Aim and Scope

The objective of the *Journal of Residuals Science & Technology* (JRS&T) 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 are also welcome.

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Research

Book Review

Sludge Conditioning: Impact of Polymers on Floc Structure

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ABSTRACT: In order to enhance mechanical dewatering, conditioning polymers are used to flocculate sewage sludge. These polymers modify floc structure, which has an impact on dewatering efficiency. However, fundamental aspects of those processes are incompletely understood, particularly the way that flocs are structurally organized and how this may relate to their mechanical and dewatering properties. Thus, this study focused on the impact of different types of polymers on sludge rheological and microscopic properties. Polymer dosage was found to be the main parameter controlling these properties and a master curve was obtained between the linear viscoelastic (LVE) complex modulus and polymer dosage, based on optimal polymer concentration. Additional research possibilities were also defined.

INTRODUCTION

With increases in the extent and efficiency of wastewater treatment, more wastewater residues, known as either sludges or biosolids, are generated. These materials are an environmental issue with economic and political overtones as well, due to the cost and pollution concerns associated with their disposal. This is true globally, and consequently there are international efforts to address these issues. One of the challenges for professionals is then to limit the produced volumes of sludge and above all, to remove as much water as possible, while minimizing environmental and energy costs. In wastewater treatment plants, the specific processes for accomplishing this are known as biosolids conditioning and dewatering.

Perhaps surprisingly, fundamental aspects of these processes are still incompletely understood. This is notably due to the composition of sludges, which is not only complex but also time variable. Though such difficulties hinder attempts at defining sludge behavior during conditioning and dewatering, many studies have examined these phenomena as reviewed by Dentel (2001a). Some of them have focused on the dewatering processes whereas others have dealt with sludge properties, and especially their interactions with conditioners that are used to improve mechanical dewatering.

Indeed, in order to improve mechanical dewatering, flocculating agents are commonly used: they react with sludge components to induce flocculation which expedites water release. In order to accomplish this, these flocculants necessarily reinforce the structure of the solids so that the solid and liquid portions are more easily separable (Dentel, 2001b). This structure is subjected to mechanical stresses, which may be considerable depending on the specific dewatering device. The success of sludge treatment depends mainly on this last step. Thus, in order to understand and to improve sludge dewaterability, many researchers have tried to characterize and explain the structure and mechanical behavior following addition of the flocculant agent, which is usually a high molecular weight cationic polymer.

Because dewatering processes are usually based on mechanical techniques, and because floc strength is believed to play a significant role in sludge dewatering (Dick, 1979), rheology has been assumed to be the appropriate method to study the mechanical properties of conditioned sludge (e.g. Lolito et al., 1997; Chaari et al., 2003; Seyssiecq et al., 2003; Spinosa and Wichman, 2004). The Herschel-Bulkley rheological model has been shown to characterize the gel-like behavior of sludge (Baudez and Coussot, 2001; Tixier et al., 2003), even though it cannot entirely describe the complex behavior of sludges (Baudez, 2008). In attempting predictive approaches to dewatering, many authors have looked at the relationship between specific sludge characteristics (zeta potential, capillary suction time, total solid content, etc.) and the network strength

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measured under flow or the yield stress (Abu-Orf and Dentel, 1999, Mikkelsen and Keiding, 2002; Yen et al., 2002; Ormeci, 2007). However, most of those papers have focused on sludge liquid behavior: less work has been done to characterize the solid-like behavior of the cake or solids fraction that is not flowing during dewatering. Yet, the resilience of this fraction is crucial in assuring a high solids recovery by maintaining the integrity of the cake. Only a few researchers have focused on the influence of conditioning on sludge rheological behavior (Chen et al., 2005; Ayol et al., 2006; Chen et al., 2006; Wolny et al., 2008) and these studies are relatively new. Thus, a lack of knowledge remains about the impact of conditioning polymers on sludge flocs' solid-like behavior even though it may be significant in explaining the polymer efficiency.

Rheology gives information about sludge structure at a macroscopic scale. In order to investigate sewage sludge small-scale structure, a complementary technique is microscopy. A variety of approaches have been evaluated for this purpose, as reviewed by Chu and Lee (2004): scanning electron microscopy (SEM), confocal laser scanning microscopy (CLSM), atomic force microscopy (AFM), and transmission electron microscopy (TEM) microtome slicing. Optical techniques or camera were also used (Da Motta et al., 2001; Zhao, 2003). Because they only probe sample surfaces, the AFM and TEM techniques do not seem to be appropriate tools to investigate the morphology of flocs. However, SEM, CLSM and microtome slicing have provided satisfactory resolution with the relatively large scanning scale that is suitable for examining the sludge floc and cake structure when considering dewatering treatment (Chu and Lee, 2004).

