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Research Paper

Evaluation on applicability of a new hybrid adsorbent to waste pollution control in Lowland by complex leachate from waste landfill site

S. Juengjarernnirathorn [1], M. Ohno [2], Y. Mishima [3], H. Suhara [4] and H. Araki [5]

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ABSTRACT

There is growing social concern about water environment issue including eutrophication, water pollution in the water bodies, and hazardous contaminants in lowland groundwater. Following extensive research into wastewater characteristics, the understanding of the potential effects of wastewater on health and the environment has become more comprehensive. Soil and water in lowland areas are especially easily contaminated by heavy metals, toxicant chemicals from waste disposal landfill sites and factories, and natural disasters. These events have prompted the search for suitable solutions. Several treatment methods have been developed to deal with health and environmental concerns associated with the findings of recent research. In this paper, a new adsorbent is characterized and the adsorption of harmful substances dissolved in leachate has been studied. Nano size Layered Double Hydrotalcite (NLDH) and Zeolite (Ze) have been combined to synthesize a more powerful adsorbent, which successfully adsorb both anion and cation at the same time; cations and anions were simultaneously recovered at the same time over 3 hours, under an initial pH of 6 at 20°C using 0.5 gram and 1 gram per liter of the hybrid adsorbent (HB). Other adsorbents were used to validate the efficiency of a new hybrid adsorbent (HB).

1. Introduction

Polluted water is a serious threat not only to humans but also to other animals and the environment. Well-known effects of toxicity exist in leachates, e.g., fluoride (F^-), nitrate (NO_3^-), and heavy metals, which affect human health (chronic and cancer), the environment and can have other unexpected acute effects. Industrialization in developing countries is one of the major causes of water pollution. Leachates from landfills and other sources of toxic discharge are serious contributors to this pollution. Lowland areas are affected by tide level changes. Groundwater in lowland areas is easy to contaminate. Toxic metals such as cadmium, lead, arsenic and mercury are harmful to human health. These metals accumulate in soils, plants and other living things. In

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[1] Corresponding author, Graduate School of Science and Engineering, Saga University, Saga 840-8502, JAPAN, 14694001@cc.saga-u.ac.jp
[2] JDC Corporation, Akasaka 4-9-9, Mintoku, Tokyo 107-8566, JAPAN, mutsuhiro.ohno@n-kokuda.co.jp
[3] Lecturer & IALT member, Graduate School of Science and Engineering, Saga University, Saga 840-8502, JAPAN, sk9822@cc.saga-u.ac.jp
[4] Special appointed Professor & IALT member, Institute of Lowland and Marine Research (ILMR), Saga University, JAPAN, hideo.suhara@n-kokuda.co.jp
[5] Professor & IALT member, Institute of Lowland and Marine Research (ILMR), Saga University, JAPAN, arakih@cc.saga-u.ac.jp
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Japan, landfill sites are typically constructed in secluded mountainous areas far from populated areas because they can increases the risk of leachate pollution into natural water resources. Leachate is defined as wastewater collected at the bottom of a landfill site that contains numerous hazardous organic and inorganic chemicals at various concentrations (Shiraishi et al., 1999). It is a by-product of landfill waste degradation and contains high concentrations of heavy metals and organic materials that should be treated before being discharged to surface waters. Aged, or mature leachate, which is produced by older landfills, is difficult to manage with high humic and fulvic fractions within its organic matter (Huo et al., 2008; Kulikowska and Klimiuk et al., 2008). The safety of treated leachates released into river waters is usually evaluated by chemical analyses; however, it would not be technically or economically feasible to analyze all the contaminants contained in a leachate. (Fent et al., 2003; Lionetto et al., 2003; Triebskorn et al., 2002). Nano size Layered Double Hydrotalcite (NLDH) was used in combination with zeolite (Ze) as an adsorbent for cation and anion exchange, respectively, and together the new adsorbent is called HB. NLDH has other important uses, including the removal of environmental hazards in acid mine drainage (Lichti et al., 1998 and Seida et al., 2001), and as a procedure for the disposal of radioactive wastes (Roh et al., 2000). Zeolite materials have been extensively employed for investigations of the sorption of heavy metals. These materials have promising effective sorption capacity, mainly due to their valuable sorption characteristics that combine ion exchange and molecular-sieve properties. These properties can be easily modified (Breck et al., 1974; Barrer et al., 1978; Ouki and Kavanagh et al., 1997; Majdan et al., 2003). Consequently, zeolites have emerged as versatile alternative adsorbents, and have attracted considerable interest due to their catalytic and ion exchange properties (Bezus et al., 1986).

