Aim and Scope

The objective of the *Journal of Residuals Science & Technology* is to provide a forum for technical research on the management and disposal of residuals from pollution control activities. The Journal publishes papers that examine the characteristics, effects, and management principles of various residuals from such sources as wastewater treatment, water treatment, air pollution control, hazardous waste treatment, solid waste, industrial waste treatment, and other pollution control activities. Papers on health and the environmental effects of residuals production, management, and disposal and are also welcome.

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Research

Evaluation of Airborne Endotoxin Concentrations Associated with Management of a Crop Grown on Applied Biosolids

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ABSTRACT: Public health concerns have been expressed regarding inhalation exposure associated with the application of biosolids on cropland, which is due to the potential aerosolization of microorganisms, cell wall products, volatile chemicals, and nuisance odors. Endotoxin is a component of the cell walls of Gram-negative bacteria and is likely present in many biosolids. The application of biosolids to cropland may result in an immediate exposure or a delayed exposure to these microbial agents, such as when the crops are harvested. Upwind and downwind airborne concentrations of endotoxin were compared among and within two adjacent established hayfields, one with and one without previously applied biosolids, during grass raking and bailing activities. The mean downwind concentration of airborne endotoxin was significantly higher than the mean upwind concentration at the site where biosolids had been previously applied. The mean downwind concentration of endotoxin was not significantly different than the mean upwind concentration at the control field where biosolids had not previously been applied. When comparing the mean concentrations of airborne endotoxin among the sites, significant main effects were noticed for wind direction and field type, and an interactive effect was noticed for direction and field type. It is not known if the increased mean concentration of endotoxin associated with the downwind air samples at the applied biosolids field were due to the residual biosolids that were previously applied or due to endotoxin associated with plant material. The results apply to this investigation only since there was no treatment replication of each type of field. The downwind endotoxin concentrations observed during the raking and bailing activities were lower than various health effects criteria that have been recommended for airborne endotoxin.

INTRODUCTION

ENDOTOXIN is a term associated with the toxic characteristics of the outer membrane of Gram-negative bacteria [1], specifically the fragments of the Gram-negative cell wall that contain lipopolysaccharides [2]. Lipopolysaccharides are essential for the physical organization and function of the outer membrane, and thus for bacterial growth and multiplication [3]. Endotoxin consists of a family of molecules called lipopolysaccharide (LPS). The LPS contains a lipid region (lipid A), and a long covalently linked heteropolysaccharide. The polysaccharide portion is divided into a core portion and the O-specific chain [2,4]. Endotoxin is present in the environment as whole cells, large membrane fragments, or macromolecular aggregates of about one million Daltons [5].

The multiple biological activities associated with endotoxin reside in the lipid A component [6,7]. The biological activity of endotoxin is not dependent on bacterial viability [8]. Human inhalation studies or worker exposure cases involving endotoxin have shown adverse physiological and symptomatic respiratory responses [9,10]. Inhalation of the components of bioaerosols may result in several allergenic-type reactions or lung diseases, such as bronchitis, reactive airway disease, organic dust toxic syndrome (ODTS), and hypersensitivity pneumonitis (HP) [11]. There is debate whether early childhood exposure to endotoxin is positively or negatively associated with the onset or severity of asthma [12,13].

Endotoxin is released into the environment after bacterial cell lysis or during active cell growth [14]. Since bacteria, fungi, and endotoxin may be associated with biosolids, there is an inhalation concern with these bioaerosol components both during and after biosolids land application. Bacteria in biosolids may survive for long periods of time, depending upon the method of

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management and environmental conditions [15,16,17]. Elevated levels (above background) of endotoxin were associated with sites receiving biosolids application with a mechanical slinger [18]. There is no published study regarding airborne endotoxin concentrations during subsequent crop management activities.

The primary objective of this study was to determine if a statistically significant difference existed between the mean upwind and mean downwind airborne concentrations of endotoxin, during grass raking and bailing activities among and within two proximal hayfields (grass), with one of the sites having been previously treated with biosolids as a soil amendment.

MATERIALS AND METHODS

The sampling approach for this study involved two separate sampling events for aerosolized endotoxin. One sampling event occurred at an established hayfield that did not receive any biosolids application (control field). The other sampling event occurred at an established hayfield that had received surface applied biosolids (application field). Anaerobically digested biosolids were similar to Class B biosolids, but were pre-treated with a limited amount of lime to ensure a viable microbial population was present for monitoring purposes. The biosolids contained approximately 10^9 colony forming units per gram-dry weight (CFU gdw^{-1}) total coliforms with a solids content of 22%. The biosolids were applied to the application field within a 100 m diameter area, approximately nine months earlier, and were applied to the surface via a hopper truck with a mechanical slinger at a rate of 10 dry tons per acre.

Each of the two sampling events occurred during separate grass raking and bailing activities (3 dry-days after grass cutting) for approximately 60 minutes. For each sampling event, five upwind (UW) and five downwind (DW) stations (containing two endotoxin sampling devices each) were placed along parallel lines, perpendicular to the prevailing wind direction, as shown in Figure 1. The exact orientation of the zones was determined based upon the weather station wind direction data collected by a Davis Instruments Weather Monitor II weather station (Hayward, California). The samplers were oriented around a 40 m × 40 m monitoring area (within a 40 m × 80 m area that had been cut). For the application site, the monitoring area was within the original 100 m diameter biosolids application area. Five upwind and five downwind sampling stations, each containing two endotoxin samplers, were located 10 m apart from each other within the respective zone. For both the upwind and downwind zones, the distance from the samplers to the corresponding external edge of the biosolids raking and bailing area was 10 m. The bailing machine was operated parallel to the sampler lines. After each pass, the raking and bailing equipment (two distinct farm machine vehicles in series) temporarily left the sampling zone, turned around, and performed another pass in the opposite direction (endotoxin samplers continued to operate during the turn-around). The samples were collected near the personal breathing zone (PBZ) height at 1.5 m above the ground surface by mounting the endotoxin samplers on portable tripods. The weather station was placed 20 m upwind and on the mid-line of the upwind sampling line.

Figure 1. Sampling station orientation for both control and application fields.

The control field (of the same size) contained the same grass cover as the biosolids field. It was located approximately 400–500 m from the biosolids field. To reduce field variation, one initial fertilizer application was applied to the control field within three months of the demonstration, since the application site received nitrogen loading from the applied biosolids.

Prolonged wind direction changes of more than 45 degrees, for longer than two minutes, or any strong wind gust (greater than 15 MPH for at least two minutes), or any precipitation event would immediately halt sample collection activities until they subsided. The bailing equipment was instructed to shut-down at this time as well. If the sampling was shut down for more than 30 continuous minutes, the sampling event would have been considered to be invalid.

Various sampling methods for collecting airborne endotoxin have been used in occupational settings [9, 19]. There are several variables which will possibly influence the endotoxin concentration collected in air samples, such as filter type, extractant fluid, and sample preservation time [20]. The sampling method used involved the use of commercially available 37-mm cassette filter (0.45 µm polycarbonate filters) assemblies (Aerotech Laboratories, Phoenix, AZ), which were manufactured to be endotoxin-free. Two cassettes were mounted to each tripod for each of the sampling stations. The cassettes were separately attached to a vacuum pump (GAST Manufacturing, Benton Harbor, MI). The desired collection flow rate for the cassette assemblies was 4.0 L min^{-1}. Each air collection pump was calibrated pre- and post-sampling in the field immediately before and after each sampling event with a primary standard calibrator (Gillian Model 2 primary standard pump calibrator). Any pre- and post-flow rates that differed by more than 10% were not used in subsequent data calculations.

After each sampling event, the cassettes were capped, placed in plastic bags, and then placed into an iced cooler for transport back to the analytical laboratory within 8 hours. After arrival at the laboratory, cassettes were opened, cassette filters were aseptically removed, and then the filters were placed into a pyrogen free 50 ml centrifuge tube containing 6 ml of pyrogen free water. The 50 ml centrifuge tube was capped and shaken on a mechanical shaker for one hour to complete the extraction procedure for endotoxin.

After the endotoxin was extracted, it was assayed using the Kinetic-QCL method [21]. The field samples were mixed with a substrate, placed in the kinetic reader, and monitored (time) for the appearance of a yellow color. A standard dilution curve ranging from 0.005–50 Endotoxin Units (EU) ml^{-1}, using a control standard endotoxin (CSE), was prepared during the assay. A positive product control spike (PPC) for each dilution was incorporated into the assay to determine recovery (−50%–200%). The solutions were delivered onto a 96-well microplate, which was then inserted into the BioWhittaker Kinetic QCL reader.

Descriptive and inferential statistical methods were used on the collected data. Two approaches were considered for the analysis. In the first approach, the sites were considered independent of each other. Inferential statistics included the parametric student t-test assuming normality of the data distribution. The null hypothesis was that there is no statistically significant difference in airborne endotoxin concentration between the mean upwind zone concentration (10 samples) and mean downwind zone concentration (10 samples) of endotoxin, for each sampling event. The second approach analyzed the data as a completely randomized design with a two-way treatment structure (2 × 2), wind direction (upwind, downwind) and field type (control, biosolids) using ANOVA (PROC GLM Procedure). The *t*-test and ANOVA analyses were performed using SAS [22].

RESULTS AND DISCUSSION

The airborne concentrations of endotoxin at each identified station, and the mean concentrations for each trial, are provided in Table 1. The values in Table 1 were adjusted for concentrations of endotoxin detected in the field and blank samples. Interactive box plots (field type by wind direction) of the endotoxin data is presented in Figure 2, showing a potential outlier sample value for each trial. None of the environmental conditions that would have invalidated the results were encountered, so the sample collection effort was considered valid.

Table 1. Concentration of Airborne Endotoxin at Individual Sampling Stations (EU m^{-3}).

Field	Zone	1	2	3	4	5	6	7	8	9	10	Mean
Control	Upwind	11.3	6.1	4.8	3.1	8.6	9.5	8.7	8.7**	7.9	10.6	7.8
Control	Downwind	11.6	38.1*	14.9**	6.3	9.7	15.6	16.1	7.4	14.2	11.9	14.5
Application	Upwind	7.7	2.9	2.0	2.5	0.3	0.4	0.0	2.5**	1.5	2.0	2.1
Application	Downwind	24.3	27.1	38.2**	28.9	43.5	44.8	42.7	34.2	39.9	38.3	36.0

*Represent potential outlier data.

**Stations greater than 10% difference in pre/post flow calibration.

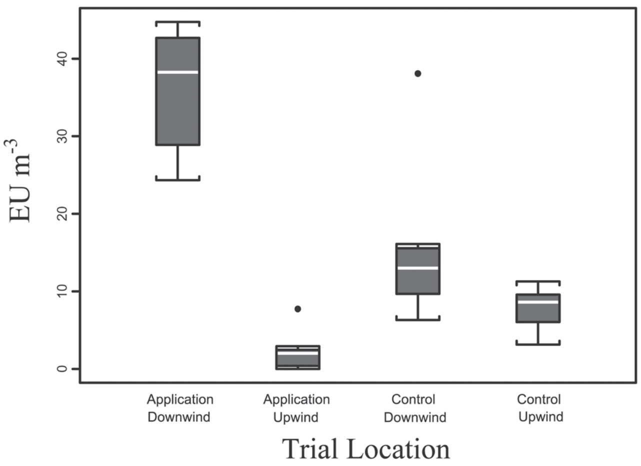

Figure 2. *Boxplots of upwind and downwind endotoxin concentrations for control and biosolids application trials.*

For relative comparisons, the mean airborne endotoxin concentrations observed for each trial were greater than some of the other published background range levels detected in outside environments that vary from 0.0005–0.74 EU m^{-3} in outdoor environments in Germany to 2.0–3.8 EU m^{-3} for outdoor sites in the United States [23,24]. The levels observed were lower than the mean concentration of 114 EU m^{-3} observed within 10 m downwind of a limited number of biosolids application sites in the southwestern United States, but in the range of the mean concentration of 6 EU m^{-3} observed further downwind on these sites [18].

The mean airborne endotoxin concentrations observed for each trial were less than published occupation exposure levels, and less than the large range of other published human exposure criteria for endotoxin. Inhalation of endotoxin in concentrations as low as 4–15 ng m^{-3} (40–150 EU m^{-3}) has been associated with acute and chronic airway inflammation and lung function decrements [23]. The International Committee on Occupational Health (ICOH) Committee on Organic Dust observed toxic pneumonitis at endotoxin levels of 200 ng m^{-3} (2000 EU m^{-3}), systemic reactions at 100 ng m^{-3} (1000 EU m^{-3}), and airway inflammation at 10 ng m^{-3} (100 EU m^{-3}) [25]. Experimental studies of human exposure to cotton dust and field studies suggest an endotoxin threshold for acute airflow obstruction in the range of 45 to 330 EU m^{-3} [26]. The ACGIH has recommended an indoor endotoxin concentration less than 30 to 100 times the ambient (outdoor) concentration [26]. The Dutch Expert Committee on Occupational Standards of the National Health Council has proposed a health-based recommended limit value of 4.5 ng m^{-3} (0.45 EU m^{-3}) over an eight-hour exposure period [27]. The NIOSH Recommended Exposure Limit (REL) for airborne metalworking particulates, that may contain endotoxin from recirculated fluids, is limited to 0.4 mg m^{-3} for thoracic particle mass (0.5 mg m^{-3} total particulate mass) [28].

The mean concentration of downwind airborne endotoxin samples was significantly higher than upwind concentration mean during grass raking and bailing operations within the application trial field where biosolids had previously been applied. The mean upwind and downwind concentrations were not statistically significantly different within the control trial field where biosolids had not previously been applied. It was not determined if the increased concentrations of endotoxin in the downwind air samples at the biosolids application field were due to the biosolids residual or due to plant material grown on the field. Even though the control field did receive fertilizer, the density of plant material appeared to be visually higher on the biosolids application site, though any type of measurement for this property was not performed.