Thus, confocal microscopy is one of the most cited techniques to analyze sludge (Thill et al., 1999; Chung and Lee, 2003; Schmid et al., 2003; Chu and Lee, 2004): pictures are essentially used to estimate floc size and fractal dimension. However, sludge conditioning has not been extensively examined through such an analysis: most of the authors have focused on activated sludge and its microbial population, quite independent of any conditioning polymer effect.

This study represents a first step toward our final goal: relating properties of the three-dimensional network (resulting from interactions between the sludge and the flocculant conditioner) to dewatering and mechanical properties. Thus, after introducing the protocols we used, this paper shows the main results concerning sludge conditioning and their characterization with rheology and microscopy. Results suggest that polymer dosage is the main parameter influencing sludge rheological and structural properties. A master curve is shown to relate linear viscoelastic complex modulus and polymer dosage.

MATERIALS AND METHODS

Material

Anaerobically digested and activated sludges were used (denoted as DS and AS hereafter). Anaerobically digested sewage sludge was sampled from the Wilmington (Delaware, USA) waste water treatment plant, whereas activated sludge came from a rural treatment plant in Varennes sur Allier (central France). Activated sludges were thickened by decantation. Samples were stored at 4°C to maintain constant behavior as long as possible.

Dry content (DC) was determined by drying at 105°C for 24h. The measured DC values were around 2.5% for digested sludge and 1.2% for the thickened activated sludges.

Conditioning

Conditioning polymers were provided by Ciba. They are all acrylamide-based copolymers (quaternized 40/60 mole ratio AETAC/AM DMAEA-Q: MeCl) but have different structure (cross-linked or linear), surface charges or molecular weight (Table 1). Solutions were prepared with demineralized water at a 5 g.L^{-1} concentration, 24 h prior to application (Saveyn et al., 2005).

For sludge conditioning, a jar test was used, operating at 200 rpm during 30 s to mix the sludge and the polymer and at 15 rpm during 120 s to promote flocs growth. Half a liter of sample was mixed with different dosages of polymers.

Table 1. Zetag Polymer Characteristics (Ciba references).

Polymer	7557	8140	8160	8165	8190	8846FS	8848FS
Cationic charge	Medium-high	Medium	Medium-high	Medium-high	Very high	Medium-high	High
Molecular weight	Medium	High	High	Very high	High	Very high	Very high
Structure	Linear	Linear	Linear	Linear	Linear	Cross-linked	Cross-linked

Optimal dosage was commonly determined based on capillary suction time (CST) measurements. CST measurements were done five times each with a Triton Electronics 304M CSTmeter to determine the best dosage for each polymer. Then, sludges were drained to remove supernatant with a coffee filter during 4h (dry content is shown for the optimal dosage in Table 2).

Rheology

Rheological measurements were performed on conditioned and drained sludge. They were realized on a Paar Physica MCR300 rheometer assisted by US200 software and equipped with soft parallel planes geometry (2 mm gap, 25 mm radius). Amplitude sweeps from 0.01 to 10% were performed at 1Hz frequency to determine the linear viscoelastic (LVE) range, i.e. the range of deformation for which shear stress and shear rate are linearly proportional: in the LVE zone, the complex modulus $G^* = (G'^2 + G''^2)^{1/2}$ is independent of the shear strain.

Supernatant viscosity was determined using a Paar Physica MCR301 rheometer assisted by Rheoplus software and equipped with cone plane geometry (0.1 mm gap, 25 mm radius). Samples were submitted to increasing and decreasing 120 s ramps from 0 to 1400 s^{-1}. The supernatant being a Newtonian fluid, the slope of the curves $\tau = f(\dot{\gamma})$ represents the viscosity.

All the measurements were repeated at least three times, with satisfactory repeatability: the mean results are presented.

Microscopy

Microscopy was performed with a confocal laser scanning microscope (CLSM) Zeiss LSM 510 VIS on samples of drained conditioned digested sludge fixed with paraformaldehyde. The settings are the following: 10× Plan-Apochromat 0.45 NA, wavelength 560nm at 4.9% laser power in reflection mode. According to our protocol, the pictures obtained with the microscope are composed by around 15 slices, each composed by 4 × 4 square pictures. The global picture is a 4 700 μm width and corresponds to a depth of 80–100 μm according to the quality of the reflection. Such a protocol allows the analysis of a large sample, which is of major importance for sewage sludge analysis to compensate for their potential heterogeneity. This method was repeated twice on each sample.

