leachates may contain high concentrations of biodegradable and refractory organic compounds, ammonium, heavy metals, phosphorus, chloride, sulfate and other toxic compounds requiring their removal from the solution (Torretta et al. 2017). Some reactive filter materials have been investigated for their potential in removing selective compounds from landfill leachates. Kietlińska and Renman (2005) evaluated mixtures of sand, peat, polonite and blast furnace slag using bench-scale column experiments for the removal of heavy metals and nitrogen from a landfill leachate. Modin et al. (2011) studied metal sorption onto granulated activated carbon (GAC), bone meal and iron fines. The mentioned studies generally cover selected contaminants (e.g., heavy metals, ammonium and chemical oxygen demand

(COD)) and do not cover the changes in the complex mixture of constituents in landfill leachates. Little emphasis has been given to the effectiveness of volcanic slag and sepiolite in removing landfill leachate constituents. The objective of this study was to investigate the use of some natural materials like volcanic slag and pumice, and sepiolite obtained as a commercial residue, steel slag as industrial waste and activated carbon and compost for their potential use in reactive barriers aiming the removal of landfill leachate constituents. For this purpose, (1) leaching tests were conducted to examine the potential of the reactive materials to leach chemical compounds and (2) batch experiments were performed to assess the capability of the reactive materials to remove the chemical constituents from solution with respect to the treatment time. The capacity of the reactive materials to adsorb heavy metals, chloride, fluoride, sulfate, phosphate, ammonium and organic matter (COD) from the landfill leachate was evaluated by following their changes in the solution composition.

MATERIAL AND METHODS

Residues/wastes used as reactive material. The organic compost (OC) was received from a consulting firm that was running a 'Zero Waste' project. During the project, the compost was produced from fine-sized kitchen residue in four weeks using a composting machine (Özten et al. 2009). The sepiolite rasping (SE) was provided by Yılmaz Lületaş Pipo, which is a company producing pipes as touristic gifts from sea foam in Eskişehir, Turkey. The volcanic slag (VS) was taken from the lava flow area of the Kula Volcanic Geopark located in Manisa, Turkey (<http://www.kulasalihli-geopark.com/default.aspx>). The pumice (PU) was supplied by Acerler Bims, which is a company producing construction materials in Nevşehir, Turkey. The steel slag (StS) was obtained from the Yeşilyurt Steel Plant located in Samsun (<http://www.yesilyurtdc.com.tr/en/index.html#>), which is a scrap-based steel industry producing electric arc furnace slag. All the inorganic materials were air-dried, ground and screened to obtain a fraction below 2 mm. The organic materials were air-dried and sieved to obtain a fraction below 4 mm (Page et al. 2014).

Landfill leachate. The leachate was collected from the sanitary landfill site of Samsun, which is a city with a population of about 1 335 716 people in Turkey (Turkish Statistical Institute 2019). The

<https://doi.org/10.17221/71/2021-SWR>

landfill receives about 319 000 t of mixed municipal solid waste per year. The site is located south-east of Samsun and has a total capacity of about 2 775 000 m³ and a total surface area of about 20.7 ha (Özkaraova Güngör et al. 2010). The characteristics of the raw leachate are presented in Table 1.

Leaching experiments. Leaching tests were performed to determine leaching potential of the reactive materials. Samples of 10.00 g volcanic slag, sepiolite, pumice, steel slag, compost and activated carbon were placed into Erlenmeyer flasks with 100 mL of deionised water, yielding a liquid to solid ratio of 10 L/kg. The flasks were placed on a horizontal shaker for a time period varying between 15 min and 4 days at 150 rpm. The pH was recorded prior to and after the experiments. Following centrifugation, the supernatant was filtered using 0.45 µm MF-Millipore MCE Membrane syringe filters (Merck, Germany) and then analysed for sulfate (SO₄²⁻), phosphate (PO₄³⁻), fluoride (F⁻), chloride (Cl⁻), ammonium (NH₄⁺), zinc (Zn²⁺), copper (Cu²⁺), cadmium (Cd²⁺), nickel (Ni²⁺) and COD.

Batch experiments. Batch tests were carried out to investigate the capability of the reactive materials to remove constituents from the leachate with respect to the treatment time. The same experimental conditions were used during the treatment of the landfill leachate with the reactive materials. The pH was recorded prior to and after all the experiments to understand the environmental conditions. All the suspensions were initially centrifuged and afterwards filtered using 0.45 µm MF-Millipore MCE

Membrane syringe filters. The clear solutions were analysed for SO₄²⁻, PO₄³⁻, F⁻, Cl⁻, NH₄⁺, Zn²⁺, Cu²⁺, Cd²⁺, Ni²⁺ and COD.