The mean concentration of the downwind air samples at the application site was statistically different than the other three means (upwind control, downwind control, upwind application). However, the downwind control trial mean was higher than the upwind means for both trials (before multiple comparison adjustment) and higher than the upwind application trial site mean even after adjustment (via Scheffe's approach). ANOVA analysis between the two sites (four groups) indicated that there were statistically significant main effects among the sites in wind direction and field type; there was also a statistically significant interaction effect with wind direction and field type. The residuals from the ANOVA are not normal, but also are not skewed, so a transformation (such as the logarithmic) was not useful to normalize the distributions. However, the box plots did identify possible influential outliers. Suspected outliers made no difference in interpretation, and after removing these outliers, the relationship between the endotoxin concentration and the type of field and sampler location is strengthened. After removal of the outliers, the distribution of the residuals becomes normal, indicating that the two outliers contributed to the non-normality of the original data distribution but were not influential. The results apply to this investigation only since there was no treatment replication of each type of field.

CONCLUSIONS

The mean downwind concentration of airborne endotoxin associated with raking and bailing of grass was significantly higher than the mean upwind concentration at a specific hayfield site where biosolids had been applied approximately nine months prior to the sampling event. It was not determined if the increased mean concentration of endotoxin in the downwind air samples at the biosolids application field were due to biosolids residuals or due to plant material grown on the field. In contrast, the mean downwind concentration of airborne endotoxin for the same activities at a close proximity site (control site) that did not receive biosolids application was not significantly higher than the mean upwind concentration.

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Determination of Optimum Polymer Dose for Single and Dual Polymer Conditioning of Wastewater Sludge

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ABSTRACT: Determination of the optimum dose for a dual-polymer system is more difficult than for a single polymer system, and there has been little research in this area. This study investigates rheology as a possible tool for the determination of optimum dose for single and dual polymer conditioning. The rheogram peaks observed after polymer injection were analyzed and correlated to the optimum polymer dose. The results showed that dual polymer conditioning achieved better dewatering at lower conditioner doses, and torque rheology provides a promising tool for the determination of optimum dose and optimum combination of polymers in dual polymer systems.

INTRODUCTION

DEWATERING and thickening of sludge for both water treatment and wastewater treatment applications can represent a significant portion of the operating budget for treatment plants. Chemical conditioners are frequently used to enhance floc formation and increase the dewaterability of the sludge. Determination of the optimum dose of conditioner to add can be difficult, and cannot yet be effectively achieved in-line. Sludge rheology has been suggested as a possible method for optimum dose determination, and is ideal for in-line application [1,2,3,4,5].

Traditionally, jar tests are used to test different polymers and to determine the optimum dose, and it can be difficult and time consuming for treatment plant operators to choose the correct polymer and the correct dose. Capillary suction time and filtration tests are the most common methods by which the polymers are tested. Many other laboratory tests also exist, but most are indirect indicators of dewaterability and can be time consuming if many different samples must be tested [6]. A faster method of determining optimum dewatering is especially important for wastewater sludges, for which the properties and therefore optimum dose can change from day to day.

Sludge rheology has been identified as one possible in-line and real-time method to determine the optimum polymer dose of sludge. Rheology is defined as the deformation of a body under the influence of stress [7]. The degree of deformation, or the ability of the sludge to resist deformation, can provide information about the dewaterability of the sludge. Rheology can measure the degree of the flocculation of the sludge and the ability of the flocs to resist deformation due to stress, which can be an indirect measure of floc strength [7]. Since dewatering devices require certain floc strengths, this in turn can be used as a measure of dewaterability for a specific device.

Langer et al. [2] studied the mechanisms of floc formation in relation to the rheological properties of anaerobically digested wastewater sludge. They observed increasing peaks up to the optimum dose and then decreasing peaks following the optimum dose. They proposed that the increase in viscosity (the upwards part of the peak) was due to the formation of an elastic floc network. The energy dissipation following the peak (the downwards part of the peak) represented the energy released due to the rupture of the network bonds and deformation of the elastic network. Therefore, the peak height is indicative of the amount of energy required to disrupt the elastic floc network with a high peak height indicating a strong floc network which is indicative of good dewaterability.

Örmeci and Abu-Orf defined a term called totalized torque, which referred to the area under a torque time rheogram [4]. They suggested that totalized torque could be used to determine the network strength of an elastic floc network by converting the totalized torque

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to units of work energy. They found that the totalized torque was linearly proportional to the network strength, and so could be used directly for comparison of network strength of samples for a given sludge. They suggested that the network strength could be used to match the strength of the sludge network to a particular dewatering device if the intensity of the shear forces experienced in the particular device were known.

Örmeci et al. tested waste activated, alum, aerobically digested, and anaerobically digested sludge to develop a protocol for measurement of network strength [3]. Good reproducibility was demonstrated with the use of a torque rheometer. They found that the magnitude of the peaks increased with increasing polymer dose and with increasing impeller speeds, and that in the overdosed range the peaks became wide and erratic. They also observed peaks when tap water was used instead of sludge, indicating that the peaks were at least partially due to the turbulence created by switching on the impeller of the rheometer. Abu-Orf and Örmeci [5] studied the ability of network strength measurements to predict dewaterability in laboratory and full-scale experiments. They found a dip in the network strength at the optimum dose. This was explained by the decrease in the drag force due to the flocculation of particles and the release of some of the floc water as free water. The dip in the network strength at the optimum polymer dose was observed both at the laboratory and full-scale tests.

Dual polymer conditioning has been shown to lead to better dewatering or equivalent dewatering at lower doses in many cases [8,9,10,11] and can be accomplished with an inorganic polymer followed by an organic polymer, or with two organic polymers usually of different charges. Dual polymer conditioning is an emerging area of research and offers a tool in designing sludge flocs with the desired strength and characteristics using conditioners sequentially. This would allow fully controlling the floc characteristics to maximize the water release. The mechanisms behind dual polymer conditioning and determination of the optimum dose using dual polymer conditioning are not well-studied or well-understood yet [8]. Dual polymer conditioning is a complicated task since the optimum doses of chemical conditioners are typically determined empirically, and there are many possible combinations when two polymers are used. Therefore, there is a need for an analytical tool that can test a number of combinations for polymer type and dose rapidly. The goal of this research is to evaluate the use of torque rheology as a tool for determining the optimum polymer type and dose in single and dual polymer conditioning.

MATERIALS AND METHODS

Sludge Samples

For tests with mixed primary and secondary sludge, full-scale tests were conducted at the Plum Island Wastewater Treatment Plant in Charleston, South Carolina, U.S.A. For tests involving anaerobically digested sludge, samples were taken from the Robert O. Pickard Environmental Centre in Ottawa, Canada. The anaerobically digested sludge was used for both single and dual polymer tests. To ensure consistent sludge characteristics throughout the tests, the same sludge sample was used for all tests, the tests were completed in a single day, and the sample was well-mixed prior to drawing sub-samples for testing. Solids concentration of the digested sludge remained same between different sampling events.

Polymers

The mixed primary and secondary sludge was tested with Clarifloc C-9545 (SNF Polydyne Inc.), which is a high charge cationic polyacrylamide polymer in emulsion form. The polymer was prepared at a concentration of 0.25%.

FloPolymer CA 4600 (SNF Canada), which is currently used at the Robert O. Pickard Environmental Centre, was used to condition the anaerobically digested sludge. CA 4600 is a high charge density, high molecular weight, dry cationic polymer, and was prepared by mixing for 1 hour with a magnetic bar mixer followed by 10 seconds with an electric hand mixer and let to sit for an additional hour before use. The polymer solution was prepared at a concentration of 0.5%.

For dual polymer conditioning, anaerobically digested wastewater sludge was conditioned with a combination of an inorganic conditioner (alum) and a cationic organic polymer (FloPolymer CA 4600). The inorganic conditioner was prepared in a concentration of 20%, and the FloPolymer CA 4600 was prepared in a concentration of 0.5%.

Single-polymer Conditioning

For single polymer conditioning, the optimum polymer dose was determined using CST (capillary suction time) and filtration results taken alongside rheological measurements. The CST and filtration results were then compared with the rheological measurements to investigate the use of rheology as an indicator for the optimum polymer dose.

Dual-polymer Conditioning

The design of the dual-polymer conditioning experiments required knowledge of the optimum dose prior to the start of the experiments. Therefore, prior to dual-chemical conditioning, the optimum dose of each of the conditioner was determined using the CST measurements and peak heights as described below. The doses of each one of the inorganic and organic conditioners were then varied in fractions of the optimum dose. Rheological characteristics of the samples were measured and the optimum dose combination was determined. CST and centrifuge tests were completed at this time to confirm the optimum combination and to study the rheograms characteristics for conditioning optimisation in a dual-conditioner system. From this optimum combination, the dose of the inorganic conditioner was kept constant and that of the organic conditioner varied to further optimise the dose. Results were again compared to CST and centrifuge tests. This dose was then compared with the dose of the organic polymer alone.

Rheological Measurements

Two different rheological methods were used for single and dual polymer conditioning as explained below.

Single-polymer Conditioning

A torque rheometer (Floccky Tester, Koei Industries Inc.) was used for all rheological measurements. The Floccky Tester has variable impeller speeds, and can be programmed in different steps. It uses 200 mL samples. The optimum speed for the sludge was determined each day, by varying the impeller speed in 10-rpm increments between 250 rpm and 350 rpm. The optimum impeller speed was taken as the speed, which created the biggest increase in the rheogram when the speed was changed. The Floccky tester was set to rotate at a speed of 420 rpm for 10 seconds and then at 300 rpm for 40 seconds. This was followed by polymer addition and 2 more minutes of mixing at 300 rpm. These mixing speeds were chosen to simulate the total mixing and shear introduced at treatment plants. The initial high mixing speed was provided to ensure that the sample was well-mixed prior to sample injection, and the second mixing at 300 rpm for 40 seconds provided a background reading before the injection of the polymer. Mixing regimes generally vary for sludge conditioned at different treatment plants and shear that sludge is exposed to during conditioning is a combination of shear from mixing and shear encountered in pipes and pumping. Increased mixing will lead to increased polymer demand, however some shear is required to ensure that the polymer is well mixed and to promote floc formation [12]. Injecting the polymer once the impeller had been started eliminated interference due to the motor starting as observed by Örmeci et al. [3]. The polymer was inserted directly into the Floccky Tester's reservoir. Two replicates were taken for each polymer dose.

Dual-polymer Conditioning

The Floccky tester was set to rotate at a speed of 420 rpm for 10 seconds, then 300 rpm for 40 seconds. After this point, the inorganic conditioner was inserted. The mixing was continued at 300 rpm for 1 minute. The organic polymer was then inserted, and the mixing continued at the optimum speed for 2 minutes. This mixing regime was chosen so that the peaks produced by each of the two conditioners would be clearly visible and distinct. Two replicates were taken for each polymer dose.

Dewaterability Measurements

Single-polymer Conditioning

Capillary suction time (CST) and filtration tests were used for dewaterability measurements. The CST tests were conducted by placing 7 mL of conditioned sludge in the CST reservoir. The CST device then measured the time required for water to drain from the conditioned sludge onto a piece of paper and between two water sensors on the paper. The dose producing the sample with the lowest CST was taken as the optimum polymer dose. The filtration tests were completed by applying vacuum filtration to the entire 200 mL sample from the rheometer for 10 minutes. Following filtration, the filter cake was divided into two separate samples and the percent solids of each were measured and averaged. The filtrate volume was also measured. The dose producing the highest quantity of filtrate and the sludge cake with the highest solids content was taken as the optimum dose. The polymer was mixed into the sludge samples using the Floccky tester impeller to ensure uniformity between conditioned samples. The rheological measurement steps were followed as outlined above. All dewaterability measurements were completed in duplicate.

Dual-polymer Conditioning

CST tests were used for dewaterability measurements according to the *Standard Methods* [13]. The CST measurements were used to predict dewaterability with filtration. Centrifuge tests were also completed to predict dewaterability with centrifugation. For single-polymer conditioning and full-scale testing, centrifuge testing was not carried out. Centrifuge testing was added for dual-polymer conditioning because one of the advantages of dual-polymer conditioning is that it provides greater flexibility to design flocs for different types of dewatering devices. CST and filtration are both measures of filterability. The centrifuge testing provided an additional indication of centrifuge dewaterability. 50 mL samples were placed in 50 mL centrifuge tubes and were centrifuged for 1 min. at 4,000 rpm. The cake heights in the graduated centrifuge tubes and turbidity of the samples were recorded. All dewaterability measurements were completed in duplicate.

RESULTS AND DISCUSSION

Single Polymer Conditioning for Mixed Primary and Secondary Sludge

Three polymers were tested with mixed primary and secondary sludge from the Plumb Island Wastewater Treatment Plant in South Carolina. The results shown here are for Clarifloc C9545. Similar results were obtained with other polymers tested. Tests were completed to determine whether or not rheological measurements could be used to predict the optimum dose for mixed primary and secondary sludge. Results from CST and filtration tests indicated that the optimum dose for the sludge was around 5–6% polymer-to-sludge ratio as the unit used at the treatment plant (Figure 1). Based on the solids concentration of sludge, 1% corresponded to 1 g polymer/kg DS. Figure 2 shows that the peak heights increase by increasing the polymer dose until the optimum dose and then decrease following the optimum dose, providing a clear indication of the optimum dose.

Single Polymer Conditioning for Anaerobically Digested Sludge

During the second phase of experiments, anaerobically digested sludge from the Robert O. Pickard Environmental Centre was tested with FloPolymer CA 4600. FloPolymer CA 4600 is a high charge density, high molecular weight, cationic polymer.