Pictures were analyzed using three software products: LSM Image Examiner, Volocity and ImageJ. We especially focused on the matter distribution. First, the maximal part of the pictures that can be analyzed was determined (based on the quality of the picture). Then, the floc surface (named *A*) was determined with Volocity software. Because the global analyzed area was not exactly the same for each sample, results are compared based on the ratio colored surface/total surface.

RESULTS AND DISCUSSION

Polymer Dosage and Filterability

For the purposes of this research, the optimum polymer dosage is defined at the lowest CST value (Figure 1). This is a commonly used research approach, even though the CST test emphasizes filtrate flow in the absence of applied force.

The polymers we used all belong to the same chemical family, but it appears that the best dosage is different for each polymer (Table 2). Within the group tested, higher molecular weight tends to decrease the dosage (Zetag 8140 to 8190), consistent with a bridging effect (Saveyn et al., 2005). A higher amount is needed for the highly cross-linked (structured) polymers (Zetag 8846FS and 8848FS) as also shown previously (Dentel et al., 2000a). Optimal dosage also depends on the type of sludge, digested sludge needing higher amounts of polymer than activated sludge.

Rheological Behavior of Drained Conditioned Sludge

Being conditioned and drained, both activated and

Table 2. Value of the Optimal Dosage and Corresponding CST, and Dry Content (of drained samples) for Each Polymer, According to the Type of Sludge.

Polymer	Dosage [g/kg DC]	CST [s]	Drained Samples DC [%]
Digested Sludge			
Zetag 7557	12.35	8.18	10.03
Zetag 8160	7.65	7.75	8.47
Zetag 8165	10.05	7.26	8.31
Zetag 8846FS	17.86	9.30	9.57
Zetag 8848FS	23.11	9.13	10.31
Activated Sludge			
Zetag 7557	4.17	9.80	8.01
Zetag 8140	2.00	8.65	7.30
Zetag 8160	1.87	7.53	7.52
Zetag 8190	2.17	9.06	8.63

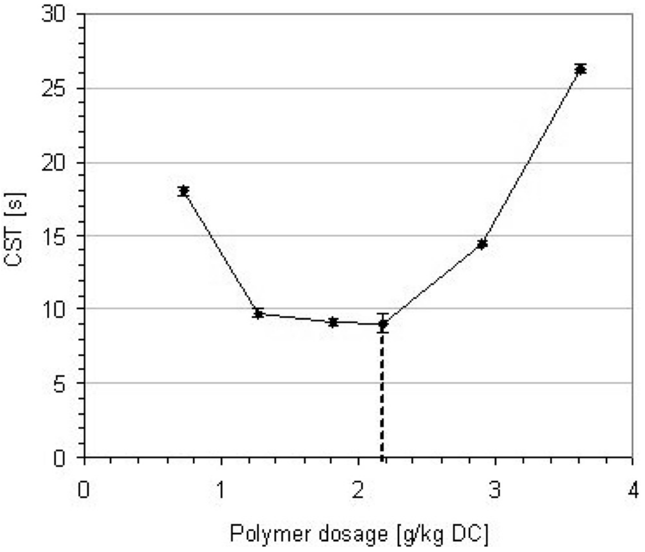

Figure 1. *Typical CST measurement results—Capillary suction time regarding to polymer dosage (Zetag 8190) for an activated sludge.*

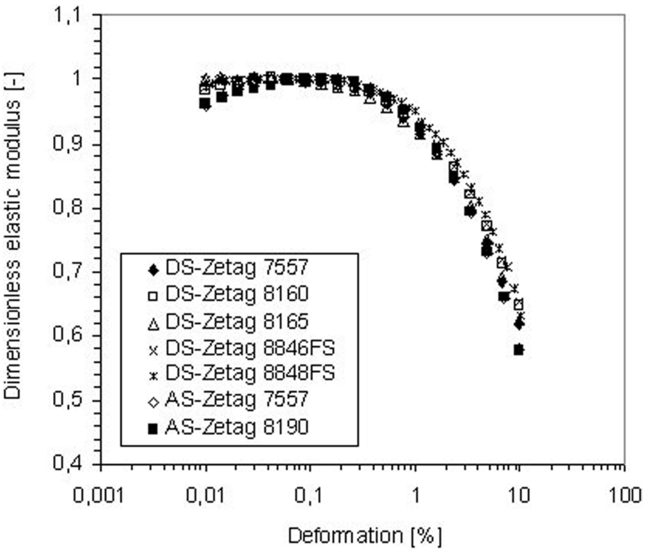

Figure 3. *Dimensionless elastic modulus (G^*/G^*_{LVE}) vs. amplitude for both activated and digested sludge at optimal dosage.*

digested sludge present a similar rheological behavior. As already shown by Ayol et al. (2006), when submitted to small amplitude sweep, their complex modulus $G^* = (G'^2 + G''^2)^{1/2}$ remains constant until a defined deformation then decreases (Figure 2): this strain, γ_{LVE}, corresponds to the end of the linear viscoelastic zone. As for the complex modulus, the elastic and loss moduli (Figures 3–4) decrease with the amplitude. It should also be noticed that the loss modulus is smaller than elastic modulus, so complex and elastic moduli are quite similar.