Analytical techniques. The aqueous solutions obtained from the experiments with landfill leachate were analysed for SO₄²⁻, PO₄³⁻, F⁻, Cl⁻, NH₄⁺ using a Dionex ICS-5000 ion chromatography system as described by the Operator's Manual (Thermo Fisher Scientific Inc. 2012). The pH of the solutions was determined with a Sartorius PB 20 pH meter (Sartorius, Germany) equipped with an SP10T electrode. The analyses of Zn²⁺, Cu²⁺, Cd²⁺, Ni²⁺ were performed according to the atomic absorption spectrometric method using a UNICAM 929 AAS flame atomic absorption spectrometer (APHA/AWWA/WPCF 1998). The chemical oxygen demand was determined according to the closed reflux method as described by the American Public Health Association, American Water Works Association and Water Pollution Control Federation (APHA, AWWA and WPCF) (1998). All the experiments have been carried out in duplicate at least and have been repeated when the relative standard deviations of the means of duplicate measurements were less than 10%. The results of the analyses were reported as average values.

Quality control. The operational conditions were set according to the manufacturer's guidelines to observe optimal determinations. Merck and Dionex standard solutions are always used during the preparation of calibration solutions. The detection limit values of the Dionex ICS-5000 ion chromatography system (Thermo Scientific, USA) were 0.4 mg/L for PO₄³⁻, 0.2 mg/L for SO₄²⁻, 0.2 mg/L for NO₃⁻, 0.04 mg/L for F⁻, 0.2 mg/L for Cl⁻, 0.5 mg/L for NH₄⁺, 1 mg/L for Ca²⁺ and 0.5 mg/L for Mg²⁺. Precise quality procedures and precautions were used to guarantee the reliability of the results. The precision and accuracy of the measurements were monitored by analysing the quality control samples of various concentration levels (low, medium and high; in mg/L). The calculated standard deviations and deviations (the relative difference between the measured and certified concentrations) were found to be 0.002–0.016 and 2.1–8.4% for Cu²⁺; 0.003–0.008 and 2.6–8.5% for Zn²⁺; 0.013–0.022 and 4.7–7.2% for Pb²⁺ and 0.006–0.008 and 2.9–9.6% for Cd²⁺, respectively.

RESULTS AND DISCUSSION

Leaching experiments. The potential of the reactive materials to leach chemical compounds was

Table 1. Landfill leachate characteristics

Parameter	Range	Average
pH	7.03–7.24	7
COD (mg O ₂ /L)	8 775–15 584	10 773
PO ₄ ³⁻ (mg/L)	12.3–15.4	14.2
SO ₄ ²⁻ (mg/L)	445–721	583
NO ₃ ⁻ (mg/L)	5.9–10.4	7.9
Cl ⁻ (mg/L)	3 313–4 921	4 477
NH ₄ ⁺ (mg/L)	1 631–1 688	1 669
Zn ²⁺ (mg/L)	0.17–2.47	1.17
Cu ²⁺ (mg/L)	0–0.16	0.09
Cd ²⁺ (mg/L)	bdl	bdl
Ni ²⁺ (mg/L)	0.45–1.03	0.71
Ca ²⁺ (mg/L)	206–1721	895
Mg ²⁺ (mg/L)	252–635	466

bdl – below detection limit

determined using deionised water in treatments with respect to time. The degree of release from the reactive materials changed with respect to the material and reaction time. The reactive material having the ability to release the highest number of chemical compounds, were the OC. The OC, which was produced from kitchen waste, leached high amounts of NH_4^+ (30.87 mg/g) and Cl^- (20.32 mg/g). NH_4^+ (17.07 mg/g) was also released from the VS at high levels. The OC was the only reactive material leaching organic matter as reflected by the COD. The SE represented only the heavy metal release at lower levels. Additionally, the activated carbon (AC) reflected a high potential to release Cl^- (12.66 mg/g) and SO_4^{2-} (1.08 mg/g). The PU and StS similarly released high levels of Cl^- and SO_4^{2-} . Regarding the pH changes of the solutions, it can be concluded that all the deionised water leaching tests revealed neutral to slightly alkaline conditions. The average amounts of the compounds released by the reactive materials are listed in more detail in Table 2.

