Organic Matter Removal from Leachate Using a Mixed Soil-Activated Carbon

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Abstract

A sustainable proposal was developed for environmental protection to the area around a landfill without control. Diverse columns for simulated permeable barrier packed with semi-wasted activated carbon (AC) from water treatment coming from a deionized equipment and soil samples taken from a landfill without any contamination control located in Mexicaltzingo (México) were studied to remove natural organic matter (NOM) from leachate samples (LS), taken from a landfill site, and laboratory prepared samples (LLS). Natural organic matter measured like chemical oxygen demand (COD), biochemical oxygen demand (BOD), nitrates and nitrites was removed through packed columns. Two different packed forms were tested; in column A, the AC was placed as a support for the landfill soil samples and, in column B, a homogeneous mixed of AC and landfill soil was used. Experiments showed that a short time, 60 min is optimal for a fast NOM removal, COD and BOD decreased up to 94% from the initial concentration in LS; for column B, the same parameters plus nitrates and nitrites were removed up to 100%, making it the most efficient treatment. There are not significant differences in NOM removal for soil samples taken at 3 or 12 meters and the used AC is a semi-wasted revalorized residue. The proposal in this work, for NOM removal through packed columns measured by 4 parameters, shows to be viable as an initial proposal to be used as a permeable barrier to reduce a contamination risk associated to the landfill area.

Keywords: Activated carbon; Leachate; Natural organic matter; Soil; Sustainable

Introduction

Commonly, organic matter (OM) is used to describe a mixture of heterogeneous chemical fractions [1]. So normally the term “natural organic matter (NOM)” is used for all the organic matter in a reservoir or natural ecosystem. NOM is formed by a wide variety of organic compounds that are primarily derived from the decomposition of plant and animal residues that contribute to offensive taste and odors [2,3]. Particularly, NOM from landfill leachates includes volatile fatty acids and refractory humic and fulvic-like compounds, depending on the stage of degradation in the landfill [3]. To measure NOM in synthetic conditions, some carbohydrates, hydrous metal oxides are used as standards to obtain an analytical signal to let follow NOM concentration in lab samples [2]. The main risk generated by NOM in soil and water is totally or partially diminished oxygen, thus the aquatic life and aerobic process are limited for nutrients [4]. As result, NOM is one of the major pollutant materials in leached liquids.

In Mexico, every year only 39% of 30 tons of municipal solid waste (MSW) was disposed of in a landfill [5]. In San Mateo Mexicaltzingo, which is a representative town located in central Mexico due to its commercial activity, there is an MSW disposal site that is outside Mexican Standards and environmental regulations [6-8]. Originally, sand mine has been used as a final disposal site for the last 20 years and is still in operation. The site covers 8705 m², of which approximately 5600 m² are in use. Among the material disposed at the site were pork meat residues and some other animal-derivates, resulting in high NOM content composed mainly humic-like materials, due to the age of the landfill [3].

Many studies focus on the removal of NOM with by different methods, such as ion exchange, membrane filtration, coagulation and adsorption in several materials [3]. Usually, activated carbon is used as a universal adsorbent for water and treated wastewater with heavy metals, phenols, colorant and organic matter [1,9]. One disadvantage of organic matter removal with activated carbon is the large molecular size of the NOM, but a great advantage is that it is low cost, available and environment friendly [4]. In this work, we propose the use of semi-wasted activated carbon (AC) from deionized water equipment to reduce NOM from natural and synthetic leachate samples. The AC in deionized water equipment is replaced every 6 months and after it has no another use, therefore it was important for this work to revalorize this residue by testing a new use after his in end of life in these devices.

The stratigraphic profile shows that the soil in Mexicaltzingo is sandy [10] so NOM could seep through the soil into the phreatic zone, where drinkable water is extracted, becoming a risk for groundwater [4,11]. Unfortunately, in Mexico there are many sites without any type of contamination control where no real action is taken to diminish the generated pollution [8].

