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CONVERSION OF SLUDGE FROM A WASTEWATER TREATMENT PLANT TO A FERTILIZER

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ABSTRACT: Preventing wastage of resources is an important priority for sustainability. Sludge from a wastewater treatment plant (WWTP) is such a resource that it often wasted. It is a source of nutrients and organic materials that can be used as a fertilizer. At a waste water treatment plant in Montreal, the sludge is currently incinerated and sent for disposal. Alternatives to the practice are thus desirable. Elevated concentrations of cadmium, copper, cobalt and selenium are found in the sludge and therefore a treatment process is required before use as a fertilizer according to the Province of Quebec regulations. Leaching was selected as there is potential for heavy metal removal. However, nutrient loss must be minimized to preserve its use as a fertilizer. To meet these goals, a new leaching agent (K_2HPO_4) was proposed, and investigated for heavy metal removal efficiency on the sludge. A correlation of heavy metal removal and preserved nutrient concentration with time and pH was found. Removal efficiencies of cadmium, copper, cobalt and selenium of 80%, 44%, 70% and 93%, respectively were determined. In addition, concentrations of nitrogen, phosphorus and potassium of 17%, 17% and 25%, respectively, resulted in the treated sludge. In conclusion, the use of dipotassium phosphate is an effective leaching method to remove heavy metals and simultaneously increase the primary macro nutrients at an acceptable cost.

Keywords: Heavy metals, Nutrients, WWTP, Sludge, Leaching

1. INTRODUCTION

Sludge is produced as the results of the wastewater treatment process, dewatered and disposed of in landfills. Disposal of sludge has many disadvantages but is utilized due to its simplicity. However sustainability concerns, resource depletion and increased sludge production due to population growth, require better solutions to this problem.

New cost effective methods for treating and recycling of sludge must be employed to prevent resources wastage and damaging the environment. High concentrations of different nutrients and organic materials enable use of sludge as a fertilizer in agriculture fields. Chemical fertilizers can easily leach through the soil where they are no longer available for plant usage. This problem can be solved by humus in the soil which is stable organic matter in the soil that can preserve nutrients for plants. Using sludge as a fertilizer can increase organic matter. In comparison to chemical fertilizers, using sludge as fertilizer can add various nutrients to the soil, and enhance soil fertility, while preserving nutrients in the root area.

One of the largest wastewater treatment plant (WWTP) in the world is located in Montreal (Jean-R. Marcotte). This WWTP produces a large volume of sludge daily, sending their sludge to landfill for disposal. To decrease the volume of sludge and to control biological pollution, incineration facilities were built at the plant and its bottom and fly ashes are disposed of instead of the raw sludge.

As heavy metals are found in the influent flow to the Montreal WWTP, the resulting ashes contain heavy metals. Therefore disposing of the ash can have harmful effects on the Montreal environment. Also the useful resources of the nutrient content of the sludge have been wasted up to now. An alternative solution must be proposed for this problem to remedy the existing procedures. Instead of disposing of the ashes in the landfill, it is possible to use the sludge as a fertilizer in an agriculture field. However, heavy metal removal is a necessity prior for use as a fertilizer while the nutrient content must be conserved.

High concentrations of pathogens and chemicals in the sludge can be harmful for environment and living organisms so that reducing the dangerous contents to below acceptable levels before returning the sludge contents to the environment or reuse is necessary. Common methods for sludge treatment are aerobic or anaerobic digestion, alkaline stabilization, composting, and incineration [1]. Each method produces different products.

Among the various treatment methods, leaching was selected for evaluation. This method is simple and does not require any expensive or complex facilities. The leaching method is usually effective for heavy metals but nutrients can also be removed. In this research an attempt is made to remove this disadvantage and convert the sludge of

Montreal WWTP to a fertilizer by a leaching method.

The general objective of this research was to develop a method for conversion of the sludge to a high quality fertilizer. The specific objectives were to evaluate the effects of the proposed leachant on the sludge, and determine the correlation between pH and reaction time with treated sludge concentrations of heavy metals and nutrients.