The optimum dose determined through CST, filtration, and cake solids analysis tests was 10.5 g polymer/kg DS (Figure 3). The rheograms are illustrated in Figure 4. The peak height of the rheograms increased up to the optimum dose (10.5 g polymer/kg solids) and then decreased after the optimum dose (11 g polymer/kg sol-

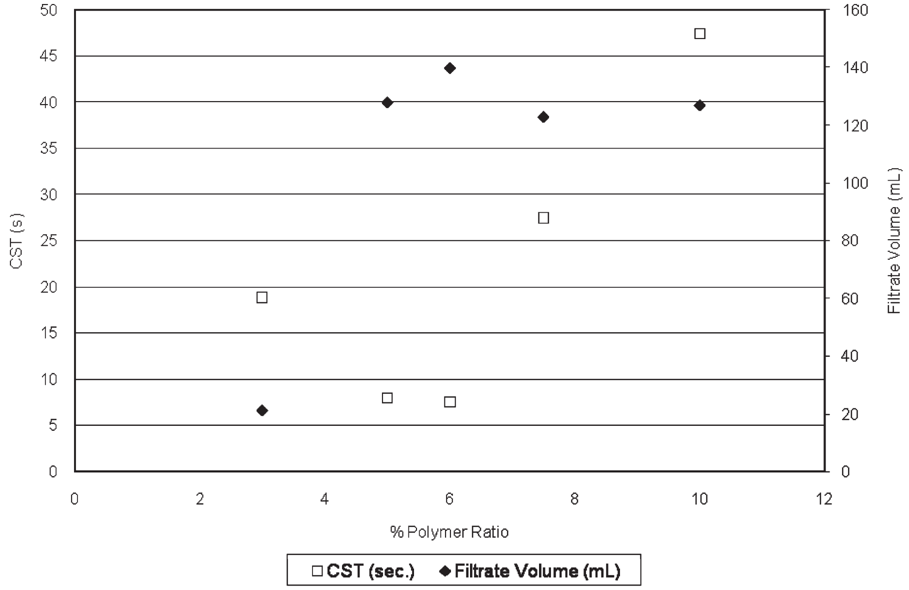

Figure 1. CST and filtration results for mixed primary and secondary sludge with Clarifloc C9545.

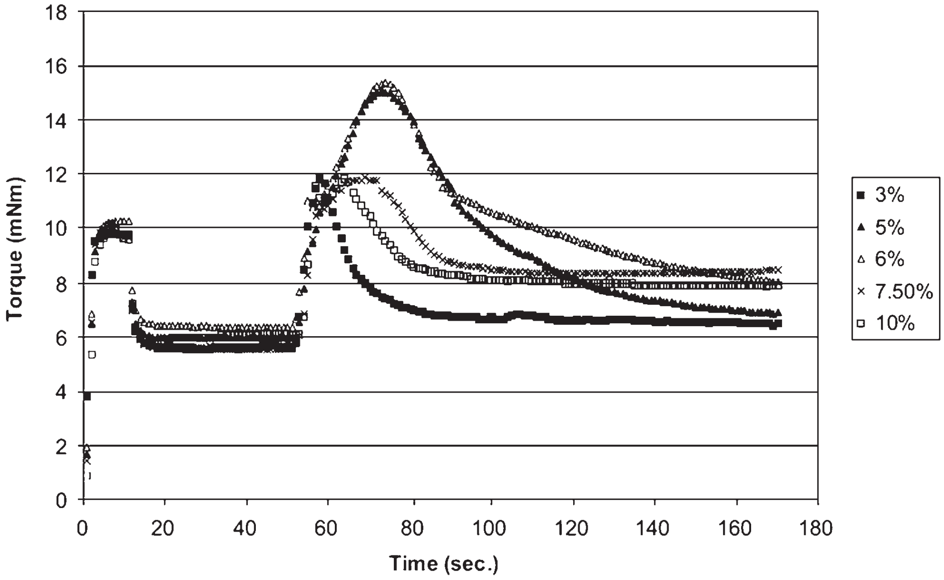

Figure 2. Rheograms for mixed primary and secondary sludge with Clarifloc C9545.

ids) as previously observed (Figure 2). At higher polymer doses (12 g polymer/kg solids), however, the peaks started to increase again due to the resistance caused by the excess polymer in the sample. Previous research conducted using several low and high molecular weight and cationic charge polymers reported that the optimum dose was observed at or around the peak height [14].

Dual Polymer Conditioning for Anaerobically Digested Sludge

Results from the single polymer conditioning tests indicated that the rheograms and peak heights can possibly be used for the optimisation of dual polymer conditioning. For the third phase of experiments, anaerobically digested sludge was taken from the Robert O. Pickard Environmental Centre and conditioned with a combination of alum and FloPolymer CA 4600.

Use of Peak Heights to Determine the Optimum Dose for Dual Polymer Systems

This set of experiments was performed to determine whether or not the rheogram peak heights could be used to determine the optimum dose for dual polymer systems. First, the optimum dose was determined for each of alum and FloPolymer CA 4600 alone (800 g alum/kg DS and 14 g polymer/ kg DS, respectively). The per-

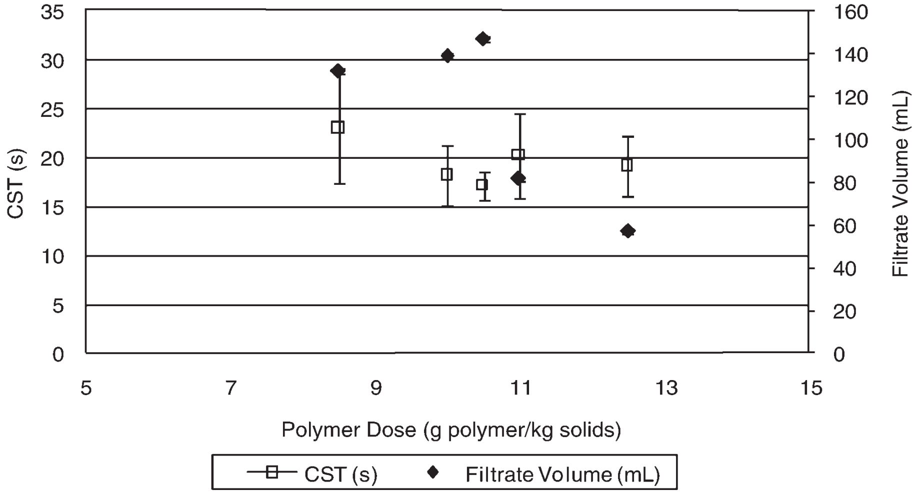

Figure 3. CST and filtration results for anaerobically digested sludge with Flopolymer CA 4600.

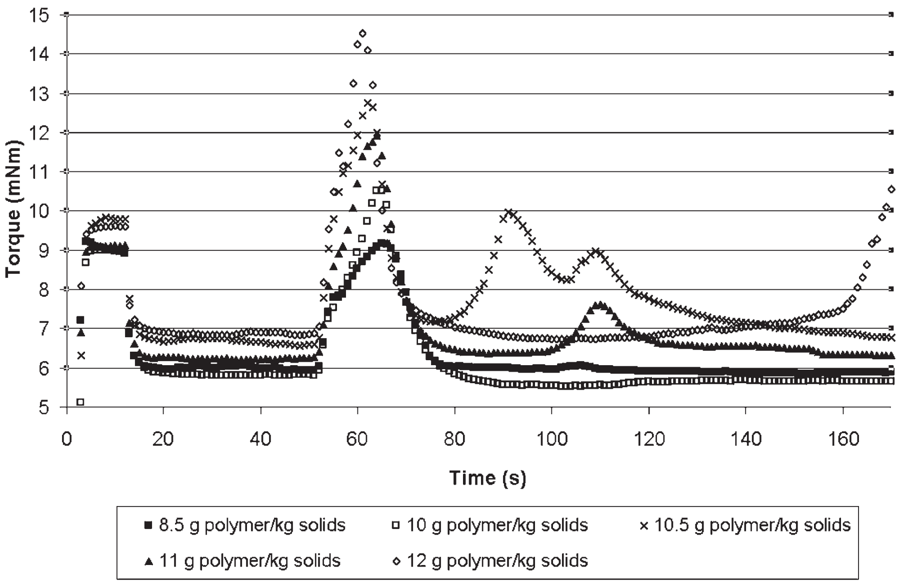

Figure 4. *Rheograms for anaerobically digested sludge with Flopolymer CA 4600.*

centages of the optimum doses of each of these were varied to determine the optimum ratio of inorganic to organic conditioner. Doses of 25% of the optimum dose of the alum and 75% of the optimum dose of the FloPolymer CA 4600; 50% of the optimum dose of the alum and 50% of the optimum dose of the FloPolymer CA 4600; and 25% of the optimum dose of the alum and 75% of the optimum dose of FloPolymer CA 4600 were tested (Table 1). The best of these three doses was then determined. Since this is a dual-conditioner system however, there are actually an infinite number of possible combinations of doses. It would not be possible to test all possible combinations of doses. Therefore, from this optimum ratio of conditioners, the amount of inorganic conditioner was kept constant while adjusting the amount of the organic polymer to further optimise the system (Table 2).

Results from dewaterability tests are presented in Table 1 and show the average of two replicates. CST and centrifuge tests were used to determine which of the ratios led to the best dewaterability. For centrifugation tests, samples were centrifuged at 4,000 RPM for 1 minute in standard 50 mL centrifuge tubes. The cake depth (mL) in the centrifuge tube and the turbidity of the centrate was measured after centrifugation. The CST results were in the same range for all of the doses tested. However, the centrate turbidity was much lower for the dose of 25% of the optimum dose of alum followed by 75% of the optimum dose of the organic polymer. This can be expected because the floc strength required for centrifugation is generally higher than that required for CST or filtration tests [15].Therefore, the sludge conditioned at all of the doses might have adequate strength to survive the CST test but additional strength is required for the centrifuge tests. This dose was therefore taken as the optimum dose.

Further Optimisation of the Dual-Conditioner System

The dose of the inorganic conditioner (alum) was then maintained at 25% of the optimum dose (taken from the optimum ratio determined from Table 1). The dose of the organic polymer (FloPolymer CA 4600) was then varied to further optimise the system. Table 2

Table 1. Dewaterability for Dual-polymer Conditioning.

DOSE (alum/polymer)	CST (s)	Cake Height After Centrifugation (mL)	Turbidity After Centrifugation (NTU)
25%/75%	54.8	15.3	46.9
50%/50%	54.2	19.4	86.3
75%/25%	53.1	15.3	165.7

Table 2. Dewaterability for Dual-polymer Conditioning with 25% of the Optimum Dose of Alum.

DOSE (alum/polymer)	CST (s)	Cake Height After Centrifugation (mL)	Turbidity After Centrifugation (NTU)
25%/25%	55.5	14.4	131.3
25%/50%	37.0	15.3	36.2
25%/75%	54.8	14.1	48.6
25%/100%	109.1	15.0	55.0

below shows the average of two replicates of the dewaterability data recorded. The lowest turbidity (36.2 NTU) and also the lowest CST (37 s) occurred at a dose of 25% of the optimum dose of the alum and 50% of the optimum dose of the FloPolymer CA 4600. This was compared to the optimum dose of FloPolymer CA 4600 (14 g polymer/ kg DS), which led to an average CST of 52.2 seconds and a turbidity of 40.2 NTU. Better dewaterability was achieved with a much lower dose of FloPolymer CA 4600 when dual conditioning was used.

Rheograms were produced for each of the four doses in Table 2. The rheograms shown in Figure 5 are averages of two and error bars are not shown for clarity. The peaks formed after alum addition (at 50 s) were at the same height because the dose of the alum was the same for all four samples. The next peaks show the effect of the addition of increasing doses of FloPolymer CA 4600 (at 110 s). The peak heights increased to 25% of the optimum dose of the inorganic conditioner followed by 50% of the optimum dose of the organic polymer, remained relatively constant for a dose of 25% of the optimum dose of the inorganic conditioner followed by 75% of the optimum dose of the organic conditioner, and then started increasing again in the overdosed range. It was previously reported that based on the chemical interaction of polymers with sludge, after the optimum dose is reached the peaks may decrease in size or stay relatively same until the polymer dose is very high [13]. Maintaining the same peak height with addition of additional polymer is indicative of the optimum dose because further polymer addition confers minimal additional floc strength. In the overdose range, an increase in the peak height is observed and the peaks eventually get very large and erratic due to the unmixed polymer in the samples.

CONCLUSIONS

The use of the peaks of torque-time rheograms was shown to predict the optimum dose for both mixed primary and secondary, and anaerobically digested wastewater sludge. The peak heights either increased to the optimum dose and then decreased following the optimum dose or increased to the optimum dose and then remained relatively constant. The highest peak was observed at or around the optimum polymer dose. In the overdose range, the peaks started to increase again due to the excess polymer and increased viscosity of samples.

The use of the peak heights to determine the optimum dose for dual-chemical conditioning was also studied. The results from the preliminary tests show that dual polymer conditioning help to achieve the same level or better dewatering at significantly lower polymer doses. Considering the cost of the polymers and their effect on the environment, dual polymer conditioning offers im-

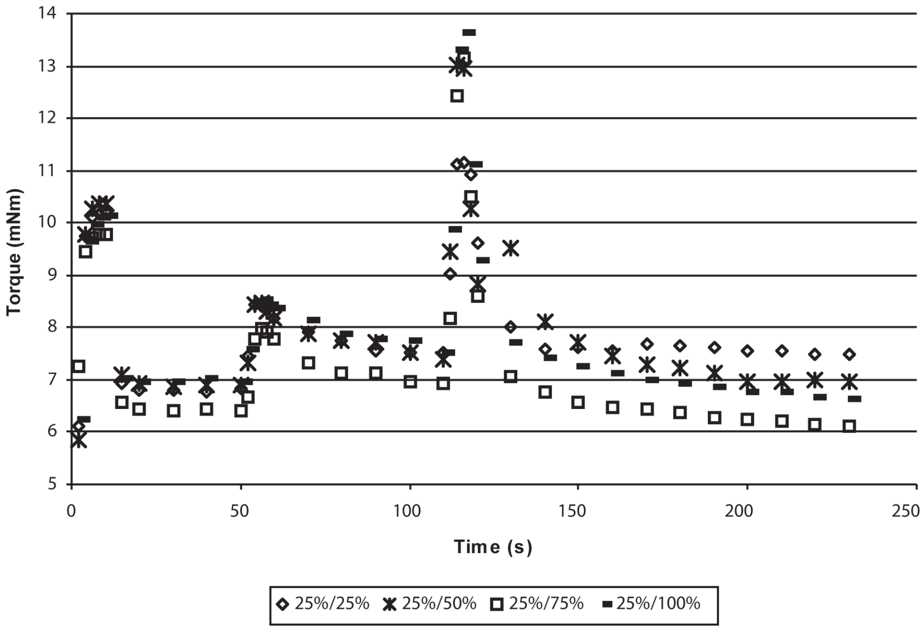

Figure 5. Rheograms for dual-polymer conditioning of anaerobically digested sludge with alum and Flopolymer 4600.

portant advantages. Little research is available on dual-chemical conditioning in the literature so far, and rheology offers a tool to advance this area of research. Results presented herein indicate that torque rheology can be a useful tool in determining the most effective polymer and dose combination by studying the formation of peaks after the addition of polymers. However, more research is required to fully understand the interaction of multiple polymers with sludge, and how that information can be used to design flocs that yield the best dewaterability.