Permeable reactive barriers (PRB) have been used successfully to treat a wide range of contaminants [12]. A PRB consists of making a long trench around the soil and filling it with a reactive material, they are no toxic for humans and are functional to adsorb dangerous chemical compounds present in groundwater, and the system can be
Characteristics of natural soil [10].

| Soil depth (m) | Texture    | pH   | E.C. (dS/m) | C.E.C. (cmol/Kg) | Clay (%) | Silt (%) | Sand (%) |
|---------------|------------|------|-------------|------------------|----------|----------|----------|
| 3             | Sandy      | 5.9  | 1.42        | 7.52             | 5.9      | 12.6     | 81.4     |
| 12            | Sandy clay | 7.4  | 1.79        | 7.57             | 14.3     | 0.7      | 85.6     |

Table 1: Characteristics of natural soil [10].
100.75%) previously standardized using a K₂Cr₂O₇ standard (Aldrich, 99.99%) potassium dichromate 0.025 eq/L.

**BOD determination:** The procedure for BOD determination is described by NMX-AA-028-CUF-2001 [22]. A winkler bottle is prepared with an aliquot of leachate sample (LS or LLS) and filled with oxygen saturated water, previously prepared with a specific solution which contains 8.5 g of KH₂PO₄, 21.75 g de K₂HPO₄, 33.4 g de NaH₂PO₄ •7H₂O, 22.5 MgSO₄ •7H₂O, 0.25 g FeCl₃ •6H₂O, 27.5 g of CaCl₂ in 1.0 L of solvent and aired. The initial dissolved oxygen is measured by an oxygen dissolved calibrated meter YSI S1000 and then the winker bottle is closed and incubated at 20°C for 5 days in a Memmert IPS749 incubator. At the end of the 5th day, the final oxygen dissolved can be measured in the same way.

**Nitrites and nitrates determination:** Nitrites were determined by NMX-079-CUF-1987 [22] as follows; first a standard curve is prepared using NaNO₂ from 0 to 0.25 mg/L (0 to 3.6 × 10⁻³ mol/L). Then 10 ml of leachate sample (LS or LLS) without turbidity is placed in different tubes, to each tube 1.0 ml of sulfurilamine was added and left stand during 8 minutes, after 1.0 ml of NEDA solution [CH₃NH₂•HCl •2H₂O, 99.99%] which contains 8.5 g of KH₂PO₄, 22.5 g of MgSO₄ •7H₂O, 0.25 g FeCl₃ •6H₂O, 27.5 g of CaCl₂, 1.0 L of water was added. After 60 minutes, absorbance was read at 543 nm in Thermo Evolution array equipment [21]. Nitrates were determined by ion electrode selective Thermo Scientific Orion, using a calibration curve prepared with KNNO₃ solution from 0.5 to 5 mg/L, and then following the common procedure of using an electrode method.

**Results and Discussion**

A leaching sample of the piezometric well was taken in a rainy season. The well was made to determine the stratigraphic profile as describe in section 2.1; the results for COD, BOD, nitrites and nitrates are shown in Table 2. The obtained values for the determined parameters correspond to middle-age landfill, between 10 and 20 years old [23] as a reference results are compared with Mexican standard limits. It is observed that the amounts of COD and BOD are high; therefore the leachate potentially contributes to the increase of NOM within the environment. These results are due to the municipal solid wastes (MSW) deposited in the landfill which degrade with time resulting in an important source of organic matter pollution in the site.

The characterization study of MSW for quartering method [24] is shown in Table 3. This characterization was made to identify a kind waste deposited in landfill where LS is produced. The sample tested and separated in this work was taken from 1 day of collected MSW is deposited in landfill; the main residue found was guts and feathers (47.2%). Overall, organic waste corresponds to 75% of the domestic waste stream. Discarded plastic, paper, diapers, glass and other represented 25% of the MSW and other wastes, like textiles, wood, aluminum, etc., were also found but in less proportion. The high content of organic matter found in the MSW, which later is disposed in Mexicaltzingo’s landfill, degrades and produces leachate for 20 years according with landfill age identify by leachate characterization, therefore, high quantities of these residues will increase the volume of leachate resulting in a higher probability of aquifers, land and plants polluted for a long exposition to generated NOM in site [25]. According with this result, MSW contributes to NOM in this site for 20 years, and NOM detected quantity is according with landfill age as the same other typical organoleptic properties like color, taste and odor also identified [17].