2. MATERIALS AND METHODS

2.1 Materials

2.1.1 Chemicals

Dipotassium phosphate, 70% (K_2HPO_4), nitric acid (70%, trace metal), hydrogen peroxide (30%): and hydrochloric acid (70%, trace metal)) were purchased from Fisher Scientific Co.

2.1.2 Sludge samples

The samples were obtained from the Montreal Jean.R.Marcotte WWTP. After pumping the water, the pre-treatment is started with screening units to remove large solids and continued with grit removal to protect subsequent treatment processes. The main treatment unit in this WWTP is primary treatment, a coagulant, ferric chloride or alum, is added before the screening units. Also an additional flocculation aid, a long string polymer, is added after the grit chamber units. Coagulation and flocculation occur in the primary clarifiers. The total solid in the primary sludge is around 3%. This sludge is sent to be homogenized, conditioned and dewatered. Also there are mechanical traversing bridges to remove the scum from the surface of the water. The treated water is discharged to the nearby river. There are four reservoirs after the primary clarifier to help manage the sludge treatment. Sludge is pumped from these reservoirs to a homogenization unit. Polymer is added before dewatering to increase efficiency of filter presses. After producing cake, it is sent to incineration and the ash is sent for disposal.

Samplings were done in August and November 2012 and February and May 2013. The samples were obtained from the primary sludge after dewatering and before sending the cake to the incinerator. Also the samples were kept in plastic containers inside the refrigerator at 4 ºC .

2.2 Experimental Methods

The experiments were divided into two parts, one for determining initial concentrations of elements in the sludge, and the other one for determining the final concentrations of the sludge after leaching at different pHs and reaction times.

Leaching solutions (pH 1, 2 and 3) were prepared with 1 M di-potassium phosphate (K_2HPO_4) solution, deionized water and HNO_3 (for pH adjustment). The adjusted pH was 1, 2 or 3. One gram of dewatered sludge was added to 50 ml leachate in a 50 ml tube. The samples were shaken at 150 rpm. Different reaction times on a horizontal shaker were used for the various experiments (1, 2 or 4 hours). At the end of the experiment, the samples were centrifuged at 3000 rpm for 15 minutes. The leachate was then decanted from the sludge and then analyzed. The leaching experiments were performed in triplicate. The final result was the average of these three experiments.

2.3 Heavy Metal Analysis

All heavy metal analysis was done by ICP-MS (Agilent Technology 7700 X ICP-MS). All samples were digested by the EPA 3050B method. For digestion, 1 gram of dewatered sludge (cake) was separated, 10 ml of 1:1 (vol/vol) HNO_3 and water were added, and then heated to 95º C by a hot plate for 15 min. After cooling the sample, 5 ml HNO_3 were added and heated for 2 hours. After cooling the sample, 2 ml of deionized (DI) water and 3 ml H_2O_2 were added. The solution was heated while adding 1 ml H_2O_2 until the general appearance of the sample did not change. The final step of the digestion was to heat the sample with a hotplate for two hours. After cooling and diluting with DI water 100 times, the sample was filtered with a 0.7 micrometer filter paper. All samples were diluted 500 times by 2% HNO_3 and 1% HCl to obtain a final concentration be less than 200 ppb. The concentrations of all analyzed samples were calculated based on the calibration curve. In this case, five calibration samples with 0.1, 1, 10, 100 and 300 µg/L were prepared.

2.4 Nutrient Analysis

Persulfate digestion was used before nitrogen analysis based on the Hach manufacturer instructions. It has been developed for soil and fresh water [2]. The sample and persulfate powder were added to the HR total nitrogen hydroxide digestion vial and after 30 seconds of mixing it was heated to 105ºC for 30 minutes by the Hach Digital Reactor Block 200. Nitrogen concentrations in the samples were read by the DR2800 product of Hach Company, a portable spectrophotometer. The digested sample was cooled before nitrogen analysis.