To counteract the environmental harm caused by various types of wastewater in lowland areas we evaluate the applicability of this new hybrid adsorbent, introduced to provide a new choice for adsorbing heavy metal and toxic chemicals dissolved through processing complex leachate from waste disposal landfill sites.

2. Materials and Methods

2.1 Leachate

This research was conducted using artificial leachate and raw leachate. Artificial leachate was used to clarify the efficiency of the new hybrid adsorbent and then raw leachate was used to confirm its efficiency in practical use, which more difficult to treat than artificial leachate. The leachates used in this research were collected from municipal landfill sites in Japan.

2.2 Artificial Leachate

All chemicals were prepared for immediate use using standard solution with deionized water the initial concentrations as shown in Table 1. A standard solution and reagent grade chemical were used to prepare the artificial leachate (Table 2). The pH of the artificial leachate was adjusted using 0.1 mol/L NaOH or 0.1 mol/L HCl solutions.

Table 1. Initial concentrations of chemical compounds in the artificial leachate. (Kashiwada et al., 2005)

Chemicals	Initial concentration (ppm)
F^-	1.74
Cl^-	3060
NO_3^-	468
B	2.242
Na	1503
Mg	106.9
Ca	216.4
K	706.4
Cd	0.001166
Cr	0.001205
Pb	0.002488
As	0.000648
Hg	0.0005
P	0.3633
Se	0.001

Table 2. Chemicals and reagents.

Items	Chemicals
F^-	F standard solution
P	P standard solution
NO_3^-	KNO_3
B	B standard solution
Na	NaCl
Mg	$MgCl_2 \cdot 6H_2O$
Ca	$CaCl_2$
K	KI
Cd	Cd standard solution
Cr	Cr standard solution
Pb	Pb standard solution
As	As standard solution
Hg	Hg standard solution
Se	Se standard solution

2.3 *Raw Leachate*

Raw leachates were received from waste disposal landfill sites in Japan. Each landfill site was seepage-controlled, i.e., rubber sheets had been laid on the bottom of the site to prevent leakage of leachate into the ground. Collected leachates are delivered to water-treatment works and released, primarily as treated leachates, into rivers downstream. We expected the leachates to be contaminated with environmentally and biologically hazardous compounds. The characteristics of the raw leachates are shown in Table 3.

2.4 *Adsorbents*

This study used five types of adsorbent consisting of powdered activated carbon (PAC), resins (cation and anion resin and chelating), zeolite (Ze), Nano size Layered Double Hydroxide (NLDH) and the new hybrid adsorbent (HB).

2.5 *Synthesis of the new hybrid adsorbent*

The new hybrid adsorbent was synthesized by combining appropriate ratios of NLDH with Ze (1.14:1) then grinding the compound to powder according to Ohno's method (Ohno et al., 2014). NLDH is an inorganic ion adsorbent having a crystallite size adjusted to a nano-size when the aforementioned hydrotalcite substances are artificially synthesized. NLDH is the general name for various compounds represented $\left[M^{2+}_{1-x}M^{3+}_{x}(OH)_2\right]\left[A^{n-}_{x/n}\cdot mH_2O\right]$, that have anions in a nano-sized layered structure. In this molecular formula, M2+ and M3+ are divalent and trivalent metal ions, respectively, and $A^{n-}_{x/n}$ is the exchangeable anion between the layers. The hydratalcites (HT) employed in the experiments were Mg and Ca as the divalent metal ion, Al as the trivalent metal ion, and Cl- as the exchangeable anion, therefore, it was a Mg-Al-Cl-type HT. The NLDH powder was size adjusted using the sieve method to a diameter of 0.8 to 2.0 mm.

The composition of Ze, a Na-A type zeolite, is expressed as $Na_2{\bullet}2SiO_2{\bullet}AlO_3{\bullet}4.5H_2O$. Its diameter is 2 to 5 mm and its Cation Exchange Capacity (CEC) is 250 meq/100 g. This type of Ze can exchange its Na^+ and NH_4^+ in water (Mishima et al., 2011).

Table 3. Concentrations of chemicals detected in leachates from the waste disposal landfill sites.