Figure 1 shows the results obtained for COD for simulated packed columns, it presents COD concentrations for soil samples taken at 12 meters deep for a) laboratory leachate sample (LLS) and c) leachate sample (LS) from the landfill and for the soil samples taken at 3 meters deep for b) LLS and d) LS. In all cases, it can appreciated the same behavior for all soil samples, a fast removal of COD during the first 60 min followed by a semi-stable quantity of COD until reach 350 min. For the leachate lab sample, COD decreased from 3485 mg/L to 115 mg/L during the first 60 minutes in the soil at 3 m deep, representing a decrease of 96% of the initial COD concentration. While for the leachate sample extracted at 12 m deep, it presented a decrease from 1718 mg/L to 912 mg/L, having only a 53% removal of the original COD concentration.

![Figure 1: COD in packed columns](image)

A characteristic of the tested leaching sample (LS) is that COD concentration corresponds to half of the laboratory prepared leachate (LLS). Samples originated from the piezometric well had also other chemical compounds like suspended and total solids, carbonates, fatty acids and refractory compounds as humic acids, which presence is consistent to the landfill age and can be removed in the same column. While the prepared lab leachate sample only presented carbohydrates, hydrous metals, and others that simulated the NOM. These explain the higher COD removal in LLS than in LS; LLS samples had higher organic content and did not present a competition between all the others chemical compounds, like existed carbonates in LS [26].

Also, in the packed columns it can be observed an additional effect associated with the pH value; when the lab leachate sample passed through the packed column the pH value changed from 4.77 to 6.1,
while the pH value for LS changed from 7.02 to 8.02 units. In both cases, a pH increase is due to organic matter decomposition and it is associated to microbial action since the packed columns were exposed to the light.

BOD results obtained for the soil sample taken at 12 meters deep for a) laboratory leachate sample (LLS) and c) leachate sample (LS) from the landfill and taken at 3 meters deep for b) LLS and d) LS, are presented in Figure 2. For the LS, after 60 min it is observed the initial BOD concentration decreased 50% at 12 m deep, while at 3 m deep it was possible to remove 80% of the initial BOD concentration. This shows that there is not real effect for BOD removal associated with the depth of the soil, deeper soil does not guaranty an increase in NOM removal. In the lab leachate samples, it can be observed the same behavior, which confirms that there is no effect in the soil depth; the removal percentage is higher in 3 m soil (94%) than in 12 m soil (60%). For longer times, up to 350 min, a different behavior is observed for both LS and LLS; removal of BOD in 12 m soil decreases at this time while the rest of the samples reach equilibrium at 270 min.

The carboxylic acids and phenolic compounds of the NOM had high molecular masses, high degree of aromaticity and, sometimes, formed complexes with other substances present in the water or sorbent material. This factor is common when activated carbon is used to reduce NOM in water samples, and in this case, it explains the decreased adsorption of BOD in the packed columns with soil-activated carbon [17]. However, NOM removal in each column showed that the soil taken from Mexicaltzingo landfill acts like a natural permeable barrier against the organic matter pollution, expressed like COD and BOD. This effect is improved by adding activated carbon as support, which represents only 20% of the additional weight of the soil used for the packed columns. In the tested packed columns for COD and BOD removal, the saturation point was not reached with the sandy soil (3 m) or with the sandy clay soil (12 m). This last type of soil had a low exchange capacity that not had influence in the removal process, which confirms that there is not a real influence in NOM removal when using different soil samples of depths.

Table 4 shows the results obtained for nitrites and nitrates in the packed columns for LS and LLS. This results show that nitrites and nitrates were best removed in LS in all the columns. For example, nitrites in column A changed its initial concentration from 53.4 mg/L to 30.8 mg/L for LLS; removing a 43% of the initial concentration, while for LS the concentration changed from 2.7 mg/L to 0.98 mg/L; which is a 64% of nitrite removal. A similar behavior is observed for nitrates in both columns. For the LS, the column B removed 68% of the initial concentration (IC) which is a decrease from 49.1 to 15.3 mg/L, while in column A, concentration was decreased up to 15.3 mg/L which represents a 75% removal.

Nitrites and nitrates removal is influenced by the amount of NOM present [27], therefore the simultaneous removal of BOD and COD decrease the nitrites and nitrates elimination. The initial concentration of both does not affect the removal capacity of the packed columns.