The nitrogen analysis was also followed based on the Hach instructions. It included adding two different powders (A and B) to the digested sample and taking 2 ml from the produced solution for mixing with a new solution called C. At the end nitrogen analysis results were shown by the DR 2800 Hach device.

Analysis for all nutrients except for nitrogen was done by ICP-MS. As the nutrient concentration range was higher than the heavy metals, more dilution was required with the same dilution solution. A 50000 times dilution was used for calcium, magnesium and iron and 1000000 times dilution for potassium and phosphorus.

3. RESULTS AND DISCUSSION

3.1 Initial Content of Heavy Metals in Sludge

The initial concentrations of heavy metals of the untreated sludge were determined based on an average of 28 samples. Seven samples were taken each three month period over seven consecutive days. The samplings were done in February, May, August and November. The average concentrations were compared to the C1 and C2 levels according to the Guide for Recycling of Residual Materials for Fertilizers [3].

As seen in Table 1, by comparison of the Quebec regulations and the average concentrations in 2014, heavy metals can be divided into two groups. The first group includes As, Cr, Ni, Pb, Zn, Co, and Cu and Se can pass both regulations without any treatment. The second group includes Hg, Mo and Cd that can pass C2 and thus the prepared sludge is acceptable but improving the quality of sludge is needed to decrease their concentration to the C1 limit.

The concentrations of the various heavy metals in historical data were provided by the WWTP and therefore a comparison was made between those values in 2007, 2011 and 2014. The concentration of Cd increased from 9 in 2007 to 16.7 in 2011 and now has decreased to 3.9. Therefore at one time it could not even pass C2 guidelines. Cobalt levels increased from 19 in 2007 to 72 mg/kg in 2011 where it could not pass the C1 level but now it can. Selenium on the other hand has decreased from 2007 (9 mg/kg) to 8.1 mg/kg in 2011 to current levels. Therefore it seems to be no longer problematic. Copper has also decreased over the years (from 477 to 468 to 146 mg/kg in 2007, 2011 and 2014, respectively).

Therefore Cd can be defined as the major problem for use of the sludge as a fertilizer. As currently copper and cobalt are below C1 levels, they can be classified as non-problems currently. Se is currently very close to C1 levels so it can be classified as potential problematic. However all four heavy metals were followed during the leaching tests.

Table 1 Comparison of metal sludge contents (mg/kg dry basis) to Quebec guidelines [3]

Element	Concentration	C1	C2
Co	15.7	64	150
Cu	145.9	400	1000
Se	1.25	2	14
Cd	3.9	3	10

3.2 Leaching Test Results for Heavy Metals

To decrease metal concentrations in the sludge, leaching tests were performed to ensure the produced sludge will reach an acceptable cadmium removal for passing C1 Quebec regulations. In addition a decrease in copper, cobalt and selenium contents were desirable while preserving or increasing the nutrient concentrations of the sludge. pH and time were the two important factors evaluated.

Figure 1 shows the average removal percentage for cadmium at different pHs over a 4 hour time period. Only a short time period is required as most of the removal occurred in the first hour. Also there is an indirect correlation between removal percentage and pH as decreasing the pH increased the removal percentage. Moreover the removal percentage by this method for cadmium reached its maximum removal percentage, around 80%, Also the difference between using a salt and using only acid is shown in Fig. 1. The salt and acid combination is much more effective than the salt alone. The experiments also show that an acceptable removal at pH 3 is possible to pass the C1 regulation after four hours reaction at pH 1.

Similar trends were obtained for all three other metals (graphs not shown). pH 1 with the salt gave maximal results.

Only copper showed a less significant difference between the results at pH 1 and pH 3.

Table 2 shows the final content for all metals after leaching with the salt and pH 1. It can be seen that substantial removal is obtained for all 4 metals.