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Adsorption of Hexavalent Chromium from Aqueous Solutions by Compost: Adsorption Equilibrium and Kinetics

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ABSTRACT: In this research, adsorption of Cr(VI) on municipal compost has been studied. The main objectives are (1) investigating chromium adsorption from aqueous solutions by compost, (2) studying the influence of contact time, pH and initial chromium concentration on adsorption process and (3) determining appropriate adsorption isotherm and kinetics parameters of Cr(VI) adsorption. The results showed that a reasonable adsorption of chromium obtained after 180 minutes. Higher chromium Adsorption observed in lower pHs, and maximum chromium removal (74.63%) obtained in pH = 2. The adsorption of chromium by compost decreased at the higher initial chromium concentration. The adsorption process follows Freundlich isotherm equation (R^2 = 0.976) and the pseudo-second order kinetic model.

INTRODUCTION

ENVIRONMENTAL contamination by heavy metals is a widespread problem, with sources of pollution arising from industrial activities. One of the most important heavy metals in aqueous solutions is chromium. Chromium commonly found in liquid wastes in two oxidation states, Cr^{+3} and Cr^{+6}. Cr(VI) poses a serious risk to the environment and endangers public health as well as the environment. It is highly toxic, extremely mobile in groundwater at wide ranges of pH and according to National Toxicology Program (NTP, US), there is sufficient evidence for carcinogenicity of Cr(VI) [1]. Chromium (VI) generated from industrial processes such as electroplating, wood preservation, metal finishing, textile industry, pigment, chrome plating and leather tanning [1, 2]. The untreated effluent from electroplating industry contains approximately 100mg/L Cr(VI) [3]. It is essential that industries treat their effluents to reduce the Cr(VI) to acceptable levels.

A number of treatment methods for the removal of metal ions from aqueous solutions have been reported, mainly reduction, ion exchange, electrodialysis, electrochemical precipitation, evaporation, solvent extraction, reverse osmosis and chemical precipitation [4]. Most of these methods suffer from drawbacks such as high capital and operational costs or the disposal of the residual metal sludge. Efficient and environment friendly methods are thus needed to be developed to reduce heavy metal content [5].

As an alternative to conventional methods, recently, the method of the removal of heavy metal contaminants by means of natural adsorbents has been focused on. A variety of materials have been tried as adsorbents for Cr(VI) and a number of studies have been reported using adsorbents like cactus, olive cake, wool, charcoal, pine needles [6], Soya cake [7], rubber tyres, sawdust [8], fly ash [9], rice husk based activated carbon [10], wheat bran [11] and etc.

In most of other researches, removal of chromium(VI) from dilute polluted solutions has been studied. In this paper adsorption process in high chromium concentrations was investigated. In addition a new and economical adsorbent, municipal waste compost from a compost plant in Iran (GILAN compost plant), for removal of chromium(VI) was used. The effect of contact time, pH and concentration of chromium on percentage of adsorption were been investigated. In addition, adsorption isotherms were studied and also a kinetic study was carried out to elucidate the equilibrium adsorption kinetics behavior.

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MATERIAL AND METHODS

Adsorbent

The compost grinded and particle sizes between 297 and 595 μm was obtained by passing the milled material through standard steel sieves and then used for experiments without any physical or chemical treatments.

Batch Adsorption Studies

Batch experiments were conducted to investigate the parametric effects of different factors on Cr(VI) adsorption. Chromium samples were prepared by dissolving a known quantity of potassium dichromate ($K_2Cr_2O_7$), supplied by Merck company, in double-distilled water and used as a stock solution and diluted to the required initial concentration (range: 50 to 300 mg/L). Fresh dilutions were used for each step of the study. The initial pH of the solutions was adjusted by using either 0.1 N NaOH or 0.1 N H_2SO_4. 100 mL of Cr(VI) solution of known concentration and initial pH, with a required amount of adsorbent was agitated at a speed of 250 rpm at 25°C for a specified period of contact time. Then, the solution was filtered through filter paper. The Cr(VI) ions concentrations were determined in the filtrate using DR/4000U spectrophotometer by colorimetric techniques according to the standard method No. 3500-Cr B [12]. The amount of Cr(VI) adsorbed in mg/g at time t was computed by using the following equation:

$$q_t = (C_0 - C_t) \cdot V / W \tag{1}$$

where C_0, and C_t are the Cr(VI) concentrations in mg/L initially and at a given time t, respectively. V is the volume of the Cr(VI) solutions in mL and W is the weight of adsorbent in g. The percentage of removed Cr(VI) ions (R_{em} %) in solution was calculated using Equation (2):

$$R_{em}(\%) = (C_0 - C_t) / C_0 \times 100 \tag{2}$$

The effects of contact time, t (5, 10, 15, 20, 30, 45, 60, 120, 240 and 300 min), initial chromium concentration, C_0 (50, 100, 150, 200, 250 and 300 mg/L) and initial pH of solution (2, 3, 5, 7, 9 and 11) was investigated by varying any one of the parameters and keeping the other parameters constant. To increase the accuracy of the data, each experiment was repeated 3 times.

Adsorption Isotherms

Adsorption isotherm studies were carried out with different adsorbent doses ranging from 1 to 6 g/100mL in pH of 3, while maintaining the initial chromium concentration at 200mg/L. Langmuir, Freundlich and BET models were applied to the adsorption isotherm and adsorption parameters and correlation coefficients were also calculated from the adsorption isotherm data. The isotherms were summarized in Table 1.

Adsorption Kinetics

The study of adsorption kinetics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. The kinetics of Cr(VI) adsorption on the compost was analysed using pseudo first-order [13], pseudo second-order [14], Elovich [15,16] and intraparticle diffusion [17,18] kinetic models. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R^2). A relatively high R^2 value indicates

Table 1. Isotherm Equations.

Isotherm Name	Isotherm Equation	Parameters
Langmuir	$q_e = \dfrac{\theta \cdot b \cdot C_e}{1 + b \cdot C_e}$	C_e = the equilibrium concentration(mg/L) q_e = the amount adsorbed per amount of adsorbent at the equilibrium(mg/g) θ (mg/g) and b (L/mg) = the Langmuir constants related to the maximum sorption capacity and energy of adsorption, respectively.
Freundlich	$q_e = KC_e^{1/n}$	K(mg/g)= an indicator of the adsorption capacity $1/n$ (mg/L) = adsorption intensity q_m = the amount of solute adsorbed in forming a complete monolayer (mg/g)
BET	$q_e = \dfrac{q_m K_b C_e}{(C_s - C_e)\left[1 + (K_b - 1)\dfrac{C_e}{C_s}\right]}$	K_b = a constant expressive of the energy of interaction with the surface C_s = saturation concentration of solute (mg/L)

that the model successfully describes the kinetics of Cr(VI) adsorption.

The pseudo first-order equation: The pseudo first-order equation [13] is generally expressed as follows:

$$dq_t / dt = k_1(q_e - q_t) \tag{3}$$

where q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg/g) and k_1 is the rate constant of pseudo first-order adsorption (min^{-1}). After integration and applying boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of Equation (3) becomes:

$$\log(q_e - q_t) = \log q_e - k_1 / 2.303 \times t \tag{4}$$

The values of log ($q_e - q_t$) were linearly correlated with t. The plot of log ($q_e - q_t$) vs. t should give a linear relationship from which k_1 and q_e can be determined from the slope and intercept of the plot, respectively.

The pseudo second-order equation: The pseudo second-order adsorption kinetic rate equation is expressed as [14]:

$$dq_t / dt = k_2(q_e - q_t)^2 \tag{5}$$

where k_2 is the rate constant of pseudo second-order adsorption (g/mg.min). For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of Equation (5) becomes:

$$1/(q_e - q_t) = 1/q_e + kt \tag{6}$$

This is the integrated rate law for a pseudo second-order reaction. Equation (6) can be rearranged to obtain Equation (7), which has a linear form:

$$t / q_t = 1/(k_2 \cdot q_e^2) + 1/q_e(t) \tag{7}$$

If the initial adsorption rate, h (mg/g.min) is $h = k_2\ q_e^2$ then Equation (7) becomes:

$$t / q_t = 1/h + 1/q_e(t) \tag{8}$$

The plot of (t/q_t) and t of Equation (8) should give a linear relationship from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively.

The Elovich equation: The Elovich model equation is generally expressed as [15,16]:

$$dq_t / dt = \alpha \exp(-\beta q_t) \tag{9}$$

where α is the initial adsorption rate (mg/g.min), β is the desorption constant (g/mg) during any one experiment. To simplify the Elovich equation, Chien and Clayton assumed $\alpha\beta t >> t$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ Equation (8) becomes [15]:

$$q_t = 1/\beta \times Ln(\alpha\beta) + 1/\beta \times Ln(t) \tag{10}$$

If Cr(VI) adsorption fits the Elovich model, a plot of q_t vs. ln(t) should yield a linear relationship with a slope of (1/β) and an intercept of (1/β) ln(αβ).

The intraparticle diffusion model: The intraparticle diffusion model is expressed as [17,18]:

$$R = k_{id}(t)^a \tag{11}$$

A linearised form of the equation is followed by:

$$\log R = \log k_{id} + a \log(t) \tag{12}$$

where R is the percent Cr(VI) adsorbed, t is the contact time (h), a is the gradient of linear plots, k_{id} is the intraparticle diffusion rate constant (h^{-1}), a depicts the adsorption mechanism, ki_d may be taken as a rate factor, i.e., percent Cr(VI) adsorbed per unit time. The values of ki_d were calculated from the slope of the plot of log R (%) vs. log (t) and the R^2 values led to the conclusion that the intraparticle diffusion process is the rate limiting step. Higher values of k_{id} illustrate an enhancement in the rate of adsorption, whereas larger k_{id} values illustrate a better adsorption mechanism, which is related to an improved bonding between Cr(VI) ions and the adsorbent particles.

RESULTS AND DISCUSSION

Effect of Contact Time

A plot of percentage adsorption versus adsorption time is shown in Figure 1. It is obvious that the increase in contact time from 5 to 300 min increased the removal percent of Cr(VI). It revealed that the rate of uptake was rapid in the early stages but gradually decreased and became constant when equilibrium was reached. A further increase in contact time had a negligible effect on the removal percent. The nature of the adsorbent and its compactness affected the time needed to reach equilibrium. Obtained results showed that a contact time of 180 minutes enables a reasonable removal of chromium.

Effect of pH

The pH of the system exerts profound influence on the adsorptive uptake of adsorbate molecule presumably due to its influence on the surface properties of the adsorbent [19]. The variations in removal of Cr(VI) from solution at various pHs are shown in Figure 2.

From Figure 2, it is evident that the maximum removal of chromium (7.46 mg/g) was observed at pH of 2. Chromium exists mostly in two oxidation states which are Cr(VI) and Cr(III) and the stability of these forms is dependent on the pH of the system [20]. It is well known that the dominant form of Cr(VI) at pH 2 is $HCrO_4^-$, which indicates that this is the active species adsorbed by the adsorbents [21]. Increasing the pH will shift the concentration of $HCrO_4^-$ to other forms, CrO_4^{2-} and $Cr_2O_7^{2-}$ [5]. The $HCrO_4^-$ species are most easily exchanged with OH^- ions at active surfaces of adsorbent under acidic conditions according to equation 13 (Ar is adsorbent surface) [22]:

$$ArOH + HCrO_4^- + H^+ \rightarrow ArHCrO_4 + H_2O \quad (13)$$

In the other hand, changing in surface potential of compost in lower pHs is possible and increasing of adsorption capacity can be related to variation of surface potential of applied adsorbent.

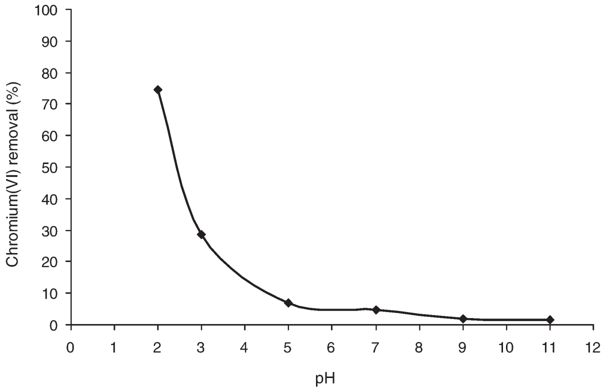

Figure 2. *Effect of pH on adsorption of Cr(VI) by compost (contact time = 3h; adsorbent dose = 2 gr/100 mL; initial Cr conc. = 200ppm; agitation speed = 250 rpm; t = 25±1°C).*

Effect of Initial Chromium Concentration

The effect of Cr(VI) concentration on the adsorption by compost was investigated by varying the initial Cr(VI) concentration (50, 100, 150, 200, 250 and 300 mg/L) at initial pH of 3 for 3 *h* contact time (Figure 3).

Cr(VI) removal percent by compost reduced with increase in Cr(VI) concentration. Cr(VI) uptake was reduced from 74% (1.85 mg/g) to 23.17% (3.48 mg/g) as concentration was increased from 50 to 300 mg/L. Though the removal percent was decreased with increase in Cr(VI) concentration, but the actual amount of Cr(VI) adsorbed per unit mass of the adsorbent was increased. Several researches found similar results with other adsorbents, as an example removal of chromium by activated carbons prepared from Casurina equisatifolia leaves [23].