Category	Chemical	Concentration (mg/L)		Effluent standard (mg/L)
		sample A	sample B	
Elements	K	872	1184.5	
	Na	2082	2530	
	Mg	71.2	74.4	
	Ca	924.8	1742	
	Al	0.505	1.036	
	Cd	0.0006	0.0164	0.1
	Cr	0.006	0.0022	0.5
	Pb	0.0024	0.0049	0.1
	As	0	0.0044	0.1
	Hg	0	0	0.005
	Se	0.0393	0.0059	0.1
	Br	27.8	37.046	
	B	2.99	1.953	10
Inorganic chemicals	F^-	0.059	0.074	8
	Cl^-	5015.10	7705.8	
Water Quality Para-meters	PO_4^{3-}	0	0	
	NO_2^-	63.253	0	
	NO_3^-	9	280.84	
	SO_4^{2-}	24.523	310.55	
	P	0.1735	0.0413	16
	pH	7.05	6.51	

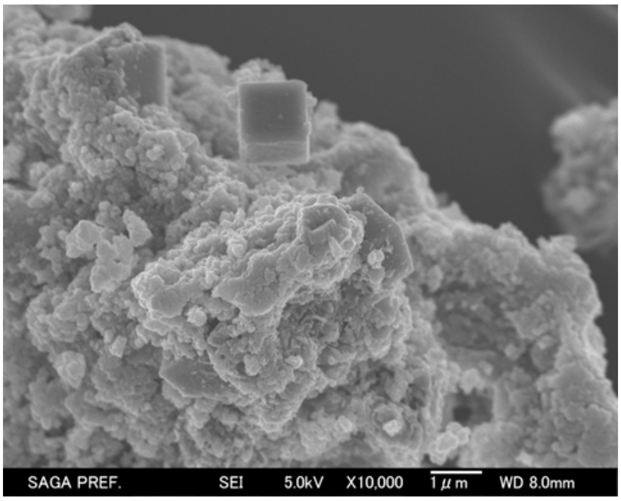

Fig. 1. SEM image of HB.

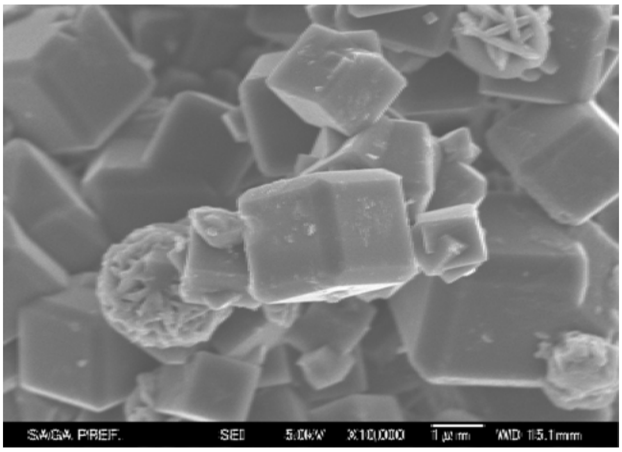

Fig. 2. SEM image of Zeolite.

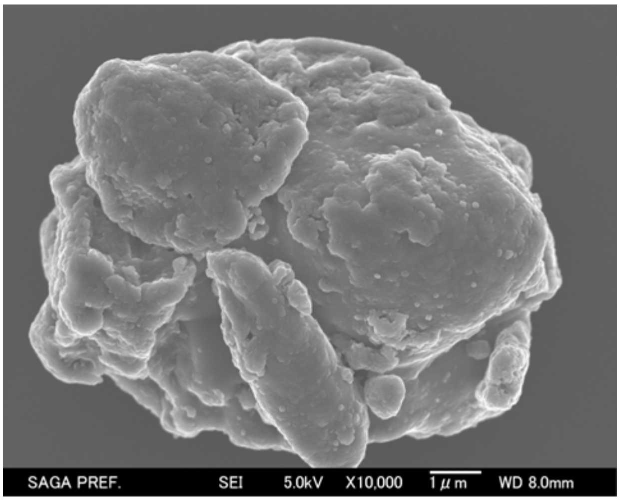

Fig. 3. SEM image of NLDH.

The particle morphologies were examined using Scanning Electron Microscopy (SEM) images. SEM images of HB, zeolite and NLDH are shown in Figs.1 to 3, respectively. The SEM image of HB shows a rough exchangeable surface compared to the exchangeable surfaces of Ze and NLDH and therefore has a high ion exchange performance.