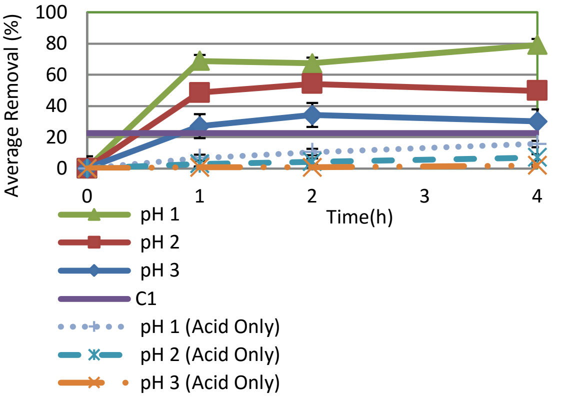

Fig. 1 Cadmium removal under various conditions

Table 2 Heavy metal content of the sludge after treatment (pH 1 & time of 4 h)

Heavy Metal	Final content after leaching (mg/kg, dry basis)	% Removal
Cd	0.8	79.5
Co	4.9	69.9
Cu	81.4	44.2
Se	0.02	98.4

3.3 Nutrient Content of the Sludge

In addition to removing harmful heavy metals from the sludge, it is important to preserve or increase the existing nutrients. As the most important nutrients are nitrogen, phosphorus and potassium, these were chosen for monitoring during the treatment method. The selected acid and salt were also chosen because three of these elements are present in their composition. The effect of this leaching method on the concentration of six different nutrients was thus investigated.

From Table 3, it can be seen that there is a large difference between primary macro nutrients in the initial and final macro nutrient contents. Potassium exchange is the main mechanism for heavy metal removal and the increase of potassium in the final product.

Table 3 Comparison of primary macronutrients before and after treatment

Primary Macro Nutrients	Initial sludge 2014 (mg/kg, dry basis)	Treated sludge (pH 1 & Time = 4 h) (mg/kg dry basis)
N	1.36	17.07
P	0.00	17.57
K	0.63	25.20

Figure 2 shows the effect of pH during the leaching test on the nitrogen content the method increases the nitrogen concentration in the sludge. The increase in nitrogen is due to the use of nitric acid for adjusting pH during the experiments. Also it is seen that the initial amount of nitrogen is 1.36% and the highest amount is reached at pH 1 and pH 2 which is more than 17%. Also at these pH, after one hour there was no significant increase in the nitrogen content. However at pH 3, the maximum content was reached at four hours.

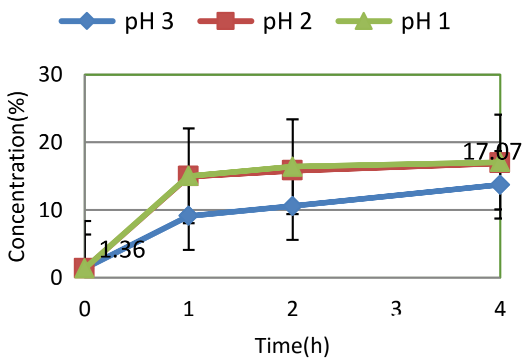

Fig. 2 Nitrogen contents after leaching at various pH

Although phosphorus had the lowest concentration of the nutrients, a significant enhancement was obtained by this method. A 17% concentration after 2 hours was achieved at pH 1 or 2. Therefore decreasing the pH to less than two was not necessary. The same trends as for nitrogen were obtained. A pH of 3 gave inferior results.

The increase of phosphorus during the experiment is likely the result of producing salts with low solubility salts such as magnesium phosphate, calcium phosphate and sodium phosphate Corresponding solubilities of these salts are 0.002, 0.02 and 121 g/L respectively [4].

Other nutrients including magnesium, calcium and iron were also monitored. All three showed a decrease in content. Magnesium showed the smallest decrease. A pH of 3 showed the lowest decrease (data not shown). Decreasing the pH to 1 further increased the leaching of magnesium. It takes more time for higher pH solutions to reach the maximum. For example it takes one hour when pH 1 and two hours when pH 2 and more than two hours at pH 3. The maximum loss of magnesium is also around 52% which occurs at pH 1 after four hours reaction time.

Although calcium loss (78%) was more significant than magnesium, the same trends were found. For pH 1, the maximum occurred at 1 hour for pH 2 it was 2 hours (35%) and for pH 3, 4 hours. Therefore decreasing the reaction time and increasing the pH can help to retain more calcium in the produced sludge.