Batch experiments. The capability of the reactive materials to remove chemical constituents from a complex mixture of solutes like landfill leachate was evaluated with batch experiments. The results, representing the influence of treatment time on solute concentrations, were interpreted as the ratio of effluent concentration to influent concentration (C_e/C_0), which is also able to reflect the dissolution of the chemical compounds from the reactive materials by the landfill leachate (Figure 1).

As known, the strength and composition of solution influences the amount of the constituents removed from solution. The composition of the raw leachate was variable reaching concentrations above 10.773 mg COD/L, 1669 mg NH_4^+ /L, 4477 mg Cl^- /L, 583 mg SO_4^{2-} /L and 14.2 mg PO_4^{3-} /L within this study (Table 1). In general, the results showed that the

capability of the reactive materials was different from each other and for each leachate constituent.

Activated carbon has been widely used in wastewater treatment and water purification systems, due to its affinity to various chemical compounds and its high adsorption capacity. AC was, therefore, selected as a reactive material in this study. As can be seen from Figure 1A, AC was only capable in removing NH_4^+ (25%), COD (75%), PO_4^{3-} and heavy metals like Zn^{2+} and Ni^{2+} (100%) from the landfill leachate. The concentrations of SO_4^{2-} , F^- and Cl^- seem to have increased in the effluent, which is in agreement with the results of the leaching experiments. Studies conducted on landfill leachate treatment with activated carbon presented an effective removal of organic carbon, heavy metals, ammonium and phosphate (Foo & Hameed 2009). In a study carried out by Modin et al. (2011), heavy metal removal from landfill leachate with granular activated carbon was found to occur at different degrees. The heavy metal removal from the leachate was attributed to sorption to basic sites, since a drop in the pH was not observed. Another possible mechanism was explained to be sorption together with organic matter since more than 90% of the total organic carbon (TOC) (240 mg/L) was also removed.

It was interesting to observe that the OC represented a high potential to remove the COD (80%), despite its organic nature. Landfill leachate seems to have a higher potential to solubilise compounds like PO_4^{3-} (Figure 1B). This potential was higher than that determined in the deionised water leaching tests. Different chemical reactions with the strong landfill leachate, e.g., ion exchange and the mineralisation of organic compounds, can increase this release (Kietlińska & Renman 2005). NH_4^+ was similarly released at high levels from the OC. Similarly, bone meal was reported to release large quantities of ni-

Table 2. Average leachable amounts of compounds (mg/g)

	PO_4^{3-}	SO_4^{2-}	F^-	Cl^-	NH_4^+	Zn^{2+}	Cu^{2+}	Cd^{2+}	Ni^{2+}
AC	bdl	1.08	0.02	12.66	bdl	bdl	bdl	bdl	bdl
OC	0.33	0.25	0.02	20.32	30.87	0.001	bdl	bdl	0.002
StS	bdl	0.60	0.007	16.44	bdl	bdl	bdl	bdl	0.003
PU	bdl	0.52	0.02	9.63	bdl	bdl	bdl	bdl	0.003
VS	bdl	0.48	0.002	bdl	17.07	0.0003	bdl	bdl	0.003
SE	bdl	bdl	bdl	bdl	bdl	0.001	bdl	0.0002	0.026

AC – activated carbon; OC – organic compost; StS – steel slag; PU – pumice; VS – volcanic slag; SE – sepiolite rasping; bdl – below detection limit