2.6 Adsorption Experiments

All solutions were prepared and used immediately. A standard solution and reagent grade chemical were used to prepare the artificial leachate. The pH of the artificial leachate was adjusted using 0.1 M NaOH or 0.1 M HCl solutions. The efficiency of the adsorbent quantity on ion removal was investigated using 1 L of leachate. The mixture was stirred for 24 hrs. in 2 L beakers covered with a plastic film at 20°C in a temperature-controlled room. The mixture was filtrated and analyzed using chemical analysis equipment (Table 4). Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and Ion spectrometer were used to determine the amount of ions in the leachate at different wave ranges. The percentage of ion removal was calculated using the following equation;

$$\%removal = \frac{C_0 - C}{C_0} \times 100 \qquad [1]$$

3. Results and Discussions

3.1 Adsorption of ions onto the new hybrid adsorbent

HB was prepared under two conditions (*HB*-1, the neutral condition (pH=7) and HB-2, the acidic condition (pH=4)) to test the efficiency of ion removal in artificial leachate. After the adsorption process was complete, the samples were filtered and analyzed for the presence of residual ions. The percentages of anion and cation removal were separated as shown in Figs. 4 and 5, respectively. The percentage of ion removal with HB-1 was higher than with HB-2 due to the acidic conditions created, In case of B acidic condition affect and changed into neutral charge and Cl, Na, Mg, Ca and k are exchangeable ions of HB, which become easier to be changed into another form. Moreover, from Figs. 4 and 5, it can be seen that HB can remove F and B (toxic chemicals) and Cr, Pb and As (hazardous ion) and be used in a wide pH range. Thus, HB-1 was selected for further study.

Table 4. Analyzed chemicals and the analysis methods.

Chemicals	Method
Br	Ion spectrometer
B	ICP-AES
Na	ICP-AES
Mg	ICP-AES
Ca	ICP-AES
Al	ICP-AES
Cd	ICP-AES
Cr	ICP-AES
Pb	ICP-AES
As	ICP-AES
H-As	H-ICP
Hg	ICP-AES
H-Hg	H-ICP
Se	ICP-AES
H-Se	H-ICP
F^-	Ion spectrometer
Cl^-	Ion spectrometer
PO_4^{3-}	Ion spectrometer
NO_3^-	Ion spectrometer
SO_4^{2-}	Ion spectrometer
P	Ion spectrometer

3.2 Comparison of adsorption of ions in artificial leachate onto each adsorbent

The next step was to compare the ion adsorption efficiency of HB on ion removal from the artificial leachate with other adsorbents. Adsorbents were selected based on their use in recent work. The analysis results indicated that NLDH showed the highest potential for ion removal, and half of HB is NLDH. As shown in Fig. 6 and 7, HB has an efficiency of ion removal that is more than 50% greater than NLDH because the surface of HB is rough (see Fig. 1), therefore the exchangeable area is expanded compared to the exchangeable surfaces of pure Ze and pure NLDH. In the case of cation removal HB, Ze and PAC showed higher potentials for ion

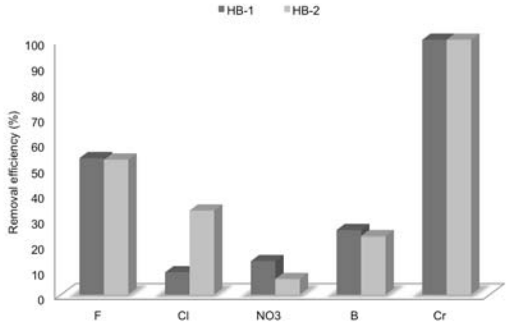

Fig. 4. Percentage removal of anions by HB.

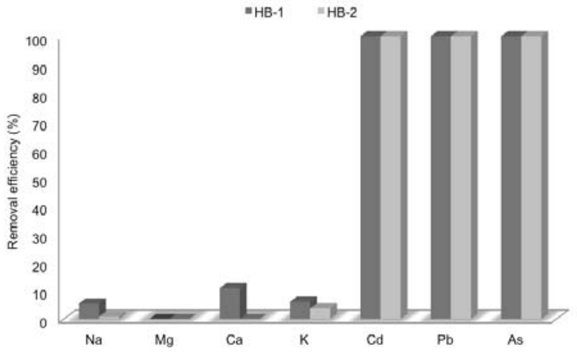

Fig. 5. Percentage removal of cations by HB.

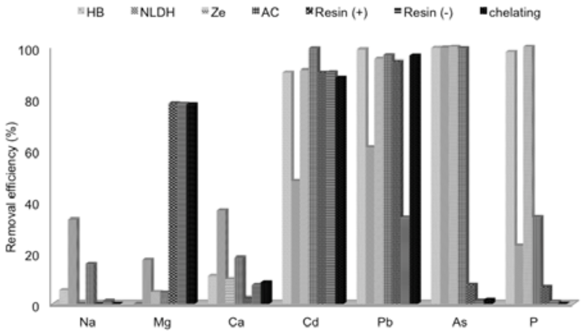

Fig. 6. Cation removal in artificial leachate.