Maximum iron removal was 68% at pH 1 and 1 hour. Slightly less removal was achieved after 2 hours at pH 2 (50%). At pH 3, 4 hours was necessary to achieve the same level of removal. It is important to mention that iron is a micro nutrient and plants use this element in very low concentration. Higher iron concentrations in the soil can be toxic for plants although this limit is dependent on the type of plant.

Overall, the treated sludge with acid and salt is lower in heavy metal content with enhanced nutrient content. Optimization of the pH and leaching can lead to an optimized product.

Table 4 Comparison of the other nutrient content in the initial and treated sludge (dry basis)

Nutrients	Initial sludge (%)	Treated sludge (pH 1 & time = 4 h (%)
Mg	0.23	0.11
Ca	0.23	0.05
Fe	1.58	0.51

3.4 Mechanism of Leaching

The main mechanism in this method using a potassium leaching solution for removing heavy metals from the sludge is by ion exchange of potassium with the heavy metal ions into the leachate solution. Therefore the treated sludge has potassium instead of heavy metals. The existence of the ion exchange process between potassium and several heavy metals cations was studied and shown by Sparks [5] in soil previously and this research shows a new application for that.

Potassium is an important nutrient for plant too during the removal of heavy metals the fertility of sludge is increased by adding potassium to it. On other hand the quality of sludge is increased by two ways at the same time, first by removal of harmful heavy metals and second, by adding a useful nutrient.

4. CONCLUSIONS

The objective of the research was to develop an alternative treatment for WWTP sludge to enable its use as a fertilizer due to its nutrient. The produced sludge needs to pass Quebec regulations for approval for agricultural usage. The removal of heavy metals with concentrations higher than the C1 regulation was required from the sludge in addition to preservation of nutrient concentration was an additional objective for high quality sludge.

Cadmium, copper, cobalt and selenium levels were higher than the C1 regulation. Three of these heavy metals passed the C2 regulations which are less strict than C1. As cadmium cannot pass the C2 level, it is in the major problem group while the others only cannot pass C1 so they are in the minor problem group.

The primary macro nutrients (nitrogen, phosphorus and potassium) and two secondary macro nutrients (magnesium and calcium) and one micro nutrient with high concentration in sludge (iron) were studied.

The most frequent leachant for heavy metal removal is usually acid or base alone. Here a dissolved salt at low pH was proposed as the leachant. The main factor for removal was found to be the salt instead of the acid or base as the main mechanism is ion exchange not acid extraction.

The leaching experiment for the sludge was performed with dipotassium phosphate (K_2HPO_4) and nitric acid (HNO_3) as leachant. The effect of pH and reaction time on removal efficiency was evaluated.

The maximal metal removal was at pH 1 with 4 hours of leaching (93% selenium, 80% cadmium, 70% cobalt and 44% copper). Although copper did not show any correlation with pH, all heavy metals have direct correlation with reaction time. Most of the removal occurred in the first hour. In contrast to other reviewed papers which show removal at very low pHs. An acceptable removal could be achieved at pH 3 in this study. Therefore this method is effective and fast for heavy metal removal and safer for employees because of less acid usage.

As all three primary macro nutrients (nitrogen, phosphorus and potassium) are involved in the removal process, the concentrations of these three are higher than expected after the experiments. Although there is a loss of the other nutrients during this method, they will be used in low concentration by plants, and thus the results should be acceptable.

Macroprimary nutrient concentration has direct and indirect correlations with time and pH but there is a maximum capacity for sludge which can be reached after 2 hours and with pH 2. Therefore increasing the time or decreasing pH is not effective after that point.

Non primary macro nutrient concentrations decreased with this method. But it can be seen that they are highly dependent on pH. Leachate with higher pH needs more time to decrease the concentration. Also it shows that after four hours in any pHs there are approximately the same results which means the maximum available amount of these elements in all pHs are equal but different times were required to reach that point at different pHs.

5. ACKNOWLEDGEMENTS

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