<https://doi.org/10.17221/71/2021-SWR>

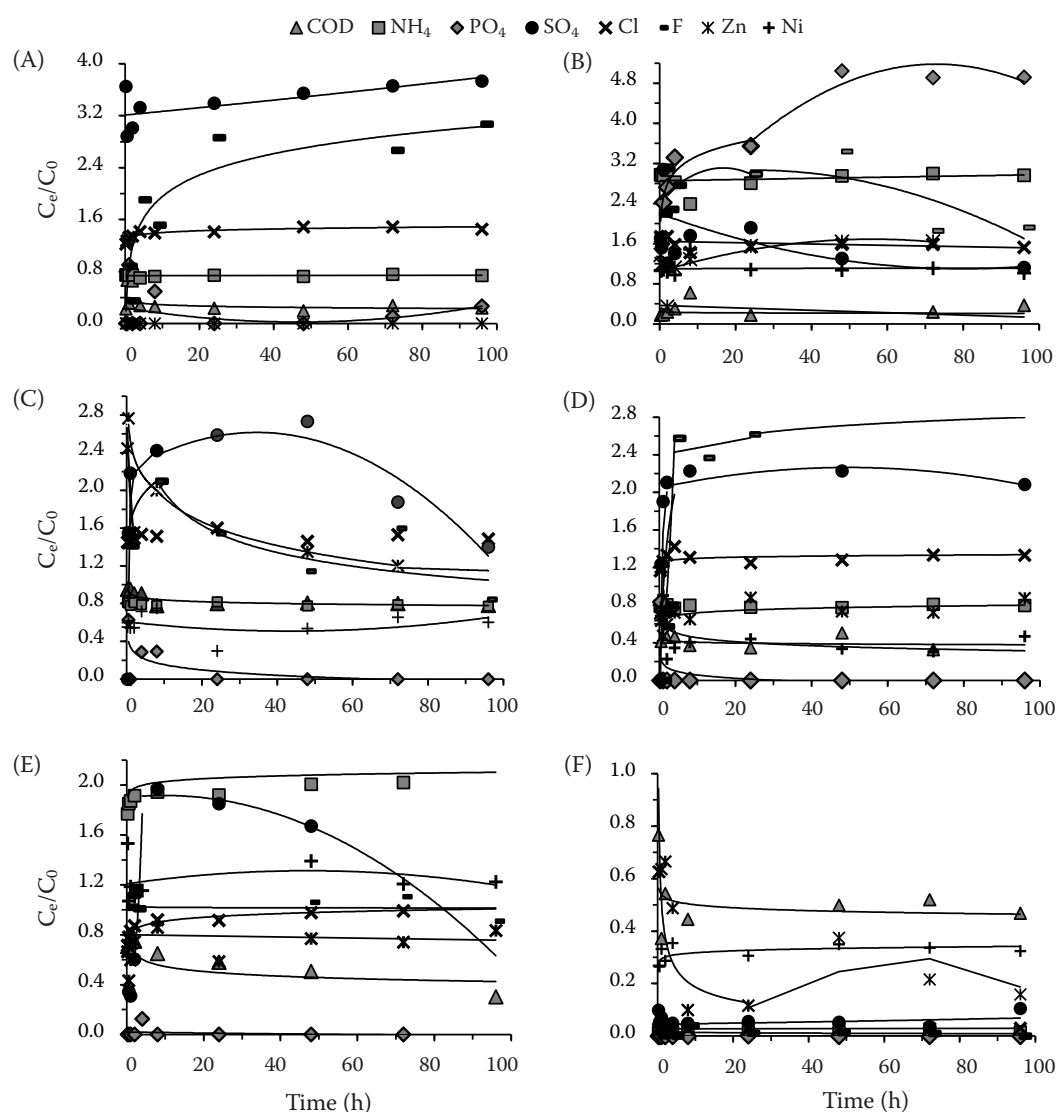


Figure 1. Relative concentration profiles vs. time for the activated carbon (A), compost (B), steel slag (C), pumice (D), volcanic slag (E) and sepiolite (F) used in the batch tests with the landfill leachate
 C_e/C_0 – the ratio of effluent to influent concentration; COD – chemical oxygen demand

trogen, phosphorus and TOC (Modin et al. 2011). In comparison, the compost used in this study was able to remove high levels of COD from the leachate.

The StS treatments reflected the low levels of the COD (10%) and NH_4^+ (22%) removal and high level of PO_4^{3-} (100%) removal (Figure 1C). A high initial release of compounds like SO_4^{2-} and F^- was followed by their removal from the solution indicating to the potential of StS to release and adsorb contaminants. The leaching of elements from a media was also observed by Kietlińska and Renman (2005). The release of high levels of calcium, silica, chromium and aluminium from polonite and blast furnace slag

was reported. It was concluded that other chemical reactions can contribute to such a release by landfill leachates. The removal of phosphate by slag originating from steel manufacturing processes is known (Kostura et al. 2005). The removal of phosphate from water solution by slag has been reported to occur by ion exchange (pH 3–8.5) and precipitation (pH \geq 8.5) (Oguz 2004).

PU removed NH_4^+ (20%), Zn^{2+} (27%), COD (65%) and PO_4^{3-} (100%) (Figure 1D). The concentration of SO_4^{2-} , F^- and Cl^- seem to have similarly increased in the effluents like in the treatments with the AC; however, at much lower levels. The experiments

represented that PU has the potential to remove NH_4^+ , COD and PO_4^{3-} . Pumice was similarly found to be effective in removing natural organic matter and phosphate from water in other studies, but its performance to remove ammonium was rather limited (Tsalakanidou 2006; Kitis et al. 2007; Mahenge 2014).