For a given polymer, moduli values depend on the polymer dosage but the curves remain qualitatively the same: this enables results to be represented with dimensionless curves, using the mean LVE value of the analyzed modulus as a reference, G/G_{LVE} (Figure 2).

Thus, the linear viscoelastic domain tends to remain constant regardless of the polymer and its dosage for both activated and digested sludge and for all the polymers we used; the differences observed at low deformation only result from the inertia of the measuring system.

It is even possible to obtain a master curve by dividing the complex (or the elastic) modulus value by its value in the LVE range. This underlines that, from a qualitative point of view, under small deformations, rheological properties do not seem to be deeply impacted by the polymer and its characteristics. On the contrary, quantitatively, moduli evolve with the polymer and its dosage.

However, looking at the loss modulus (Figure 4),

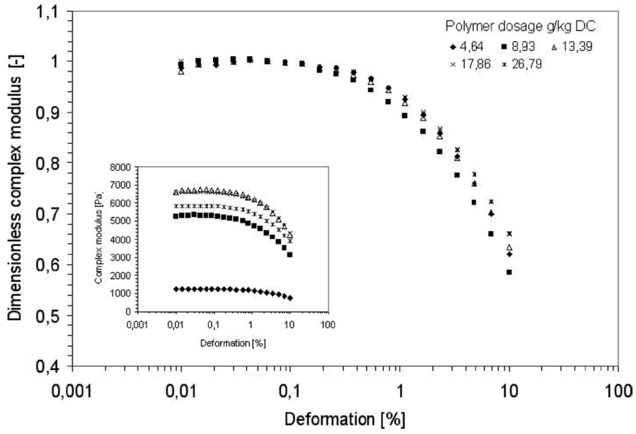

Figure 2. *Complex modulus obtained on digested sludge conditioned with Zetag 8846FS.*

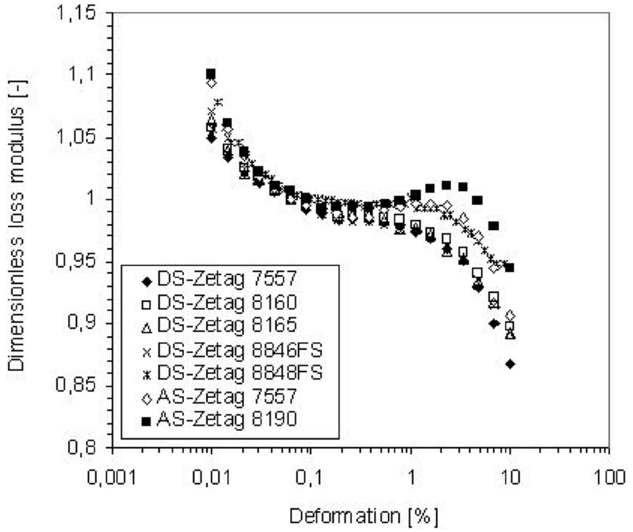

Figure 4. *Dimensionless loss modulus (G''/G''_{LVE}) vs. amplitude for both activated and digested sludge at optimal dosage.*

when the deformation increases small differences can be noticed between (i) digested and activated sludge, (ii) digested sludge conditioned with linear or cross-linked polymers: the curves are superimposed in the LVE region but not above, indicating that there is no longer proportionality between τ and γ. This means that above γ_{LVE}, the sludge structure may be rebuilt to strengthen the material and compensate for the influence of the stress (thixotropy effects) (Baudez, 2008). Such results may come from the type of sludge (activated or not), their initial concentration (activated sludge dry content is lower than for digested sludge) or from the polymer properties (cross-linkage).

Table 3. Normalized Area (average values) per Dosage and Polymer for Conditioned and Drained Digested Sludge.