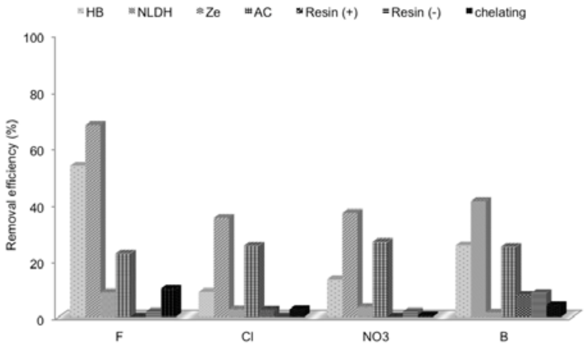

Fig. 7. Anion removal in artificial leachate.

removal. In contrast, the residual amounts of Na, Mg and Ca adsorbed under HB-2 conditions were different because of the acidic conditions created when the reactants of HB (Na, Mg and Ca) were released into the water. Moreover, It can be seen that HB is more suitable than resin without pH control as resin required. Raw leachates were used to confirm these results, as discussed in the next section.

3.3 Ion removal in raw leachate

In this experiment, raw leachates were used to confirm actual performances. Raw leachates were received from waste disposal landfill sites in a lowland area of the Kyushu region. Leachate samples were collected from both an old landfill site and a new landfill site. A batch mode was selected. For each liter of leachate, 1 g. of each adsorbent was used on the leachate. In Figs. 8 and 9 the percentage of cation adsorption is shown, HB and Ze removed target cations, such as chromium and lead efficiently. HB also demonstrated a high potential, similar to that of resin and PAC. The chemical compound characteristics of the leachates from the two sites were different; therefore, the adsorption abilities of HB, NLDH and Ze were affected by the different chemical concentrations. HB also presented a high potential for anion removal, such as boron, as shown in Figs. 10 and 11. HB has the potential to remove anions effectively, especially in young leachate. The results as shown in Figs. 12 and 13 indicate HB's high potential for P removal. In conclusion, HB is suitable for removing heavy metals and complex substances equal as PAC.

3.4 *Study of the new hybrid adsorbent considering effects of environmental factors*

Four factors were considered in this study including pH, temperature, contact time and the adsorbent dose, to investigate the effects of this new hybrid adsorbent on adsorption processes. Raw leachates were use in this study and the experiments were carried out using a batch process. To investigate the efficiency of ion removal by the new hybrid adsorbent the adsorption capacity, q_e (mg/g), was determined from the difference between the initial concentration (C_0, mg/L) and the concentration at time t (C_e, mg/L) per gram of solid adsorbent;

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad [2]$$

3.4.1 *Effects of contact time*

Time dependent adsorption of ions by the HB adsorbent was carried out using 1 liter of the leachate sample and 1 gram of the adsorbent. The objective was to determine the optimum time for the adsorption process to use as a design guideline. The kinetic curve shows the equilibrium time and the adsorption capacity of the HB adsorbent. Figures 14 show unstable graph occurred by different of adsorption strength of HB composite and the optimum on cation removal contact time ranges from 3 to 6 hours and Figures 15 show stable graph with major occurred by NLDH (a part of composition of HB), which Cl^- doesn't release into the solution (Nakahara et al., 2013) and the optimum on anion contact time range from 3 to 48 hours. Thus, these show HB is suitable for cation and anion removal based on 3 to 48 hours of contact time.

3.4.2 Effects of new hybrid adsorbent dose

An adsorbent dose ranged from 0.5 to 2 gram per liter, to investigate performance and to find out a proper dose for use with a raw leachate. The results, as given in Figs. 16 and 17 show that one gram per liter of HB has a high potential for practical use removing cations and that 0.5 gram per liter of HB has a high potential for removing anions such as fluorine.

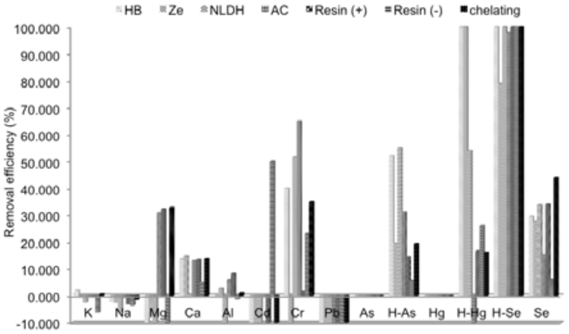

Fig. 8. Cation removal in leachate from an old landfill site.