VS, obtained from the Kula Volcanic Geopark, was also able to remove COD (50%) and PO_4^{3-} (100%), however, SO_4^{2-} , NH_4^+ and Ni^{2+} were released as well from the VS, which is in agreement with the results of leaching tests (Figure 1E). The use of volcanic slag in water purification is rather rare. However, some recent studies represent the capability of volcanic slag/rock in removing COD, phosphorus and ammonia nitrogen from rainwater runoff and wastewater (Lin et al. 2019; Wan et al. 2020). Better COD removal efficiencies were related to the affinity between the iron in slag and organic constituents in leachate (presented by COD) (Lin et al. 2019). The pH of the zero point of charge (pH_{ZPC}) of the Kula region's volcanic slag was reported to be about 9.3 (Yigit & Tozum 2012). The adsorption capacity of the volcanic slag may also be attributed to the net positive charge of the slag, as the pH of slag-leachate mixtures were between 7.5 and 8. Thus, the higher removal efficiencies observed in this study were related to these VS potential sorption sites.

In this study, the SO_4^{2-} , F^- and Cl^- release by the reactive materials seems to occur at different levels, except from SE. SE only exhibited heavy metal leaching at relatively lower degrees. SE represented the excellent removal of compounds at different levels (Figure 1F). The removal efficiencies observed within twenty-four hours were 40, 50, 65, 95, 97, 98, 98 and 100% for Ni^{2+} , COD, Zn^{2+} , SO_4^{2-} , Cl^- , F^- , NH_4^+ and PO_4^{3-} , respectively. In a study by Uğurlu et al. (2005), sepiolite was found to be effective in the removal of phosphate, ammonium, nitrite and nitrate from paper

industry wastewater. The performance of sepiolite increased at lower pH values and with thermal activation. Sepiolite is a fibrous silicate clay mineral with a high specific surface area and high surface activity (Cobas et al. 2014; Guney et al. 2014). Silanol groups (SiOH), which are present at the border of each block in the external surface of the silicate, act as neutral sites for adsorption (Alrichs et al. 1975; Santos & Boaventura 2008). The zeta potential of SE was found to change between 6.3 and 6.5 (Kara et al. 2003; Qui et al. 2013). Thus, under neutral pH, the surface of the SE exhibits a negative charge. Kara et al. (2003) showed that the zeta potential of SE from the same region exhibited the same trend, but shifted to slightly higher pH values in the presence of Co(II) . It was also concluded that adsorption of hydroxyl complexes of Co(II) ions, such as CoOH^+ , formed at $\text{pH} > 8.2$, through electrostatic attraction, can impart SE more positive charges (Kara et al. 2003). The complex nature of leachates makes it very difficult to distinguish between reaction mechanism like surface complexation, surface precipitation, ion exchange, as the status of surface materials remain rather unknown in the presence of various ions.

In order to understand the affinity of each reactive material for each constituent in the landfill leachate, the amount of constituent adsorbed per gram of reactive material was calculated. It was interesting to recognise that these adsorption capacities were much higher for constituents of higher concentrations (Table 3). The determined removal efficiencies were, in contrast, lower for these constituents. Bilardi et al. (2018) similarly explained the lower zinc removal efficiencies by a zero-valent iron/pumice mixture with a higher zinc concentration in the leachate. Halim et al. (2010) studied the removal of COD and ammonia from a leachate and reported 37.88 mg/g and 6.08 mg/g for activated carbon and 2.35 mg/g

Table 3. Adsorption capacities of the reactive materials based on the batch test data (mg/g)

	COD	PO_4^{3-}	SO_4^{2-}	F^-	Cl^-	NH_4^+	Zn^{2+}	Ni^{2+}
AC	73.86	0.135	*	*	*	4.25	0.0008	0.0065
OC	123.81	*	*	*	*	*	*	*
StS	24.44	0.131	*	*	*	3.37	*	0.0027
PU	55.82	0.142	*	*	*	3.45	0.0005	0.0033
VS	53.91	0.140	*	*	4.12	*	0.0004	*
SE	47.85	0.142	0.428	0.013	32.21	16.07	0.0019	0.0072

COD – chemical oxygen demand; AC – activated carbon; OC – organic compost; StS – steel slag; PU – pumice; VS – volcanic slag; SE – sepiolite rasping; *release

<https://doi.org/10.17221/71/2021-SWR>

Table 4. Pollutant removal potential of the reactive materials from the leachate based on the batch test data

	COD	PO ₄ ³⁻	SO ₄ ²⁻	F ⁻	Cl ⁻	NH ₄ ⁺	Zn ²⁺	Ni ²⁺	Σ
AC	++	++	---	-	-	+	+++	+++	6+
OC	++	---	-	--	-	--	--	0	9-
StS	+	+++	--	-	-	+	--	0	-
PU	++	+++	--	---	-	+++	+	0	3+
VS	++	+++	-	0	+	-	+	-	4+
SE	++	+++	+++	+++	+++	+++	++	+	20+