Polymer	Dosage [g/kg DC]	Normalized area [%]
Zetag 8848FS	7,7	27,42
	15,41	42,33
	23,11	39,17
	30,82	40,20
Zetag 8165	5,03	35,03
	10,05	61,74
	15,08	63,97
Zetag 8846FS	4,46	38,15
	8,93	45,45
	13,39	53,24
	17,86	69,35
	26,79	67,33

Microscopy

Globally, the matter distribution evolves with polymer dosage: whichever the Zetag polymer, the higher the dosage, the bigger and the denser the flocs (Figure 5) until the optimal dosage. Above optimal dosage, the floc structure tends to stabilize. This tendency can be illustrated by coloring the solid surfaces and calculating the ratio colored surface/total surface, called normalized area (Table 3). Pore size and distribution change with polymer dosage: for low dosage, there are many small flocs whereas when the dosage increases, there are bigger but less numerous flocs.

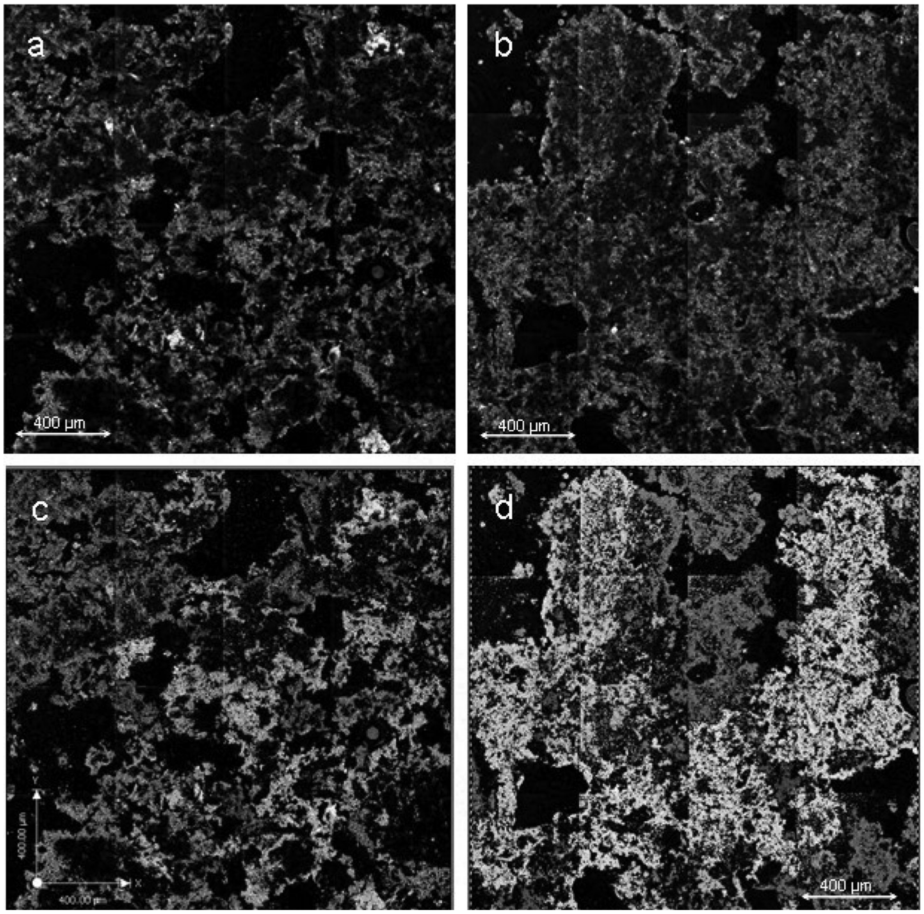

Figure 5. *CLSM pictures, analyzed (the colored ones) or not (the black and white ones)—Digested sludge flocculated with Zetag 8846FS at two dosages: 8.93 (a, c) and 13.39 (b, d) g/kg DC.*