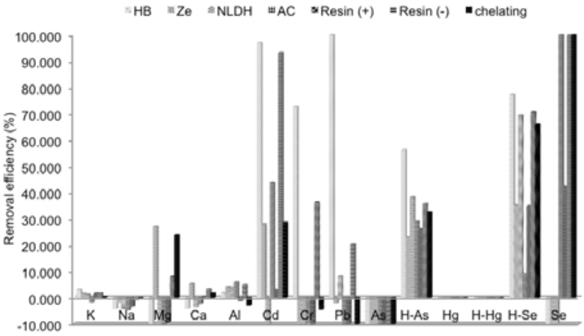

Fig. 9 . Cation removal in leachate from a new landfill site.

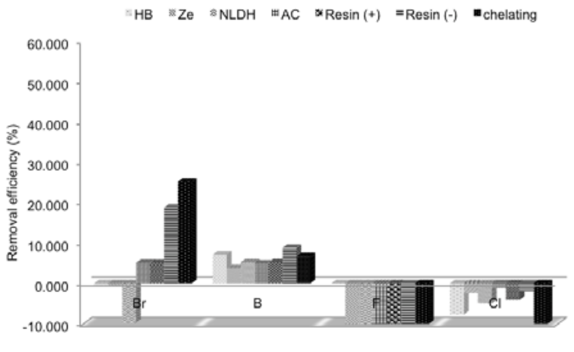

Fig. 10. Anion removal in leachate from an old landfill site.

3.4.3 Effects of temperature

The temperature also affects the efficiency of the adsorbent in adsorption process. The temperature range was set from 10°C-30°C according to the expected actual conditions. The removal the efficiency of HB is shown in Figs. 18 and 19, and indicates a high potential for anion removal at 10°C and a high efficiency of cation removal under 20°C. For anionic removal case changing of temperature not much effect with adsorption efficiency of HB adsorbent it should be clarify again in further study.

3.4.4 Effects of pH

In this experiment, a pH range of between 4 and 8 was used with 1 gram of HB and operated using a batch method for 24 hrs. In Figure 20 and 21 indicate that the

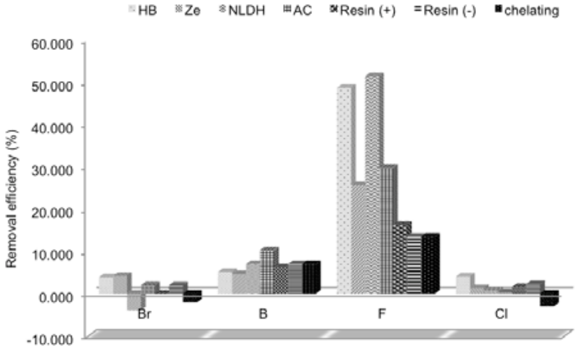

Fig. 11. Anion removal in leachate from a new landfill site.

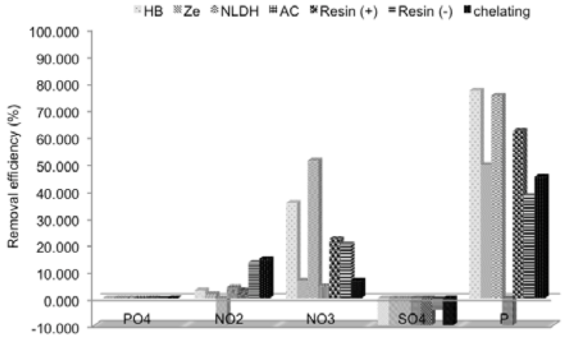

Fig. 12. Ion removal (water quality) in leachate from an old landfill site.

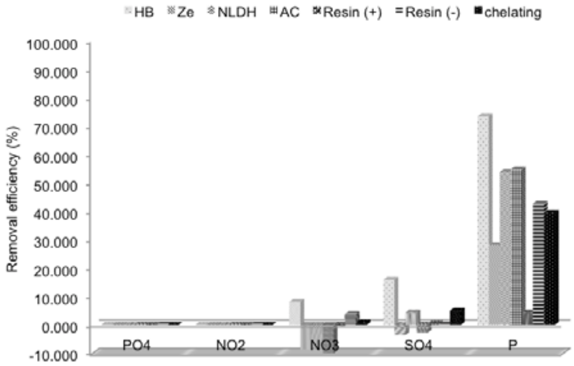

Fig. 13. Ion removal (water quality) in leachate from a new landfill site.