COD – chemical oxygen demand; AC – activated carbon; OC – organic compost; StS – steel slag; PU – pumice; VS – volcanic slag; SE – sepiolite rasping; --- – $C_e/C_0 = 3-4$; -- – $C_e/C_0 = 2-3$; - – $C_e/C_0 = 1-2$; 0 – $C_e/C_0 = \sim 1$; + – $C_e/C_0 = 0.5-1$, ++ – $C_e/C_0 = 0.1-0.5$; +++ – $C_e/C_0 < 0.1$

and 17.45 mg/g for zeolite, respectively. The adsorption capacities determined for the COD in this study were higher (≥ 47 mg/g) for all the reactive materials except for StS (24.44 mg/g). The capacity of the reactive materials to remove organic constituents from the landfill leachate was also found to be higher when compared with the other constituents (Table 3). Chávez et al. (2019) explained that the adsorption sites are first occupied by those constituents with higher adsorption affinity, leaving those of lower affinity to be poorly adsorbed.

Generally, the pH of all the solutions reflected slightly alkaline conditions (pH 7.8–8.6). It was also noticed that a slight increase in the pH (≤ 0.5) was observed at the end of the treatment time, except for SE and the AC. The pH change observed for both materials was accepted as insignificant. Thus, the complex composition of the landfill leachate does not seem to have a negative influence on the performance of these reactive compounds, especially considering that the solute concentrations were relatively higher than in most studies. Under normal conditions, such a high solute concentration should not be expected in the groundwater (Jun et al. 2009). Thus, the removal of PO₄³⁻, SO₄²⁻, COD, NH₄⁺ and/or heavy metals from landfill leachate, even at variable degrees, can be regarded to occur at remarkable levels (Table 4).

CONCLUSION

The results of this study have demonstrated that activated carbon (AC), sepiolite (SE), volcanic slag (VS) and pumice (PU) are capable in removing various compounds from complex mixtures (Table 4). Therefore, they can be regarded as potentially suitable reactive materials of a permeable reactive barrier (PRB) system treating landfill leachate contaminated groundwater. Especially, SE and VS seem promis-

ing as cheaper reactive materials in comparison to the conventional AC adsorbent. No material was efficient in removing all studied compounds from the solutions. A combination of reactive materials, considering the target compound each material is capable of removing the most, may enable optimisation in the uptake and release of a larger number of compounds from complex solutions like landfill leachates. AC presented the highest potential to remove a mixture of contaminants from the landfill leachate; however, it cannot be seen as a low-cost material. The results of the experiments conducted with the SE and VS showed that these materials are also capable of removing PO₄³⁻, SO₄²⁻, heavy metals and organic solutes from the landfill leachate. The release of unwanted substances was found to increase the retention time needed for the removal of target compounds or resulting in pollution swapping. This highlights the need to study the leaching potential of reactive materials for longer treatment times, when evaluating their usefulness for PRBs. Future studies on the investigation of measures, like pre-treatments (e.g., pre-washing of VS and SE), might help to control the release of interfering compounds from the reactive materials.

REFERENCES

- Adhikari B., Khanal S.N. (2015): Qualitative study of landfill leachate from different ages of landfill sites of various countries including Nepal. *IOSR Journal of Environmental Science, Toxicology and Food Technology*, 9: 23–26.
- Alrichs J.L., Serna J.C., Serratosa J.M. (1975): Structural hydroxyls in sepiolites. *Clays and Clay Minerals*, 23: 119–124.
- APHA/AWWA/WPCF (1998): *Standard Methods for Examination of Water and Wastewater*. 20th Ed. Washington