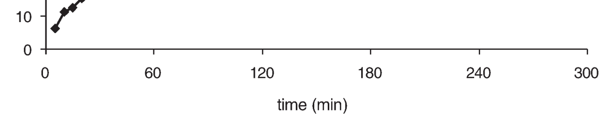

Figure 1. *Effect of contact time on Cr(VI) adsorption by compost (adsorbent dose = 2 gr/100 ml; pH = 3; iitial Cr conc. = 200 mg/l; t = 25±1°C; agitation speed = 250 rpm).*

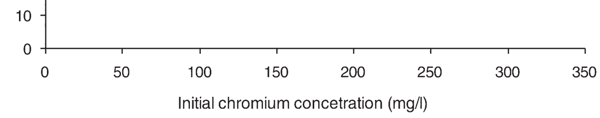

Figure 3. *Effect of initial conc. on adsorption of Cr(VI) by compost (t=25±1°C; adsorbent dose = 2 gr/100 mL; pH = 3; agitation speed=250 rpm; contact time = 3h).*

Table 2. The Quasi- Adsorption Isotherm Constants for the Adsorption of Cr(VI) on Compost.

	Langmuir			Freundlich			BET		
Parameters	**θ (mg/g)**	***b* (1/mg)**	**R^2**	***n* (mg/l)**	**K_F (mg/g)**	**R^2**	**q_m (mg/g)**	**K_b**	**R^2**
	5.97	0.012	0.941	1.965	0.312	0.976	0.953	–3.81	0.914

Adsorption Isotherms

The linearised Langmuir isotherm allows the calculation of adsorption capacities and the Langmuir constants and is equated by the following equation.

$$1/q_e = 1/(b\cdot\theta\cdot C_e) + 1/\theta \qquad (14)$$

The linear plot of $1/q_e$ vs. $1/C_e$ shows that the correlation coefficient (R^2) is 0.941 and θ was determined to be 5.97 mg/g.

The linearised forms of Freundlich adsorption isotherm was used to evaluate the sorption data and is represented as:

$$Lnq_e = LnK_F + 1/nLnC_e \qquad (15)$$

K_F and n were calculated from the slope and intercept of the Freundlich plot. The constants were found to be $K_F = 0.312$ and $n = 1.965$. n values between 1 and 10 represent beneficial adsorption [24].

Linear form of BET isotherm can be expressed by:

$$C_e/(C_s - C_e)q = 1/(K_b\cdot q_m) + (K_b - 1)/(K_b\cdot q_m)\times C_e/C_s \qquad (16)$$

The values of K_b and q_m were calculated from the linear plot of $C_e/(C_s - C_e)\cdot q$ vs. C_e/C_s. True adsorption isotherms are based on equilibrium data. As reasonable contact time is used in this study, the calculated data can be considered as the quasi-adsorption isotherm which is presented in Table 2.

According to linear regression coefficients (R^2), the Freundlich isotherm model defined best the adsorption data of Cr(VI) on compost at 25 ± 1°C. Negative value for the BET isotherm constant indicates the inadequacy of the isotherm model to explain the adsorption process for compost, since this constant is indicative of the surface binding energy [25].

Adsorption Kinetics

The calculated kinetics constants are presented in Table 3. From Table 3 and the data obtained separately for each of the kinetic models, it can be concluded that the process of Cr(VI) adsorption on compost is best fitted to pseudo second-order kinetic model, since the R^2 value matched very well.

Comparison of Adsorption Capacity of Compost with Other Adsorbents

Direct comparison of compost with other adsorbent materials is difficult, owing to the different applied experimental conditions. In the present study, compost has been compared with other adsorbents based on their maximum sorptive capacity for Cr(VI) and shown in Table 4. It can be observed that a pH of 2 was found to be an optimum in nearly all cases whatever the method of activation is. Further, it can also be seen that the compost compares well with the other adsorbents listed in Table 4.

Beech sawdust, olive oil industry waste and treated sawdust of Indian Rosewood are adsorbents that exhibited higher adsorption capacity. This could be primarily due to the initial carbon content, activation process as well as the pore development due to the basic morphology of the raw material [26]. Hence, compost can be considered to be viable adsorbent for the removal of Cr(VI) from aqueous solutions.

Table 3. The Adsorption Kinetic Model Rate Constants for Compost at Different Contact Times.

Kinetics models	**Kinetics Parameters**	**R^2**
Pseudo- first-order	q_e (mg/g) = 8.74 k_1 (min^{-1}) = 0.002	0.951
Pseudo- second-order	q_e(mg/g) = 5.49, k_2 (g/mg.min) = 0.003, h(g/mg.min) = 0.1	0.986
Elovich model	α(mg/g.min) = 0.264, β(g/mg) = 0.95	0.972
Intraparticle diffusion	k_{id} = 24.64, A = 0.472	0.983

Table 4. Comparison of Adsorption Capacities of Cr(VI) with Other Adsorbents.

Adsorbents	Adsorption Capacity (mg/g)	pH	C_0 (mg/l)	Reference
Modified steam exploded wheat straw	6.78	1–3	25	[27]
Peanut husk	7	3	50	[28]
Activated rice husk carbon	0.8	2	10	[29]
Olive cake	5.89	2	100	[6]
Pine needle	5.36	2	100	[6]
Wool	8.66	2	100	[6]
Cactus	2.48	2	100	[6]
Coconut tree sawdust	3.46	3	20	[30]
Olive oil industry waste	12.15	2	200	[31]
Beech sawdust	16.1	1	200	[32]
Treated sawdust of Indian Rosewood	10	3	100	[33]
Compost	7.46	2	200	Present study

CONCLUSION

The capacity of compost in adsorption of Cr(VI) has been investigated, and the experimental data demonstrate that compost is an effective adsorbents of chromium (VI) in solutions. The following results can be made from this study:

- Results showed that reasonable adsorption of chromium obtained after 180 minutes and at this time, the chromium removal percent was 41.38.
- Among all selected parameters, pH of solution had the more effect on chromium removal. The results showed that the highest adsorption of chromium (74.63%) was happened at pH of 2.
- It was observed that the removal percent increased at the lower initial chromium concentration.
- The Freundlich adsorption isotherm was the best model for the chromium adsorption on compost with correlation coefficient (R^2) of 0.976. The amount of n and K_F are found to be 1.965 (mg/l) and 0.312(mg/g), respectively for this isotherms.
- The kinetic analysis showed that the adsorption of Cr(VI) ions could be described well with the pseudo-second-order kinetic model with the rate constant of 0.003 g/mg.min at 25 ± 1°C

Based on the results of this research, compost can be considered as an effective, available and natural adsorbent for removal of chromium from aqueous solutions in the range of 50 to 300 mg/l. Obtained results of this study can be used for some industrial wastewaters with high Cr(VI) concentrations in the above-mentioned range. Spent adsorbent at the end of treatment, can be buried or incinerated, but the important point in this research is using a waste material for removing of Cr(VI). But in fact, pollution is transferred from liquid to solid phase and more investigations are needed for the fate of the residual adsorbent.

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Evaluation of Trace Element Concentrations in Groundwater and Classification of Endemic Disease Regions using Multilayer Perceptron Neural Network

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ABSTRACT: In this study, trace elements were measured in the groundwater in Azerbaijan and the level of the fluoride was assessed. The endemic diseases in the regions of Azerbaijan were investigated by using these data. A Multilayer Perceptron Neural Network (MLPNN) was used to classify the regions with or without an endemic disease. MLPNN employing a backprobagation training algorithm was used to predict the presence or the absence of endemic disease potential in the regions. At the end of the classification process, percentages of the towns with or without an endemic disease were calculated as 100% and 68.75% respectively. Total classification accuracy of MLPNN was determined as 75%. Therefore, we can conclude that a MLPNN is one of the most promising methods for classification of regions with endemic diseases, based on the trace elements in the groundwater.

INTRODUCTION

TRACE elements are found at very low levels in an organism's structure. Trace elements can cause toxic effects in high concentrations as well as serious health problems in low concentrations [1].

Natural concentrations of trace elements in water and soil changes according to geologyl, geomorphology, climate, and more. Since the middle of the 20th century and still growing, development of technology and increasing populations have and are still causing ever increasing adverse effects related to antropogenic pollution sources and contamination of our natural resources like water for example. Main factors responsible for creating an increase of trace elements found in natural waters are listed as follows [2]:

- Use of municipal and industrial wastewater for watering
- Use of fertilizer and pesticide for agriculture
- Storage of treatment sludge
- Emission of chimney gases
- Wastes from aviation

Trace elements from these pollutant resources make their way into surface waters, soils, and groundwater primarily from precipitation. One of the trace elements found in groundwater is fluoride. Concentrations of fluoride in groundwater are affected by geological features, climatic conditions, and existence of other regional ions [3]. Fluoride is found in low concentrations in natural waters. Carbonate stones, volcanic stones, and more are responsible for high fluoride concentrations in water. Salty waters as well as glass, aluminum, pesticide, and fertilizer production industries may create an increase in fluoride concentration [4].

Fluoride concentrations in drinking water are important for bone and tooth health. Optimum concentration is 1 mg/l and a maximum of 1.5 mg/l is permitted in regulations. Fluoride is an electronegative ion and causes a high concentration of fluorosis by connecting calcium in bones and in teeth. Higher concentrations might be related to cancer events. Health problems for various concentrations are listed below [5]:

- < 0.5 mg/l tooth sensitivity
- 0.5–1.5 mg/l beneficial for tooth health
- 1.5–4.0 mg/l dental fluorosis diseases in dental and skeleton system
- > 10.0 mg/l fluorosis diseases breaking bones.

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High fluoride concentrations are found in the groundwaters of India, China, Sri Lanka, Holland, Mexico, North America, and South America. According to a study in India, a maximum fluorine concentration was measured at 5.2 mg/l for 62 million people, including 6 million children all of whom have suffered fluorosis due to consumption of water having high fluoride concentrations [6].

There are many studies regarding classification of geological areas and their correlation with endemic based diseases. Here, we have applied an artificial model of the brain known as Artificial Neural Network (ANN) or simply Neural Networks (NNs) for classification purposes. Neural Networks have many applications [7–9]. Generally, the ANN is a cellular information processing system designed and developed on the basis of the perceived notion of the human brain and its neural system. Influence of neurons changes by altering effectiveness of synapses and therefore learning occurs. Also, note that rapid and efficient propagation of electrical and chemical impulses is a distinctive characteristic of neurons and the nervous system in general. Neurons operate collectively and simultaneously for all data and inputs that perform as summing and nonlinear mapping junctions. In some cases, they can be considered as threshold units that fire when total input exceeds a certain bias level. Neurons usually operate in parallel and are configured in regular architectures. They are often organized in layers, and feedback connections both within the layer and toward adjacent layers are allowed. Strength of each connection is expressed by a numerical value called ‘a weight’ which can be updated. Also, they are characterized by their time domain behavior which is often referred as dynamics. In general, the neuron could be modeled as a nonlinear activated function of which the total potential inputs into synaptic weights are applied.

MATERIALS AND METHODS

Groundwater samples were obtained from 10 different regions of Azerbaijan, including 65 towns, based on the possibility of endemic disease occurrence, climate, geography, soil structure, and water features. Measurements were made in 10 different parts of the Küba-Haçmaz and Şeki-Zakatala regions where endemic diseases were recorded like endemic goiter for example and in the Apşeron Peninsula which has no recorded instance of any endemic disease.

A total of 461 samples including surface water, soil, and groundwater samples were collected and 7 microelements were detected. Regions in which diseases did/did not occur were compared. Samples were kept in plastic vessels. Colorimetric measurements were carried out according to Standard Methods (15) by the Water Hygiene and Sanitation of National Medical Prophylactic Research Institute. Iodine (I) was determined to be present from tests using free iodine transformation by bromide addition in acidic pH. Fluorine (F) was analyzed following sodium fluoride transformation. During analyzes, chlorine, sulfate, nitrate, and phosphate parameters were determined to control interferences. Liquid samples were analyzed by colorimetric methods after a distillation process to detect cases of high interference by these parameters. Chemicals and solutions were prepared according to Standard Methods for all other parameters. Copper (Cu), cobalt (Co), manganese (Mn), zinc (Zn) and molybdenum (Mo) concentrations were determined via ICP-OES (Optical Emission Spectroscopy) (PERKIN ELMER; OPTIMA 2100DV).

Artificial Neural Network

An Artificial Neural Network (ANN) is an information processing paradigm that is inspired by our understanding of how biological nervous systems such as the brain process information. ANN are massivly parallel systems and highly connected structures. Artificial neural networks consist of a great number of neurons. These neurons are connected with each other. In ANN, neurons usually operate in parallel and are configured in regular architectures. They are often organized in layers and in feedback connections both within the

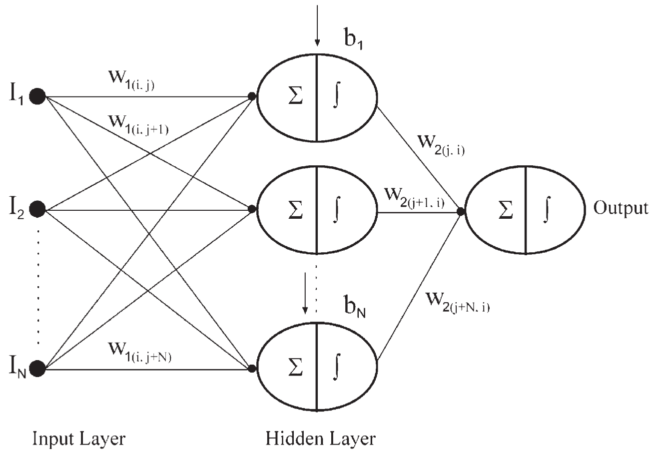

Figure 1. MLP neural network structure.

Table 1. Training Stage Weight Adjustments for Input Layer.