Finally, the last packed column was prepared mixing soil extracted at 12 m and activated carbon (column B), results of the 4 measured parameters are shown in Figure 3 for the LS. The removal percentage for COD, BOD, nitrites and nitrates in LS is better in column B than in column A. For COD, the removal percentage reaches 93% of de initial concentration; this represents almost 1150 mg/L removed in column B, while column A removed 850 mg/L. For column B, the contact time increased since the flow that passes through the packed column was slower than in column A. For BOD, the removal percentage was 85%, a similar amount to the one obtained for column A, while for nitrates, the removal percentage reached was 99%.

Figure 3 shows the results for the packed column with mixed soil-AC. It is observed that NOM removal was much more effective than in the packed column with AC as upper support. NOM removal in the packed column with mixed soil-AC exceeds 90%, although the adsorption time is longer. This increased time is due to the high molecular weight of NOM, which slows the flow through, the mixed column where the presence of different size particles exists. However, this increase in time

Table 4: Nitrites and nitrates in laboratory and leaching sample removed in four types of columns for 60 min.

| Column   | Nitrites | Nitrates |
|----------|----------|----------|
|          | LS       | LLS      | LS     |
| IC=53.4 mg/L | IC=2.7 mg/L | IC=62.4 mg/L | IC=49.1 mg/L |
| Removal  | mg/L     | percent  | mg/L    | percent  |
|          |          |          | mg/L    |          |
| A        | 30.8     | 43.4     | 0.9     | 64       |
| B        | 12.1     | 77.4     | 0.9     | 67       |

Figure 2: BOD concentration in packed columns A for 12 m and 3m soil for LLS and LS.

Figure 3: COD, BOD, nitrites and nitrates concentrations in soil plus activated carbon packed column for leachate sample (LS).
allows a higher contact time of the NOM with the soil surface and AC resulting in higher removal. Comparing the removal efficiency of NOM in columns A and B, removal rate is higher in column B for almost all parameters; very close to 100%. This high NOM removal in column B indicates that NOM is probably adsorbed in the surface of the soil and the activated carbon. Also that during this process there were not any electrostatic interactions between the samples and the activated carbon, which can exist in the AC support in column A [28]. Another possible mechanism is hydrogen bonding, which results from the combination on hydrophilic functional groups in NOM, like carboxylic groups present in the NOM [4]. The packed columns A and B show the same behavior for the 4 measured parameters at short intervals of time. It is observed a quick removal and equilibrium is reached at 480 min. The removal of contaminants, expressed as NOM, is due to the presence of activated carbon in each column.

Considering that the NOM content removed by the extracted soil depends on its structural properties (size, bonds, etc.) of the chemical compounds and the proposed experimental conditions, it is necessary to take into account the type of material to be used in the column (whether as support or mixed with soil) and the appropriate amounts of these in order to project an effective permeable reactive soil barrier for pollution control.

Conclusions

Packed columns with sandy soil, sandy-clay soil and used activated carbon for NOM removal expressed as COD, BOD, nitrates, nitrites show that, at short periods of time (60 min), it is possible to achieve a removal higher to 60%, for both natural and laboratory prepared leachate. NOM removal is not affected by the type of soil but it is influenced by the type of column packing; being the best a mixture between soil-AC. The tested columns show that a mixture of 80% soil and 20% AC is enough to create a permeable reactive barrier that controls organic pollution in an unrestricted landfill site. These results show that it is possible to valorize used activated carbon for NOM treatment in leachate generated at a landfill, and in a future implementation as a permeable barrier.