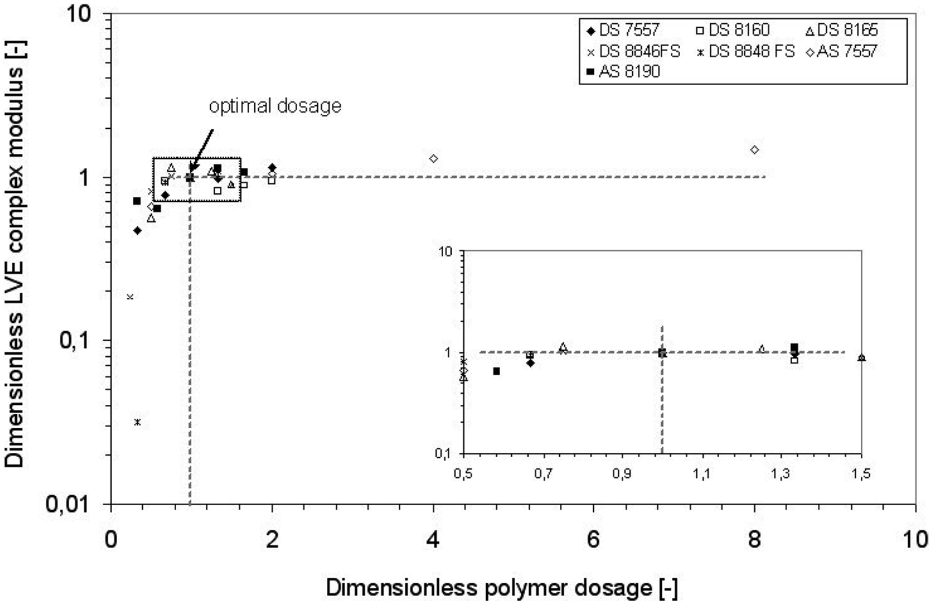

Figure 6. *Dimensionless LVE complex modulus ($G^*/G^*_{optimal}$) vs. dimensionless polymer dosage ($C/C_{optimal}$) for both activated and digested sludges.*

As for the complex modulus, it was apparently not possible to use these pictures to distinguish between these acrylamide-based polymers according to their specific properties (surface charge, molecular weight and structure). However, this last conclusion should be carefully considered: supplementary tests done with another chemical family of conditioning polymers suggest that, different microscopic properties could be observed when other properties were similar.

Discussion

In this study, three sludge characteristics were observed as a function of polymer type and dose: capillary suction time, rheology (especially the LVE complex modulus) and microscopic determination of the normalized surface of flocs.

Capillary suction time measurements are used to determine the optimum dosage with defined sludge and polymer. CST is often used to estimate sludge dewaterability. However, as written in the literature (Smiles, 1998), though it is a useful empirical tool, its weaknesses are well-known. As a consequence, CST values can only be considered as an indicator and can not be used to perform careful analysis.

This is why, in order to relate rheological behavior to filterability, the LVE complex modulus was represented as a function of polymer dosage for each polymer. By normalizing the curves with the values corresponding to the optimal dosage for each polymer, a master curve was obtained (Figure 6).

This master curve shows that above the optimal polymer dosage, the LVE complex modulus tends toward a horizontal asymptote, which means that the flocs structure is no more influenced by the polymer dosage.

This could be explained by the measurement of supernatant viscosity (Figure 7) which increases above the optimal dosage: the excess polymer can no longer react with the sludge (from a chemical point of view, all the charged sites have been neutralized) and it remains within the liquid phase. In the same way, Christensen

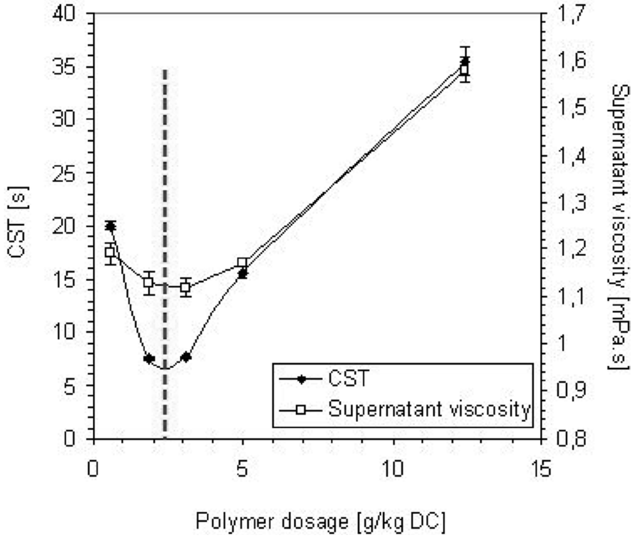

Figure 7. *CST (black diamonds) and supernatant viscosity (white squares) as a function of polymer dosage for an activated sludge conditioned with Zetag 8160. The dotted red line corresponds to the minimum of the two curves.*