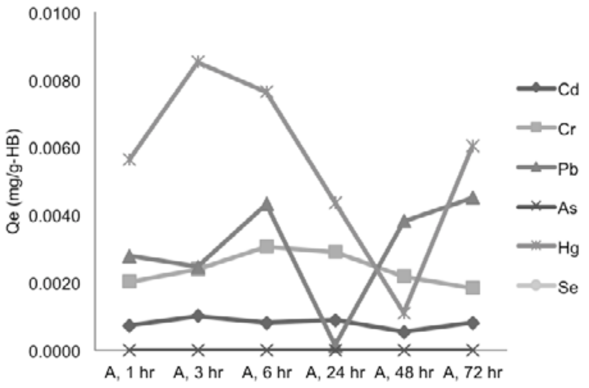

Fig. 14. Equilibrium graph of contact time (cation).

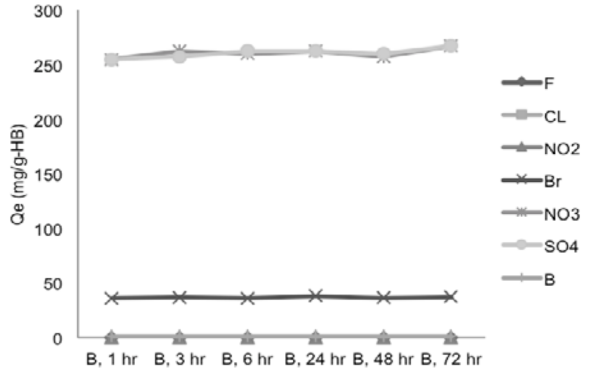

Fig. 15. Equilibrium graph of contact time (anion).

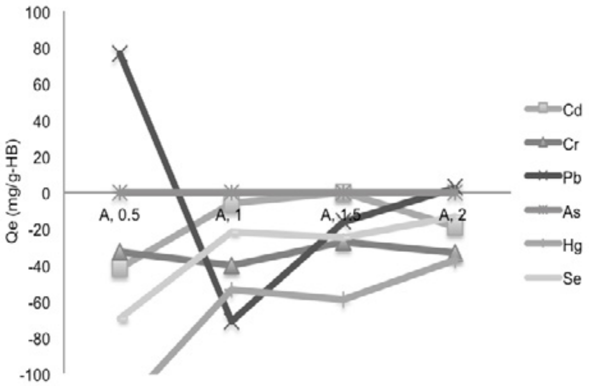

Fig. 16. Equilibrium graph of HB dose (cation).

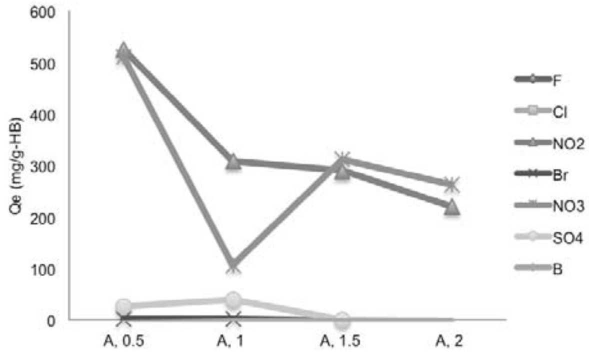

Fig. 17. Equilibrium graph of HB dose (anion).

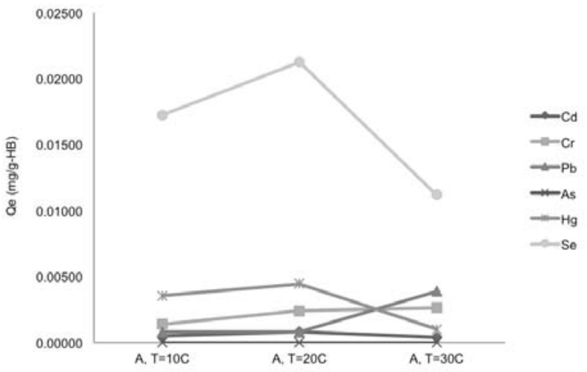

Fig. 18. Equilibrium graph of temperature (cation).