Weight Coefficients [8 × 8]								Bias
0.924169	1.183972	0.183691	–0.04567	–0.36164	0.360912	0.018763	0.038557	–3.06133
–0.15571	1.300952	0.173196	0.153311	0.002597	0.079086	0.174543	0.233566	–1.21194
0.318981	1.617396	–0.04864	–0.0743	0.563421	0.080354	0.083203	0.049027	–2.77671
–0.73516	1.007358	–0.34684	0.237968	–0.66147	0.975921	–0.36151	–0.40924	–0.77216
–0.39913	–0.584	–0.18646	–0.1368	0.448902	0.735736	0.086704	0.188459	–1.76486
–0.46108	0.267434	–0.41928	0.173931	–0.3417	0.054443	0.621825	0.004219	–3.52577
–0.13095	0.640483	–0.11838	–0.28358	0.162998	–0.19273	–0.10082	0.142626	–1.86583
–0.0832	–1.57007	–0.07385	0.282541	–0.34851	0.095528	–0.08457	–0.55679	0.654179

layer and towards adjacent layers also. Strength of each connection is called a weight which may be altered to measure algorithm sensitivity to this parameter change. They are also characterized by their time domain behavior, often referred to as dynamics. Feedforward multilayered neural network is commonly used for modeling physical systems. An important class of feedforward neural networks is Multilayer perceptron neural network (MLPNN). MLPNN is a nonparametric technique for performing a wide variety of detection and estimation tasks [8,9,11]. A MLPNN includes an input layer, an output neuron layer, and one or more hidden layers. Figure 1 displays the MLPNN architecture.

MLPNN Employing Backpropagation Training Algorithm

The MLPNN learning algorithm is very important. In most applications of MLPNN, weights are determined by a backprobagation algorithm since backprobagation algorithms have rapid execution and have been widely used in pattern classification problems. During the training stage, weights are successively adjusted based on a set of inputs and a set of desired output targets. The weights are displayed in Table 1–3. MLPNN employing backprobataion training algorithm was used to predict the presence or absence of endemic diseases in regions of Azerbaijan.

In MLPNN, a unit in the output layer determines its activity by following a two step procedure:

First, it computes the total weighted input x_j, using the formula:

$$X_j = \sum_i y_i W_{ij}$$

where y_i is the activity level of the j^{th} unit in the previous

Table 2. Training Stage Weight Adjustments for First Layer.

Weight Coefficients [20 × 8]								Bias
0.849139	–1.59552	–0.11631	–0.15604	0.517688	0.568389	–0.18823	–0.51785	–2.05075
0.096522	–0.34401	1.283149	0.959105	–0.72625	0.325536	–0.29551	–0.95117	1.800877
0.630355	–0.15091	0.409446	–1.29872	0.338106	–1.01819	–0.53934	0.882961	–1.81172
0.837131	–0.13525	–0.43248	0.950652	–0.02622	–0.68686	0.888702	1.072483	–1.35552
–1.27091	–0.02692	0.090024	0.974901	–0.00574	0.216731	1.078783	–0.88289	0.913789
1.202187	0.309911	0.385524	–0.07664	0.062305	0.694096	1.211821	–0.50994	–0.96511
0.648223	–0.80234	–0.51378	0.367238	0.738013	0.809888	0.16243	0.96776	–0.7891
0.115893	0.878913	0.640475	0.923093	–0.25348	–0.0434	–1.13162	–0.84031	–0.46013
–0.67672	0.519427	1.115819	0.351045	–0.19317	1.093957	0.318392	0.984632	0.224027
1.017393	0.983932	0.646366	–0.80046	–0.76791	0.024191	0.783957	0.871762	0.029635
–0.13671	0.374926	–1.08467	–0.04061	0.129427	0.235959	1.534921	0.65742	–0.37063
0.589418	0.417377	0.817551	–0.82658	–0.58071	0.856322	–0.73297	–0.76316	0.324093
–0.59369	–1.32978	0.140168	–0.00607	–0.59866	–1.17164	0.907737	–0.32647	–0.6326
1.417283	–0.51841	0.95231	–0.41607	0.033596	–0.17224	0.017561	–0.89999	0.76685
–1.04616	0.352619	–0.95278	–0.22592	0.263816	–0.0189	0.886524	1.014324	–0.80835
0.679729	0.372629	–0.14539	0.503863	–0.8572	1.187984	1.043091	0.331521	1.189467
–0.51069	–1.17224	–0.21274	–0.83093	–0.83133	0.152917	–0.5183	–0.49895	–1.54019
1.102943	–1.1401	–0.86547	–0.62569	–0.30864	0.019243	–0.21754	–0.18714	1.686096
–0.45927	–0.618	0.918826	–0.02833	0.039376	–0.08102	–1.10772	0.816602	–1.71232
0.306032	–0.35941	0.925806	–0.68094	–0.92687	–1.07553	1.18552	–0.52039	1.886474

Table 3. Training Stage Weight Adjustments for Second Layer.

Weights [1 × 20]	Bias
−0.931836428	−0.3835
−0.096354913	
−0.743233258	
−0.217622769	
−0.644526996	
0.242437099	
−0.48703742	
0.317824708	
−0.311516437	
1.016231976	
−0.275891224	
0.09919798	
1.048848293	
−0.338454896	
0.469453098	
−0.536252081	
−0.338498948	
0.013325265	
0.288196468	
−0.52489832	

layer and W_{ij} is the weight of the connection between the i^{th} and the j^{th} unit.

Second, the unit calculates activity, y_j, using some function of the total weighted input. Typically we use the sigmoid function:

$$y_j = \frac{1}{1 + e^{-x_j}}$$

Once activities from all output units have been determined, the network computes the error E, which is defined by the expression:

$$E = \frac{1}{2}\sum_i (y_i - d_i)^2$$

where y_i is the activity level of the j^{th} unit in the top layer and d_i is the desired output of the j^{th} unit.

Each weight is adjusted by adding an increment ΔW_{ij} to it. ΔW_{ij} is selected to reduce E. Back propagation algorithm [10] is then invoked to adjust all the weights in the network and gives the change $\Delta W_{ij}(k)$ in the weight on the connection between neurons i and j at iteration k as;

$$\Delta W_{ij}(k) = -\alpha \frac{\partial E}{\partial W_{ij}(k)} + \mu \Delta W_{ij}(k-1)$$

where, μ is momentum coefficient, α is learning coefficient, and $\Delta W_{ij}(k-1)$ is the weight change in the immediately preceeding iteration. α and μ were selected empirically, 0.5 and 0.3 respectively, for this study.

RESULTS

In this study, we used MLPNN employing the backpropagation learning algorithm for a pattern classification problem. We have applied MLPNN to predict presence or absence of endemic diseases in regions of Azerbaijan. Data from 45 of 65 subjects were used for training and the rest for testing. Outputs are represented between 0 (endemic region) and 1 (not endemic region). We aim to classify the regions with 8 inputs; sample number, fluoride, iodine, manganese, cobalt, copper, zinc, and molybdenum.

Displayed in Figure 2 is the training mean square error (MSE) curve of the MLPNN in 856 epochs and shows performance of MLPNN. As seen from the figure, MSE value reduces dramatically till 10^{-9} in 100 epochs. MSE value reaches 10^{-12} in 856 epochs. This is a very short time for the training phase. After a training phase, the testing portion of the MLPNN was conducted. During the testing phase, 20 subjects were used and are displayed in Table 4. The confusion matrix classification results for this network are provided in Table 5.

All subjects having an endemic disease potential were classified correctly; however 5 normal subjects were classified incorrectly by the network as subjects having an endemic disease potential. On the other hand, normal subjects and those having endemic disease potential were classified correctly as 68.75% and 100%, respectively. Total classification accuracy of MLPNN is determined as 75%.

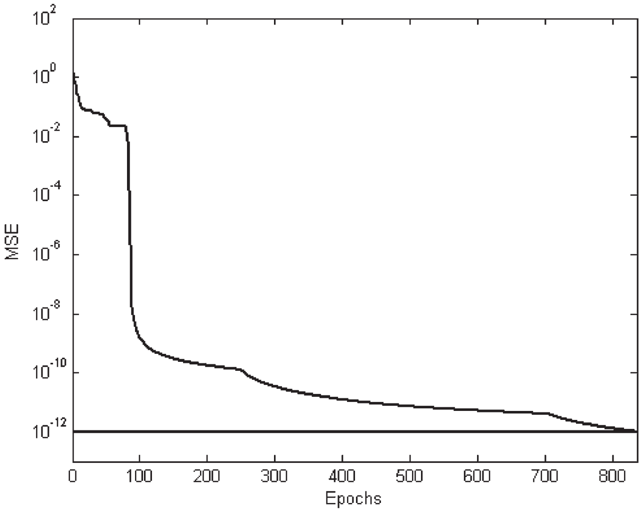

Figure 2. *Training MSE curve of MLP neural network.*

Table 4. Samples used for Testing the MLPNN.

		Inputs							Output
	Sample Number	Fluoride	Iyodine	Manganese	Cobalt	Copper	Zinc	Molybdenum	Endemic Disease
Regions		mg/L	μg/L						
I. Region of Lenkaran									
1. Lenkaran	25	0.63	62.5	32.5	2.00	3.75	88.0	11.5	Absence
2. Astara	8	0.35	11.4	24.5	2.00	5.00	12.6	4.00	Absence
3. Celilabad	20	0.59	29.8	37.5	4.75	50.5	12.6	10.8	Absence
II. Region of Küba-Haçmaz									
1. Kusar	4	0.36	5.12	32.5	7.50	36.6	8.75	11.0	Precense
2. Haçmaz	4	0.17	1.16	32.5	0.75	6.50	7.00	1.75	Precense
III. Region of Kür-Aras									
1. Salyan	2	0.60	12.53	35.0	1.00	15.0	5.00	13.3	Absence
2. Kürdemir	3	0.35	9.20	35.0	1.75	8.00	10.0	3.50	Absence
3. Saatli	8	0.60	8.26	27.0	2.00	67.5	37.0	27.0	Absence
IV. Region of Şeki-Zagatala									
1. Kah	3	0.23	5.05	45.0	1.00	3.75	4.00	3.50	Precense
V. Gence-Kazah Bölgesi									
1. Gence	17	0.35	4.17	27.5	10.9	70.5	17.0	5.32	Precense
VI. Region of Apşeron									
1. Bilge	10	1.20	199	28.5	1.55	3.00	20.0	4.50	Absence
2. Hövsan	6	1.40	32.4	34.5	1.75	22.0	30.0	20.0	Absence
3. Şuvelan	12	3.20	30.5	30.5	3.40	41.7	18.0	19.5	Absence
4. Merdekan	10	2.90	53.5	53.5	2.00	10.5	115	3.50	Absence
5. Bine	30	2.10	32.5	32.5	2.50	24.3	126	18.5	Absence
6. Zire	15	3.03	24.0	24.0	5.25	28.2	37.0	10.5	Absence
7. Buzovna	12	2.48	42.06	42.06	3.50	8.30	32.8	17.0	Absence
8. Türken	5	2.05	29.6	29.6	2.50	6.65	66.3	14.5	Absence
9. Nevhanı	3	0.68	32.7	32.7	3.40	6.25	11.5	6.00	Absence
10. Maştaha	2	1.40	53.4	53.4	2.25	5.00	77.5	21.1	Absence
11. Şağan	2	3.30	19.4	19.4	20.0	4.23	10.0	12.5	Absence
12. North hydroelectric power plant	14	3.60	16.9	16.9	1.25	3.15	17.5	24.0	Absence
13. Artyom	6	2.85	21.3	21.3	10.5	5.6	23.8	9.8	Absence
Total	**221**								

CONCLUSION

Trace element concentrations in a region are related to the regional geology and its environments. However, due to increasing and unregulated industry practices and increasing population growth, natural resources have become and are becoming more and more polluted like the increase of trace elements in our water supply or water bodies for example. Our study demonstrate that fluoride concentrations are present in amounts higher than in the drinking water standard TS 226 [1]. Fluoride concentration exceeded the 2.4 mg/l limit. Tooth fluorosis diseases are seen in these regions. Therefore, water should be subject to a first treatment to decrease fluoride concentrations. Chemical sedimentation, ion change, and reverse osmosis can be used to accomplish this for example. Cupper, zinc, and manganese do not exceed limit values. For other elements like iodine, cobalt, and molybdenum, there isn't a set regulatory limit.

Table 5. Confusion Matrix Results.

	Predicted		
Actual	Positive (endemic	Negative (normal)	Correctly Predicted (%)
Positive (endemic)	4	0	100
Negative (normal)	5	11	68.75

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Impact of Bioreactor Landfill Leachate Quality on As, Cd, Pb and Zn Leaching from Mine Residues

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ABSTRACT: In this paper, leaching of heavy metals (As, Cd, Pb and Zn) from two different metal rich wastes, namely mineral processing waste (W2) and waste derived fertilizer (W1) in batch extraction tests (TCLP, SPLP and deionized water) is presented. In addition, extraction tests using bioreactor MSW landfill leachates were also performed and results compared to the standardized tests. It was observed that the W1 (commercially available as Ironite) failed the TCLP tests, with Pb extract concentration (7.3 mg/L) higher than the TC limit. On the other hand, the W2 passed the TCLP test. Significant differences in arsenic leaching from W1 in the SPLP and deionized water extraction tests, compared to the TCLP tests reiterated the fact that TCLP underestimated the leachability of arsenic. Batch extraction tests using MSW landfill leachates were also performed. Landfill leachates were sampled from conventional (dry-tomb) and bioreactor facultative landfills. Leaching results indicated that TCLP overestimated Cd and Pb leaching in landfills. A comparison of all the batch extraction tests showed that leaching of heavy metals showed high pH dependency, with increased leaching in the acidic region (SPLP and deionized water tests). It was also observed that the dissolved organic carbon content and the volatile fatty acid content regulated the amount of heavy metals leached.