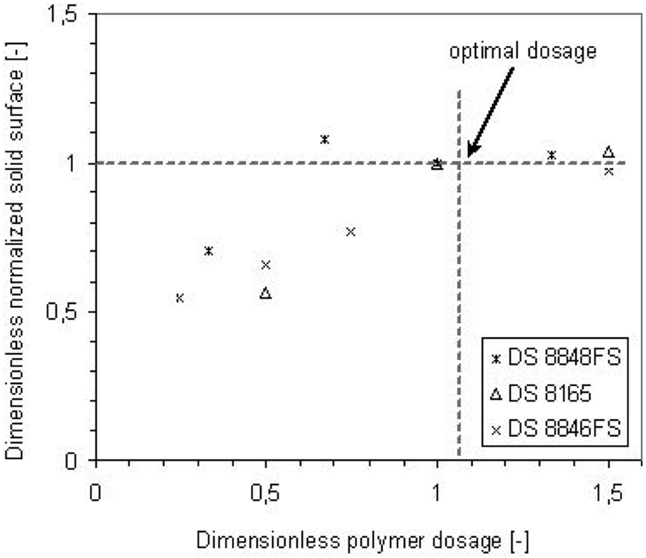

Figure 8. *Dimensionless normalized area (A/A$_{optimal}$) as a function of polymer dosage.*

et al. (1993) and Dentel et al. (2000b) found that filtrate viscosity increases in the polymer overdosing range.

In parallel, if the normalized surface determined by microscopy is normalized by the corresponding value for the optimal dosage, then plotted as a function of polymer dosage, all the samples tend to be represented on the same curve: the normalized solid surface increases with polymer dosage until the optimum is reached (Figure 8).

Such a curve resembles the corresponding plot of the LVE complex modulus vs. dimensionless polymer dosage (Figure 6). As for the rheological properties, it may seem that the total floc surface tends to stabilize above the optimal polymer dosage: we can theorize that within the tested range (and for the tested conditioners), excess polymer does not modify much more the material organization. Unless there is increased or protracted shear, it will remain within the liquid phase, increasing the viscosity as shown by rheological measurements (Figure 7).

CONCLUSION

The impact of conditioning polymers on sludge mechanical and structural properties was studied. All the polymers that were used belong to the same chemical family but vary certain characteristics such as cross-linkage, molecular weight or total cationic charges.

CST measurements were performed to determine the optimal dosage for each polymer. Rheology was used to explore the flocs mechanical properties. Whichever the polymer, rheological curves all have the same shape. They only differ by their value which depends on both the polymer and above all its dosage. In addition, microscopy was performed to characterize the flocs structure. Within the considered chemical family, flocs size increases and their amount decreases with higher polymer dosage. No tendency was found to identify the polymers according to their specific properties.

Because the literature has shown that CST values are not significant enough to be used as an index of sludge dewaterability, rheological and microscopic properties were related to polymer dosage. Thus, a unique curve was found to relate the LVE complex modulus to the polymer dosage, both being normalized by their value at the optimal dosage: LVE complex modulus increases until the optimal dosage is reached then, it remains constant. The same behavior was observed for the global area constituted by the flocs: it increases with the polymer dosage until the optimum then stabilizes. These results could be explained by the fact that the excess polymer remains in the liquid phase, as suggested by its viscosity.

Rheological and microscopic results suggest that once the optimal dosage is reached, the polymer does not really modify sludge solid structure, whereas it impacts the liquid phase properties. As a consequence, though rheological properties do not evolve like CST measurements (approximately sludge filterability), the master curve shows that finally, a relationship may exist between rheological properties and the optimal dosage, whichever the sludge and the polymer.

This study opens the way to much more work. It would especially be interesting to determine if further samples can be added to the master curve, and the curve's functional limits. In parallel, oscillatory tests could be deepened, by doing frequency sweep analysis and also by using polymers from completely different chemical families or even inorganic conditioning agents. Microscopy would also allow more developments, for example by improving the characterization of flocs distribution or doing 3D pictures. In addition, it would be interesting to relate these parameters to actual dewaterability, by employing a filtration-compression cell in order to distinguish the impact of both the structure and the liquid phase on dewatering efficiency.

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Medical Waste Management by Geographical Region in Turkey

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ABSTRACT: Medical waste management in Turkey is performed according to the Medical Waste Control Legislation that was regulated in 2005. The purpose of this work is to analyze medical waste management by regions of Turkey from the perspective of this regulation. Tables have been prepared from data obtained from the 2008–2012 Solid Waste Management Action Plan prepared by the Ministry of Environment and Forestry and covering all cities in Turkey. There are several data about number of beds in hospitals of all cities in Turkey, total medical waste produced in each city, medical waste produced per person yearly, medical waste disposal method that was used in 2007 and the method that is projected by the year 2012. Medical waste per person that is produced yearly in cities shows a parallelism with hospital bed capacity in that city and is found to be between 0.25 kg to 2.6 kg per person. The most common method used in Turkey so far in disposing of medical wastes was lime desiccation in special lots but recently there has been a tendency towards using a healthier method, namely sterilization. While the sterilization method was not used at all by 2007, the method has been employed in 15 cities as of 2009. It is projected that the number of cities using this method will be 56 by the year 2012. The number of cities using the old method of burial will be 15 in 2012. Since this method is not very appropriate for human health or the environment, these cities should also come up with projects to complete a transition towards the sterilization method.