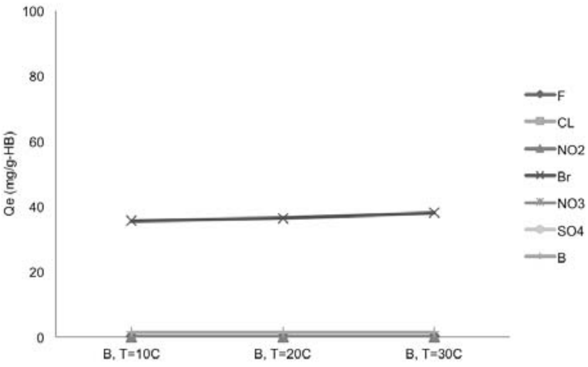

Fig. 19. Equilibrium graph of temperature (anion).

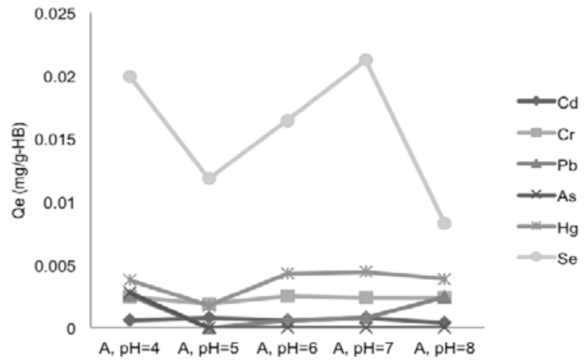

Fig. 20. Equilibrium graph of pH (cation).

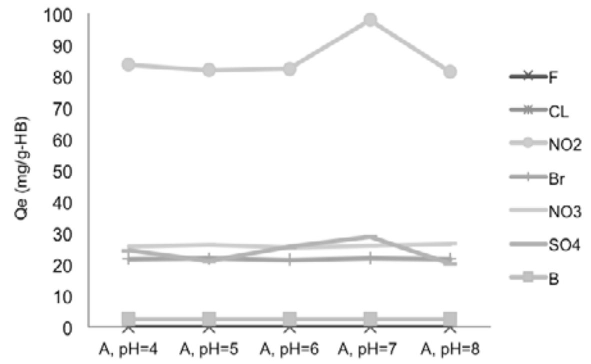

Fig. 21. Equilibrium graph of pH (anion).

adsorption of anions was favored (removal efficiency > 60%) when the initial solution pH was in the range of 5 to 7, weakly acid to neutral. In case of cation removal, when the initial pH was in range of 5 to 6 the adsorption of cations increased then slightly decreased when the initial pH was 7 or a weak base. Therefore, HB is suitable for young leachate, which has pH levels in the range approximately 6 or 7. On the other hand the residual amount of ions in raw leachate indicates that the amount of anions decreased even in acid conditions. The pH therefore has a significant effect on the adsorption of ions by HB; adsorption increases from pH 5 to 6 and slightly decreases from pH 7 to 8 as showed in the graph.

4. Conclusion

This study focused on investigating different types of adsorbents and evaluating the capability of HB using complex leachates for which treatment is usually rather difficult. The adsorption of ions by HB from artificial leachate and raw leachates occurred readily. Adsorption of ions using HB had the synergistic effect of removing anions and cations at the same time. When compared to Ze and NLDH, the percentage of ion removal indicated that heavy metals and toxic chemicals were removed to levels below regulation limits (Table 3). HB was as efficient in ion removal as the other adsorbents used in this study. Raw leachates, which are serious pollutants and appropriate water targets, having complex components (e.g., harmful substances and heavy metals) were used to evaluate the performance of HB. The results of HB removal efficiency are similar to that of PAC or resin and are therefore suitable for use with raw leachates. Although some ions can be removed efficiently using other common adsorbents, such as PAC or resins, the operational costs of HB can be reduced compared to other adsorbents, and further, HB does not require separate operational tanks or columns as PAC or resin apply to treat with landfill leachate. The study of the HB adsorbent together with the effect of environmental factors leads us to conclude that HB shows a higher potential when used for adsorption processes with young leachates under 20°C for operation times of only 3 to 6 hours.

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Symbols and abbreviations

A	The result testing with an old landfill site
B	The result testing with a new landfill site
C_o	Initial concentration (mg/L)
C	Residual concentration (mg/L)
HB	the new hybrid adsorbent
NLDH	Nano size Layered Double Hydroxide
PAC	powdered activated carbon
q_e	The adsorption capacity, (mg/g)
V	volume of the solution (L)
W	mass of adsorbent (g)
Ze	Zeolite