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References

1. Bieroza M, Baker A, Bridgeman J (2009) Relating freshwater organic matter fluorescence to organic carbon removal efficiency in drinking water treatment. Sci Total Environ 407: 1765-1774.
2. Filletta M (2014) Understanding what we are measuring: Standards and quantification of natural organic matter. Water Res 50: 287-293.
3. Joseph L, Flora JRV, Park YG, Badawy M, Saleh H (2012) Removal of natural organic matter from potential drinking water sources by combined coagulation and adsorption using carbon nanomaterials. Sep Purif Tech 29: 64-72.
4. Yang Y, Lohwacharin J, Takizawa S (2014) Hybrid ferricydrate-MFUF membrane filtration for the simultaneous removal of dissolved organic matter and phosphate. Water Res 65: 177-185.
5. Hernández-Berriel MC, Márquez-Benavides L, González-Pérez DJ, Buenrostro-Bullinger-Weber G, Le Bayon RC, Thébault A, Sclapfer R, Guenat C (2014) Carbon storage and soil organic matter stabilization in near-natural, restored and embanked Swiss floodplains. Geoderma 226-229: 122-131.
6. García-Mayo C, Macedo MG, Martínez-Gallegos S, Barrientos B, Morales-Reyes P (2011) Determination of the natural attenuation process at a disposal site in the State of Mexico. J Solid Waste Tech Manag: 217-225.
7. Renou S, Givaudan JG, Poulain S, Dirrassouyan F, Moulin P (2008) Landfill leachate treatment. Review and opportunity. J Hazard Mater 150: 468-471.
8. Suk OY, Jeen SW, Gillham RW, Gui L (2009) Effects of initial iron corrosion rate on long-term performance of iron permeable reactive barriers: Column experiments and numerical simulation. J Contam Hydro 103: 145-156.
9. Hunter WJ (2003) Accumulation of nitrite in denitrifying barriers when phosphate is limiting. J Contam Hydro 1: 79-84.
10. Korflatis GP, Demetracopoulou AC, Bourdoumis E, Nassy EW (1984) Moisture transport in a solid waste column. J Environ Eng 4: 780-785.
11. Rodríguez-Cruz MS, Sánchez-Martín MJ, Andrade MS, Sánchez-Camazano M (2007) Modification of clay barriers with a cationic surfactant to improve the retention of pesticides in soils. J Hazard Mater B 139: 363-372.
12. Scherer MN, Richter S, Valentine RL, Alvarez PJJ (2000) Chemistry and microbiology of permeable reactive barriers for in situ groundwater cleanup. Crit Rev Microbiol 30: 363-367.
13. Mohora E, Roncevic S, Dalmacía B, Agbaba J, Watson M, Karlovic E, Dalmacía M (2012) Removal of natural organic matter and arsenic from water by electrocoagulation/fluotation continuous flow reactor. J Hazard Mater 234-236: 257-264.
14. Foo KY, Hameed BH (2009) An overview of landfill leachate treatment via activated carbon adsorption process. J Hazard Mater 171: 54-60.
15. Rodríguez J, Castillón L, Marañón E, Sastre H, Fernández E (2004) Removal of non-biodegradable organic matter from landfill leachates by adsorption. Water Res 38: 3297-3299.
16. Li W, Hua T, Zhou Q, Zhang S, Li F (2010) Treatment of stabilized landfill leachate by the coaginate process of coagulation/floculation and power activated carbon adsorption. Desalination 264: 56-59.
17. SE (2001) Economy Secretary, Mexican Official Norms (in Spanish).
18. SEMARNAT (2010) Environmental and Natural Resources Secretary. Mexican Official Norms: NMX-AA-61-1985 (in Spanish).
19. Tchobanogous G, Theisen H, Vigli S (1993) Disposal of solid wastes and residual matter. Clark BJ, Morris JM, (Eds.). Integrates Solid Management, Engineering Principles and Management Issues, McGrawHill, California, USA.
20. SDS (1992) Social Development Secretary, Mexican Official Norms MX- AA-15-1985 (in Spanish).
21. Korfiatis GP, Demetracopoulou AC, Bourdoumis E, Nassy EW (1984) Moisture transport in a solid waste column. J Environ Eng 4: 780-785.
22. Sarkar D, Kumar De D, Das R, Mandal B (2014) Removal of organic matter and oxides of iron and manganese from soil influences boron adsorption in soil Geoderma 214-215: 213-216.
23. Song H, Yao Z, Wang M, Wang J, Zhu Z, Li A (2013) Effect of dissolved organic matter on nitrate-nitrogen removal by anion exchange resin and kinetics studies. J Environ Sci 25: 105-113.
24. Humbert G, Gallard H, Suty H, Croué JP (2008) Natural organic matter (NOM) and pesticides removal using a combination of ion exchange resin and powdered activated carbon (PAC) Water Res 42: 1635-1643.