- D.C., American Public Health Association (APHA), the American Water Works Association (AWWA) and the Water Environment Federation (WEF).
- Bardos P., Bakker L., Cundy A., Edgar S., Harries N., Holland K., Müller D., Nathanail P., Pijls C., Smith J. (2013): SPS9. Common themes and practice in achieving sustainable remediation worldwide, with case studies and debate. In: Special Sessions at the AquaConSoil 2013, Barcelona, Apr 16–19, 2013.
- Bekele D.H., Du J., Freitas L.G., Mallawavarapu M., Chadavada S., Naidu R. (2019): Actively facilitated permeable reactive barrier for remediation of TCE from a low permeability aquifer: Field application. *Journal of Hydrology*, 572: 592–602.
- Bilardi S., Calabrò P.S., Greco R., Moraci N. (2018): Selective removal of heavy metals from landfill leachate by reactive granular filters. *Science of the Total Environment*, 644: 335–341.
- Chávez R.P., Pizarro E.C.C., Galiano Y.L. (2019): Landfill leachate treatment using activated carbon from coffee waste. *Engenharia Sanitária Ambiental*, 24: 833–842.
- Cobas M., Ferreira L., Sanromán M.A., Pazos M. (2014): Assessment of sepiolite as a low-cost adsorbent for phenanthrene and pyrene removal: Kinetic and equilibrium studies. *Ecological Engineering*, 70: 287–294.
- Ellis D.E., Hadley P.W. (2009): Integrating sustainable principles, practices, and metrics into remediation projects. In: U.S. Sustainable Remediation Forum, Sustainable Remediation White Paper, Wiley Interscience, 5–10. Available at <https://onlinelibrary.wiley.com/doi/epdf/10.1002/rem.20210>. (accessed Apr 17, 2021)
- European Commission Directorate General (2019): Re-ground Deliverable No. D5.8 Technology Assessment Report, Ref. Ares(2019)2865097-29/04/2019. European Commission Directorate General for Research and Innovation Horizon 2020
- Foo K.Y., Hameed B.H. (2009): An overview of landfill leachate treatment via activated carbon adsorption process. *Journal of Hazardous Materials*, 171: 54–60.
- Grau-Martinez A., Torrento C., Carrey R., Soler A., Otero N. (2019): Isotopic evidence of nitrate degradation by a zero-valent iron permeable reactive barrier: Batch experiments and a field scale study. *Journal of Hydrology*, 570: 69–79.
- Guney Y., Cetin B., Aydılek A.H., Tanyu B.F., Koparal S. (2014): Utilization of sepiolite as a bottom liner material in solid waste landfills. *Waste Management*, 34: 112–124.
- Halim A.A., Aziz H.A., Johari M.A.M., Ariffin K.S. (2010): Comparison study of ammonia and COD adsorption on zeolite, activated carbon and composite materials in landfill leachate treatment. *Desalination*, 262: 31–35.
- Interstate Technology and Regulatory Council (2005): Permeable Reactive Barrier: Lessons Learned/New Directions PRB-4. Washington, D.C.
- Jun D., Yongsheng Z., Weihong Z., Mei H. (2009): Laboratory study on sequenced permeable reactive barrier remediation for landfill leachate-contaminated groundwater. *Journal of Hazardous Materials*, 161: 224–230.
- Kara M., Year H., Sabah E., Celia M.S. (2003): Adsorption of cobalt from aqueous solution onto sepiolite. *Water Resources*, 37: 224–232.
- Kietlińska A., Renman G. (2005): An evaluation of reactive filter media for treating landfill leachate. *Chemosphere*, 61: 933–940.
- Kitis M., Kaplan S.S., Karakaya E., Yigit N.O., Civelekoglu G. (2007): Adsorption of natural organic matter from waters by iron coated pumice. *Chemosphere*, 66: 130–138.
- Kostura B., Kulveitová H., Leško J. (2005): Blast furnace slag as sorbents of phosphate from water solutions. *Water Resources*, 39: 1795–1802.
- Mahenge A.S. (2014): Suitability of Moshi pumice for phosphorus sorption in constructed wetlands. *Journal of Applied Sciences and Environmental Management*, 18: 135–140.
- Maitra S. (2019): Permeable reactive barrier: A technology for groundwater remediation. *Research Journal of Life Sciences, Bioinformatics, Pharmaceutical and Chemical Sciences*, 5: 203–217.
- Modin H., Persson K.M., Andersson A., van Praagh M. (2011): Removal of metals from landfill leachate by sorption to activated carbon, bone meal and iron fines. *Journal of Hazardous Materials*, 189: 749–754.
- Lin Z., Yang H., Chen H. (2019): Influence of fillers on the removal of rainwater runoff pollutants by a permeable brick system with a frame structure base. *Water Science and Technology*, 80.11: 2131–2140.
- Oguz E. (2004): Removal of phosphate from aqueous solution with blast furnace slag. *Journal of Hazardous Materials*, B114: 131–137.
- Özkaraova E.B. (2020): Sustainable groundwater remediation with biobarriers using agricultural or plant production residues. In: Kurt H.I. (ed.): *Academic Studies in Engineering Sciences*, Lyon, Livre de Lyon: 183–213.
- Özkaraova Güngör E.B., Akın F., Erdin E., Orkun M.O. (2010): Abfallwirtschaft und Strategien in Samsun. In: Proc. Türkisch-Deutsche Abfalltage, Izmir, Nov 25–27, 2010: 499–508. (in Turkish and German)
- Özten A.F., Nişli G., Kılıç Y., Demir E., Korkmaz S. (2009): “Zero Waste” approach for evaluation of waste as a raw material: Turk Telekom Model, In: Kocasoy G., Banar M., Atabarut T., Levi A. (eds.): Proc. National Solid Waste Management Congress UKAY 2009. Eskişehir, May 27–29, 2009. (in Turkish)