INTRODUCTION

THE disposal of large amounts of metal-rich wastes is a growing environmental problem due to the leachability of toxic metals such as arsenic and lead amongst others. These wastes which also include mine and mineral processing wastes (MPW) have a very high mineral content and can be an excellent source of secondary micronutrients (U.S Environmental Protection Agency, 2002; U.S Environmental Protection Agency, 2003). In an effort to supplement plant growth, mine and mineral processing wastes are currently being recycled for the generation of waste derived fertilizers (WDF) to supplement plant growth. This process, while providing excellent fertilizer materials, also reduces waste mismanagement and unnecessary treatment procedures. However, leaching of arsenic, lead and zinc from the parent material can occur resulting in contamination of the neighboring eco-systems (Dubey and Townsend, 2004; Al-Abed et al., 2006; Al-Abed et al., 2007). Recently, a study was performed to determine the leaching potential of different W2s (Dubey and Townsend, 2004; Al-Abed et al., 2006; Al-Abed et al., 2007). The results showed that leaching of most metals in the Toxicity Characteristic Leaching Procedure (TCLP) was well below the regulated toxicity characteristic (TC) limit. Further investigation on the impact of pH on the leaching characteristics of the solid waste using deionized water showed that metal leaching was higher at low pH values, progressively decreasing to non-detectable concentrations at higher pH values (pH of 5–9). While, the materials used to produce W1s are currently exempt from hazardous waste regulations under Resource Conservation and Recovery Act (RCRA) (U.S Environmental Protection Agency, 2002; U.S Environmental Protection Agency, 2003; U.S Environmental Protection Agency, 2004), the presence of arsenic, lead and selenium in large quantities can pose a risk to human health and the environment. In a recent study, it was concluded that lead and arsenic release from a certain WDF (commercially available fertilizer called "Ironite") exceeded the TC limit (5 mg/L) for both metals (Dubey and Townsend, 2004). The same

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study also concluded that pH was the controlling factor in metal release from WDF. Similar to the leaching characteristic of MPW, the release of arsenic and lead was maximum at acidic pH (pH < 5) and alkaline pH (pH > 10), and minimal (less than 0.1 mg/L) in the pH range that was typical of MSW landfill leachate. A comparison between TCLP (pH = 4.93), Synthetic Precipitation Leaching Procedure (SPLP) (pH = 4.20) and constant pH tests using deionized water showed that metal leaching from WDF was 10-fold lower in the pH-stat tests compared to TCLP, and 5-fold lower compared to SPLP.

Municipal solid waste landfills (MSWLFs) serve as the ultimate receptors of residential, commercial and industrial wastes, amounting to more than 100 millions tons annually in the United State alone (U.S Environmental Protection Agency, 1984). In order to achieve faster waste stabilization, the US Environmental Protection Agency (USEPA) started evaluating the operation of landfills as bioreactors to determine their viability as a solid waste management technique and assess their environmental impact. The USEPA's initiative on bioreactor landfills stemmed from studies that reported enhanced waste degradation and landfill gas generation in these types of reactors (Pohland, 1975; Reinhart and Townsend, 1998; Reinhart et al., 2002). Thus, under operation as a bioreactor, the leachate produced in the MSWLFs is recirculated, thereby redistributing nutrients and microorganisms through the MSW which in turn degrades and stabilizes the solid waste much faster compared to the conventional landfills. In addition, under bioreactor conditions, the pH of the leachate is buffered, inhibitory toxins diluted, and the methanogens are recycled (Pohland, 1993; Pohland and Kim, 2000; Mehta et al., 2002; Luo et al., 2004). This results in accelerated degradation on the organic content in solid wastes and enhanced sequestration of the inorganic elements. However, changes in pH, transition between aerobic and anaerobic redox environments and dissolved organic/ fatty acid content may result in changes in the mobility of metals via oxidation, complexation or precipitation (Kjeldsen et al., 2002; Halim et al., 2003; Halim et al., 2004). Compared to conventional subtitle D landfills, bioreactor landfills may initially generate more ideal leachate in terms of the aforementioned factors, which may result in enhanced metal release from the solid wastes.

Even though, the potential for energy generation, reduction in leachate toxicity and cost saving efficiencies of landfill bioreactors have been extensively documented, limited data on the impact of leachate quality on metal leaching are available. The main purpose of this research presented here is to examine the impact of bioreactor leachates on metal leaching. Two specific sources of wastes, rich in metal content, were selected for the study. One of them was a waste-derived commercially available fertilizer (WDF, W1), available at any home departmental store, while the other was a mineral processing waste (MPW, W2) from an abandoned mine site. Both of these wastes are currently exempt from RCRA hazardous waste regulations. In addition, the leaching of specific heavy metals such as As, Cd, Pb and Zn using deionized water (pH = 3), TCLP fluid (acetic acid/acetate buffer), SPLP (sulfuric acid/nitric acid) and LLs was compared. Examining the applicability of W1 and W2 for municipal landfill disposal or evaluate accuracy of the standardized TCLP and SPLP tests was not an objective of this study. Rather, we set out to specifically to compare results on metal leaching from extraction studies using bioreactor landfill leachates (LLs) and comparing them to those from conventional "dry-tomb" landfill leachates.

EXPERIMENTAL

Chemicals

All chemicals used were of reagent grade. Trace metal grade sodium hydroxide (NaOH), nitric acid (HNO_3), sulfuric acid (H_2SO_4) and glacial acetic acid (CH_3COOH) were purchased from Fisher Scientific, PA. Distilled deionized (DI) water (Millipore Systems, MA, 18 MΩ) was used as the extractants in batch tests and as controls. Reagent blanks for all extractants were analyzed in parallel with the samples and found to have negligible levels of metals in all cases.

Solid Waste

The W1 and W2 samples were homogenized and sieved through 9.5 mm and 2 mm sieves for TCLP and deionized water (DI) tests, respectively (U.S Environmental Protection Agency, 1997). Acid extraction of metals using EPA method 3051 (microwave digestion in nitric acid) was performed to determine the total metal content in each of the two wastes. The National Institute for Standards and Technology (NIST) soil reference standard (NIST 2710) was used for calculating recoveries of the metals in all digestions.

Landfill Leachate

MSW landfill leachate used in the extractions presented here was collected from a landfill site (Outer Loop Recycling and Disposal Facility (OLDRF), Louisville, Jefferson County, Kentucky) as a part of on-going collaborative research between U.S. Environmental Protection Agency (EPA) Office of Research and Development (ORD) and Waste Management Inc (WM) under a 5-year Cooperative Research and Development Agreement (CRADA). The landfill comprise of seven individual and separate landfill units, designated Units 1 through 7. Units 1–3 and unit 6 were inactive landfill units that are not receiving waste. Unit 4 is permitted as a construction and demolition debris (C&D) landfill, and is currently active, while units 5 and 7 are permitted subtitle D landfills. The leachates for this study were collected from units 5 and 7. Six leachate samples were collected on two different sampling times (March and October of 2004). As a part of the study, the characteristics of the leachate was analyzed and summarized in Table 1. Two samples were collected from two conventional dry tomb subtitle D landfill cells (LL1), which is approximately 3–4 years old. These two samples were used as controls so as to compare leaching characteristics of wastes in conventional and bioreactor landfill. Two of the leachate samples (LL2) were collected from a retrofit bioreactor landfill cells where leachate and groundwater are re-circulated back into the landfill. Solid waste in these cells is approximately 7 years old. The last two samples (LL3) were collected from two retrofit aerobic-anaerobic bioreactor landfill cells where leachates as well as various industrial liquids were re-circulated into the landfill (LL3). The range of values reported in Table 1 were those observed in samples collected from duplicate cells of each type.

Leaching Tests

All batch leaching tests were conducted following EPA's protocols, as stipulated in the SW-846 TCLP methodology (U.S Environmental Protection Agency, 1997). All extractions were conducted at 20:1 liquid-to-solid ratio with a contact time of 18 ± 2 hours. The filtration method also followed SW 846 protocol-method 1311. The only variable in the extraction procedures was the extraction solution used in the test as outlined in Table 2. All extractions were done in triplicate. Blanks were used as controls for each extraction experiments.

Table 1. Landfill Leachate Characteristics.

Characteristic	Landfill Leachate 1[a]		Landfill Leachate 2[a]		Landfill Leachate 3[a]	
	Control conventional landfill/3–4 years old		Facultative Landfill Bioreactor/5–7 years old		Aerobic-Anaerobic Landfill Bioreactor/2 years old	
Landfill Type	Mar-04	Oct-04	Mar-04	Oct-04	Mar-04	Oct-04
pH	7.4–7.5	NA	7.2	7.1	7.2–7.8	7.5–7.6
Temp[c]	21.6–23.6	NA	21.8–23.7	28.3–28.6	27.3–37.2	35.7–38.7
COD (mg/L)	1590–2170	1970–3020	1090–1550	745–1090	4500–6020	3800–4700
BOD/COD	0.05–0.1	0.10–0.11	0.02–0.04	0.05–0.06	0.09–0.36	0.07–0.08
TDS (mg/L)	5060–7220	NA	4730–3050	NA	6760–6790	NA
Ammonia (g/L)	1000–1270	1900–1940	778–1380	422–660	1180–1520	1250–1650
Conductivity (mhos/cm)	9.7–11.6	NA	8.6–12.4	8.8–12.6	10.5–13.9	13.6–7.5
Organic Acid (mg/L)						
DOC	408–483	591–993	318–476	179–332	1870–2170	1200–1350
Butyric Acid	1.0[b]–7.6	1.0	1.0	1.0	7.4–232.0	1.0
Acetic Acid	1.8–42.0	3.0–3.9	1.0[b]	1.0	174.0–1028.0	39.0–55.0
Propionic Acid	1.0[b]–18.0	1.0	1.0	1.0	82.0–664.0	2.3–3.1
Anions (mg/L						
Chloride	1360–2710	NA	1930–1950	NA	1230–2280	NA
Sulfate	20[b]–50	NA	20–196	NA	50–100	NA

[a] Range of values observed in leachate from duplicate landill cells.
[b] Method detection limit.
[c] Temperature at time of sampling.
NA: Not analyzed.

Table 2. Summary of Leaching Test Procedures.

Leaching Experiment	TCLP	SPLP	DI	LL1	LL2	LL3
Extraction Fluid	Acetic acid/acetate buffer	Dilute sulfuric/nitric acid (60:40)	Deionized water	Landfill lechate 1	Landfill lechate 2	Landfill lechate 3
pH	4.9 ± 0.05	4.2 ± 0.05	6.9 ± 0.05	7.4 ± 0.05	7.2 ± 0.05	7.5 ± 0.05
Extraction Period (hours)	18 ± 2	18 ± 2	18 ± 2	18 ± 2	18 ± 2	18 ± 2
Liquid-solid Ratio	20:01	20:01	20:01	20:01	20:01	20:01

Instrumentation and Analysis

Before analysis solid and solid samples were digested following EPA method 3050B and 6010B respectively. After digestion, metal concentrations were analyzed using an Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, IRIS Intrepid, Thermo Electron Corporation, CA). The filtered extracts and blank samples were analyzed in triplicates.

RESULTS AND DISCUSSION

Landfill Leachate Characteristics

Table 1 presents the leachate characteristics, sampled from three different landfills, operated in duplicate, and two separate sampling times. The data in Table 1 provides the range of values for the parameters observed in leachate from duplicate cells. From the data, the pH of the leachate was almost constant and close to neutral. Historically, there may not be a difference between the leachate pH measured in conventional and in bioreactor landfills. The pH of the leachate ranges between 4.7 and 8.8 for conventional landfills (Kjeldsen et al., 2002) and between 5.4 and 8.6 in bioreactor landfills (Reinhart et al., 2002). The aerobic-anaerobic bioreactor leachate (LL3) had higher BOD/COD ratios indicative of the acid forming phase. Similar characteristics were observed for the leachates from the conventional landfill (LL2). Increased amounts of acetic, butyric and propionic acid were also present in LL3 samples; thereby enhanced metal-organic acid complexation can be expected with the LL3 leachate. It can be observed that the age of the landfills had a large influence on the VFA content. The aerobic-anaerobic reactor was only 2 years old, while the conventional and facultative landfills were 3 and 7 years old. With increased age, degradation of the organic acid content is expected, as seen in Table 1. Prior to the extraction experiments, aliquots of the leachates were acid digested using EPA method 3015 and background concentrations of the select metals were observed to be extremely low.

Waste Metal Content

Table 3 presents the data on the total metal concentration in W1 and W2 wastes, obtained via acid digestion technique performed in triplicate. As can be seen in the table, As, Pb and Zn in the W1 was extremely high, with concentrations as 2.6 g/kg, 2.3 g/kg, and 10.3 g/kg, respectively. Very low amounts of Cd was observed (0.03 g/kg) in the W1. The concentrations obtained were typical of the total metal content in the W1 waste, reported elsewhere (Dubey and Townsend, 2004). On the other hand, the total metal content of As, Pb and Zn concentrations in W2 was 0.5 g/kg, 0.98 g/kg and 0.4 g/kg, respectively. No cadmium was detected in the W2.

Leaching Results using Standardized Tests

Metal leaching obtained from the TCLP, SPLP and deionized water (DI) extraction tests on the W2 and W1 samples is presented in Table 4. Lead in the W1 leached less in the SPLP and DI tests than TCLP. The lead concentration was 3.1 and 3.2 mg/L in the SPLP and DI extracts, respectively, while that in the TCLP extract was 7.3 mg/L, which was well above the TC limit of 5 mg/L. Similar data have been reported elsewhere in literature (Dubey and Townsend, 2004). Arsenic in the W1 leached even higher in the DI and SPLP tests (39.9 mg/L), as compared to the TCLP test (0.9 mg/L). Based on the TCLP results, the W1 can be classified as a haz-

Table 3. Total Metal Content in W2 and W1.

	Concentration (mg/Kg)	
Metal	W2	W1
As	471.4 ± 18.1	2640.0 ± 28.36.2
Cd	< 0.01	33.7 ± 1.3
Pb	979.3 ± 107.9	2285.0 ± 63.6
Zn	429.2 ± 29.8	10250.0 ± 7.07

Table 4. Leaching Results from the Batch Extration Test (TCLP, SPLP and DI) on W2 and W1 Samples.