<https://doi.org/10.17221/71/2021-SWR>

- Page K., Harbottle M.J., Cleall P.J., Hutchings T.R. (2014): Heavy metal leaching and environmental risk from the use of compost-like output as an energy crop growth substrate. *Science of the Total Environment*, 487: 260–271.
- Qui Y., Yu S., Song Y., Wang Q., Zhong S., Tian W. (2013): Investigation of solution chemistry effects on sorption behaviour of Sr(II) on Sepiolite fibers. *Journal of Molecular Liquids*, 180: 244–251.
- Raymond Jr R.L., Dona C.L., Haddad E.H., Kessel L.G., McKalips P.D., Newell C., Vaské R.J. (2009): Description and current status of sustainable remediation. In: U.S. Sustainable Remediation Forum, Sustainable Remediation White Paper, Wiley Interscience: 11–33.
- Samadder S.R., Prabhakar R., Khan D., Kishan D., Chauhan M.S. (2017): Analysis of the contaminants released from municipal solid waste landfill site: A case study. *Science of the Total Environment*, 580: 593–601.
- Santos S.C.R., Boaventura R.A.R. (2008): Adsorption modelling of textile dyes by sepiolite. *Applied Clay Science*, 42: 137–145.
- Shu S., Zhu W., Wang S., Ng C.W.W., Chen Y., Chiu A.C.F. (2018): Leachate breakthrough mechanism and key pollutant indicator of municipal solid waste landfill barrier systems: Centrifuge and numerical modelling approach. *Science of the Total Environment*, 612: 1123–1131.
- Siggins A., Thorn C., Healy M.G., Abram F. (2021): Simultaneous adsorption and biodegradation of trichloroethylene occurs in a biochar packed column treating contaminated landfill leachate. *Journal of Hazardous Materials*, 403: 123676.
- Turkish Statistical Institute (2019): Population of Province/District Centres and Towns/Villages – 2018. Available at <http://www.turkstat.gov.tr>. (accessed 19.9.19)
- Thermo Fisher Scientific Inc. (2012): Dionex ICS-5000 Ion Chromatography System Operator's Manual, Document No. 065446.
- Torregrosa M., Schwarz A., Nancucheo I., Balladares E. (2019): Evaluation of the bio-protection mechanism in diffusive exchange permeable reactive barriers for the treatment of acid mine drainage. *Science of the Total Environment*, 655: 374–383.
- Torretta V., Ferronato N., Katsoyiannis I., Tolkou A.K., Airolidi M. (2017): Novel and Conventional Technologies for Landfill Leachates Treatment: A Review. *Sustainability*, 9: 1–39.
- Tsalakanidou I. (2006): Potential of reactive filter materials for small-scale wastewater treatment in Greece. [TRITA-LWR M.Sc. Thesis.] Stockholm, Division of Water Resources Engineering, Royal Institute of Technology.
- Uğurlu M., Gürses A., Yalçın M., Doğan Ç. (2005): Removal of inorganic compounds from bleached paper mill effluents by fly ash and sepiolite. In: Proc. 12th Nat. Clay Symp. Van, Sept 5–9, 2005: 552–562. (in Turkish)
- van Liedekerke M., Prokop G., Rabl-Berger S., Kibblewhite M., Louwagie G. (2014): Progress in the Management of Contaminated Sites in Europe. European Commission Joint Research Centre Reference Report, Report EUR 26376 EN, European Union.
- Wan Z., Zhang Y., Lu S., Zhang X., Liu X., Yang Y. (2020): Effect of packing substrates on the purification of municipal wastewater treatment plant effluent. *Environmental Science and Pollution Research*, 27: 15259–15266.
- Yigit N.O., Tozum S. (2012): Removal of selenium species from waters using various surface-modified natural particles and waste materials. *Clean – Soil Air Water*, 40: 735–745.

Received: May 22, 2021

Accepted: November 9, 2021

Published online: December 3, 2021