	W1			W2		
Metal (mg/L)	**DI**	**SPLP**	**TCLP**	**DI**	**SPLP**	**TCLP**
As	39.9 ± 0.5	39.8 ± 1.1	0.9 ± 0.04	0.05 ± 0.00	0.2 ± 0.02	0.06 ± 0.00
Cd	0.9 ± 0.02	1.0 ± 0.03	0.7 ± 0.02	< 0.001	< 0.001	< 0.001
Pb	3.2 ± 0.1	3.1 ± 0.06	7.3 ± 0.02	0.06 ± 0.01	0.08 ± 0.02	0.2 ± 0.00
Zn	170.7 ± 5.1	177.9 ± 6.2	168.0 ± 5.2	1.7 ± 0.3	1.7 ± 0.3	1.8 ± 0.1

ardous waste and its application as a fertilizer becomes questionable. It should be noted that almost 30% of total arsenic (based on total metal content) was extracted in the DI and SPLP tests. The difference in extractability of arsenic can be attributed to two factors: (1) the acidic pH in the DI and SPLP (pH < 3) resulting in oxidative dissolution, as compared to the conditions in TCLP; and (2) the inability of arsenic to complex with the acetate ions in the TCLP solution (Hooper et al., 1998; Halim et al., 2004). Mineralogical identification of the W1, as provided by the manufacturer indicated the presence of arsenic as arsenopyrite (Dubey and Townsend, 2004), which is known to dissolve under highly acidic conditions. The leachability of other metals such as Cd and Zn was moderately similar for all the extraction tests. The Cd extract concentration ranged from 0.7–1 mg/L amounting to almost 55 % release in the DI and SPLP test and 40 % in the TCLP test. The extract concentrations in the tests was well below to the threshold value (TC limit) of 1 mg/L. Zinc leached in very high quantities in the extraction tests (170 mg/L), corresponding to almost 32–34 % of the total metal content in W1.

As compared to the W1, leachability of the metals from the W2 was relatively low. The difference in the leached amounts from the two wastes (Table 4) can be attributed to the respective metal contents in the waste. For example, the arsenic concentration in the W2 was at least 5-fold lower than that in the W1 (Table 3), therefore lower leachability was observed (0.05-0.2 mg/L). The leaching of arsenic and lead (0.06–0.2 mg/L) was much lower than the TC limit, thereby they can be deemed as non-hazardous wastes in accordance with RCRA guidelines. A comparison of the leached amounts of As and Pb in the different extraction tests indicated some differences. In the case of arsenic, the SPLP extracted 2-fold more than the DI or the TCLP, probably due to pH effects. On the other hand, Pb concentrations were at least 2 fold higher in the TCLP, and less in SPLP and DI tests due to similar reasons. The results confirmed the findings reported previously in literature (Al-Abed et al., 2006).

Leaching Results using Landfill Leachates

The results of the batch leaching studies for the W1 and W2 samples using landfill leachates is presented in Figures 1 and 2, respectively. Batch extractions were performed using leachates sampled at two different dates, March 2004 and October 2004. The leachates

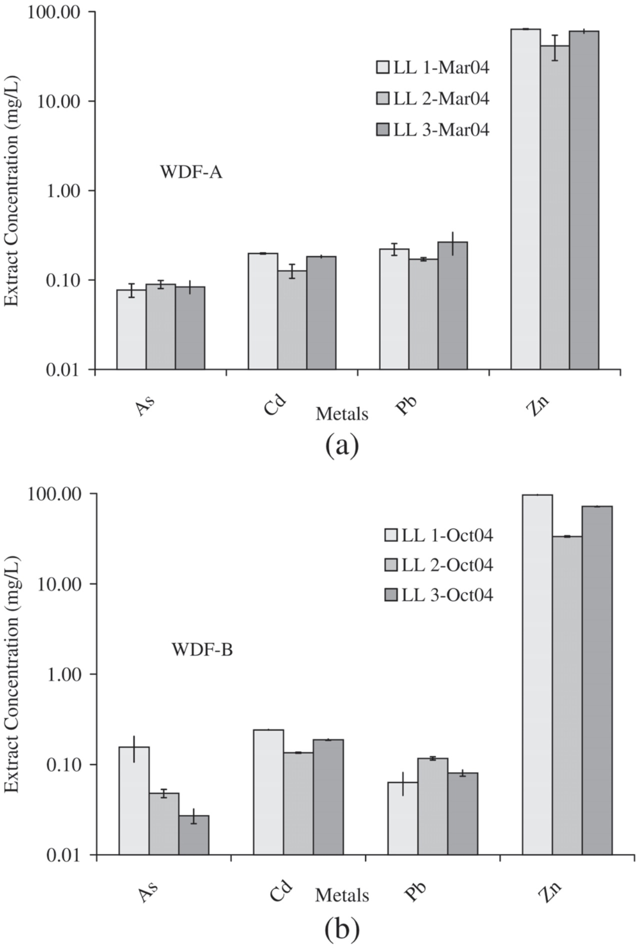

Figure 1. *Metal leaching from W1 using landfill leachates collected at different sampling times: March 2004 and October 2004.*

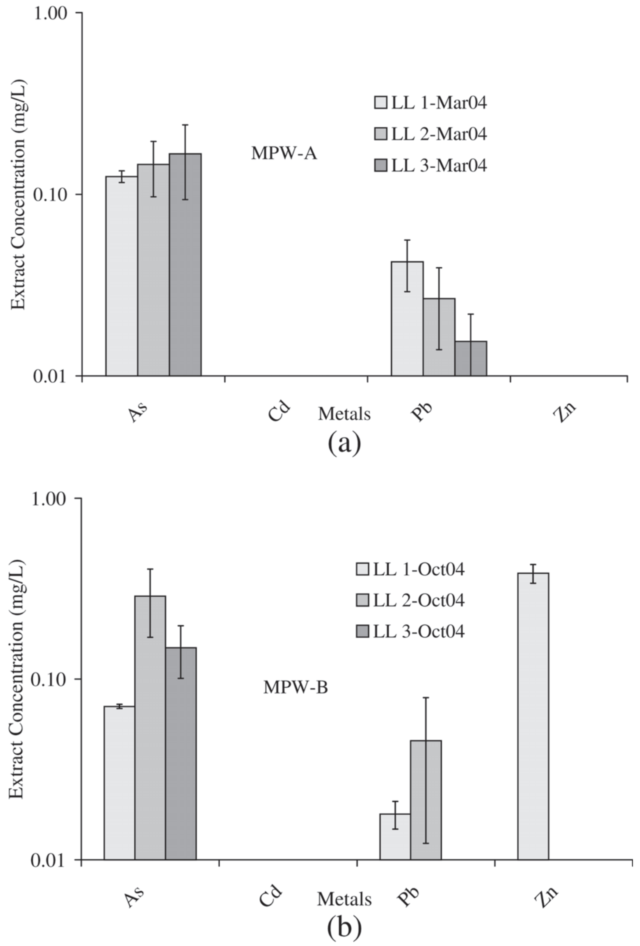

Figure 2. *Metal leaching from W2 using landfill leachates collected at different sampling times: March 2004 and October 2004.*

were collected from three cells, operated in duplicate. Prior to the experiment, the leachates were acid digested using EPA method 3015 and background concentrations of the select metal determined. The amount of metal extracted in each test was calculated by the difference of the extract and background concentration. As mentioned earlier, all extraction experiments were performed in triplicate for the leachate duplicates (similar landfill cells) and the mean of six experimental values are reported in Figures 1 and 2.

Very low amounts of arsenic leached from the W1, which was in direct contrast to the amounts extracted in the standardized leaching tests. The range of arsenic concentration extracted using the three leachates collected in March was 0.08–0.1 mg/L, amounting to less than 0.1 % of total arsenic [Figure 1(a)]. The As concentrations leached from the W1 using the October samples were similar (0.03–0.2 mg/L) [Figure 1(b)]. Similarly, Cd and Pb leached in low amounts with the extract concentrations in the range of 0.13–0.18 mg/L for Cd and 0.18–0.27 mg/L for Pb [Figure 1(a)]. Marginal yet insignificant differences in the extract concentration using leachates sampled in October were observed for both these metals. Leaching of Zn was the highest among all metals with extract concentrations as high as 100 mg/L, similar to those observed in the TCLP, SPLP and DI tests. The leachate extract concentrations of the metals in W2 were almost negligible. It was observed that the concentration of As and Pb were almost similar for all the different leachates ranging from 0.15–0.17 mg/L and 0.02–0.03 mg/L, respectively [Figure 2(a) and 2(b)]. These values were comparable to those obtained in the TCLP tests. Cd and Zn were not detected in the extracts.

Several factors can be attributed to the variation in metal release within landfill leachates, the most important being: (1) pH of the extraction fluid and; (2) organic content. Metal release as a function of pH usually showed a characteristic "V" shaped profile, with high leaching in low and high pH values, with minimum leaching in the neutral pH region (Halim et al., 2004; Al-Abed et al., 2007). The pH of the leachates in the landfill leachate extraction tests ranged between 7–7.5. Given the narrow range of pH in the leachate extraction tests and the fact that minimal leaching is observed in this range, a correlation between pH values and the leaching data could not be established. This was observed to be true for all the metals selected in this study (Cd, Pb and Zn).

It was also observed that the dissolved organic carbon (DOC) content was different in the three leachate samples and in duplicate leachates collected from similar landfill types, and so was the organic acid (volatile fatty acid) content. For the leachates obtained from different landfills (same sampling date), the DOC values were lowest for LL2 leachates with almost non-detect volatile fatty acid (VFA) content, while they were high for LL3 leachates with very high VFA content (Table 1). It is known that the presence of organic acids such as VFAs in the leachate can enhance metal mobility via complexation (Hooper et al., 1998; Halim et al., 2003; Halim et al., 2004). However, no correlation between metal leaching and VFA or DOC content could be established for the different landfill leachates. For example, in the samples collected in March 2004, the acetic acid concentration was 1, 21 and 600 mg/L in LL1, LL2 and LL3, respectively. The corresponding As extract concentrations was 0.4, 0.9 and 0.6 mg/L and that for Zn was 54.2, 41.4 and 49.5 mg/L, indicating no particular pattern. Similar observations were made upon comparing leachates collected in October 2004. Based on the values of DOC in leachates and the fact that only 5–13 % of the DOC content is comprised of organic acids, it is believed that the landfill leachate may contain other complexing agents, which may enhance or suppress the release of metals from the waste (Halim et al., 2004; Townsend et al., 2004).The leaching profiles in landfill leachate extraction tests showed that while acetic acid concentration directly influenced metal release, the presence/absence of complexing agents may inhibit metal concentration in the leachate via precipitation or complexation.

Upon comparing the leaching results using leachates collected on the same sampling time and same kind of landfill type, it was observed that metal release decreased with DOC content. For instance, the DOC content in the facultative landfill bioreactor (LL2) was in the range of 318–476 mg/L in the March samples (Table 1). Correspondingly, the arsenic and lead concentrations in the leachate extracts were 0.16–0.2 mg/L and 0.14–0.22 mg/L, respectively. Conversely, metal release increased with VFA (acetic acid) content. It is believed that the combination of pH, VFA content and dissolved organic matter influence metal leaching to varying degrees. Therefore, any leaching procedure should use extraction fluids that contain complexing agents such as organic ligands at specific pH values so as to accurately predict extent of leaching. In comparison to the W1, the effect of acetic acid concentration and DOC content was less pronounced on the W2, probably because of the characteristics of the waste itself (total metal content).

Comparison of Landfill Leachates Results with Standardized Tests

Leaching results from the different extraction tests were compared. Since no significant difference between leachate types and sampling dates was observed, the leachate results from the extraction tests using landfilled leachates were averaged. For this comparison, the average used was the extract concentration from 12 different data sets (3 types of landfills, 2 sampling dates, and duplicate cells). It can be observed from the leaching data that as the pH was increased from 3.5 (DI tests) to 4.9 (TCLP) to 7.5 (landfill leachate tests), the amount extracted decreased significantly. The leaching of arsenic from W1 decreased from 39 mg/L (DI and SPLP tests) to 0.14 mg/L in the landfill leachate extraction tests. Similar decrease was observed for Cd (0.16 mg/L), Pb (0.2 mg/L) and Zn (55.1 mg/L), in comparison to the SPLP and DI tests. As mentioned earlier, increased leaching in the SPLP and DI tests was due to the low pH, resulting in dissolution of the mineral phases present. It can also be observed that the TCLP overestimated the leaching potential of Cd and Pb, thereby incorrectly classifying the waste. The factors not accounted for in the TCLP, which may lead to the overestimation are: (1) pH variation in landfill leachate; (2) presence of dissolved organic matter and; (3) mineralogy of the waste. Even though the W1 (Ironite in this case) may leach less under landfill conditions, land application of the fertilizer may release high amounts of As, Pb and Cd, as seen in the SPLP and DI water tests. In comparison, the W2 leached less in the TCLP and LL tests. While the TCLP underestimated arsenic leaching, it over-predicted leaching of Pb and Zn.

CONCLUSION

Based on the results presented in this paper, it was concluded that, although bioreactor landfill leachates contain more DOC than conventional landfills, they tend to extract metals at levels similar to those of dry tomb landfill leachate. Thus, operating a MSW landfill as bioreactor should not have an effect on the management of metal bearing solid wastes. It is further believed that the combination of pH, VFA, DOC as well as ORP play a role in metal leaching to varying degrees. Furthermore, it may be inaccurate to base the prediction of metal mobility in a MSW landfill setting on one batch leaching test such as the TCLP. Given the fact that a variety of factors contribute towards the differences in leaching potential of these two wastes, it is uncertain to what degree do these factors influence leaching from a specific waste and therefore needs to be determined.

ACKNOWLEDGEMENTS

This paper has not been subjected to internal policy review. Therefore, the research results presented herein do not, necessarily, reflect the views of the USEPA or its policy. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Table 5. Comparison of state-of-the-art matrix resins with VPSP/BMI copolymers.

Resin System	Core Temp. (DSC peak)	T_E	Char Yield, %
Epoxy (MY720)	235	250	30
Bismaleimide (H795)	282	>400	48
VPSP/Bismaleimide copolymer			
C379: H795 = 1.9	245	>400	50
C379: H795 = 1.4	285	>400	53

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