INTRODUCTION

In modern societies almost everything (materials, devices, objects, etc.) eventually becomes waste. And while nature, in constant cycling of matter and energy reuses its waste, man has developed a series of synthetic materials that are difficult to recycle. These synthetic materials accumulate, disrupt the natural equilibrium, and create economic, ecological and health problems for society [1]. Human activities and changes in lifestyles and consumption patterns have resulted in an increase in solid waste generation rates. Pollution problems associated with the waste generation have attracted significant attention and a great deal of research has been conducted on these topics [2] as a result.

Medical waste is a special category of waste because it poses potential health and environmental risks, typically including sharp points, human tissues or body parts and other infectious materials [3]. Generally, the term 'medical waste' refers to all infectious and other hazardous or obnoxious waste generated in various health-care establishments. These wastes appear in different forms such as general waste, pathological waste, radioactive waste, chemical waste, infectious waste and potentially infectious waste, sharp needles and pharmaceutical waste and pressurized containers [4]. Medical wastes constitute a larger portion of infectious wastes, which are potentially dangerous since they may contain pathogenic agents. The production of these wastes will continue to be an on-going problem as long as there are human activities [5].

Improper disposal of medical waste may pose a significant risk to human health and the environment. Some of the problems arising from poor management of medical waste may include damage to humans by sharp instruments, diseases transmitted to humans by infectious agents, and contamination of the environment by toxic and hazardous chemicals. Thus, the management of medical waste is a subject of major concern for any regulatory agency [6]. The management of the medical waste is an emerging issue that is magnified by a lack of training, awareness, and financial resources to support solutions. The collection and disposal of this waste is of great importance as it can directly impact the health risks to both public and environmental health [7].

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As Turkey is a developing country, improvements that are observed in many areas include the medical area as well. The number of both public and private health establishments is increasing rapidly. This consequently causes an increase in the medical waste produced in Turkey. The purpose of this work is to determine the medical waste management approaches that are used by the regions in Turkey and to characterize the goals that are targeted by the city governments.

MEDICAL WASTE MANAGEMENT IN TURKEY

The first legislation dealing with medical waste management in Turkey was established by the Ministry of Environment and Forestry in 1993 in the form of "The Regulations of Medical Waste Management" [8]. Medical waste management in Turkey was executed according to these regulations for 12 years. This legislation was modified by the Ministry of Environment and Forestry in 2005 in accordance with the European Union Adaptation Process to be more in tune with the EU instructions and thus a new "Medical Waste Control Regulation" was founded. Currently, medical waste management in Turkey is performed according to this new legislation. According to the new regulations, the separate collection and temporary storage of medical wastes must be executed by the health care establishment. The transportation of the wastes from temporary waste storage, and the sterilization and the disposal of the wastes, must be executed by the municipalities.

The general practice in medical waste management in Turkey starts with the collection of medical wastes in red plastic bags by the health care establishments. This process is followed by transportation of these wastes to a Medical Waste Treatment Facility, or in case such a facility does not exist, to a sanitary landfill by vehicles that have medical waste transportation licenses, and only after a document that says "medical wastes received" is signed [9]. Out of these practices, the collection and temporary storage of the medical wastes by establishments is the same in every city in Turkey, while in the disposal of the wastes there are different practices.

There are four main methods that are used in disposing of medical wastes in Turkey. These are burial after liming (lime desiccation), sanitary landfilling, incineration and sterilization. The most commonly used method is burying after liming. Although the sterilization method was not used at all until a few years ago, there has been recent increase in the sterilization facilities.

Figure 1. Map of Turkey by geographical regions.

METHODOLOGY

Normally, Turkey is divided into seven geographical regions; The Marmara Region, the Aegean Region, the Black Sea region, the Mediterranean Region, the Central Anatolian Region, the East Anatolian Region and the South East Anatolian region. In this work, tables were constructed that represent data on medical waste management in these regions (Tables 1, 2, 3, 4, 5 and 6). The table for the Eastern and Southeastern Anatolian region is common, while every other region has its own table. These tables contain data about the yearly medical waste produced in cities, the number of hospital beds available in cities, the yearly medical waste production per person in the cities, the 2007 methods of disposal management of the medical wastes and the 2012 target methods of disposal management for the cities. The data in the tables were prepared by the Ministry of Environment and Forestry and were taken from the 2008–2012 Waste Management Action Plan (WMAP) [10].

RESULTS AND DISCUSSION

Medical Waste Management in Marmara Region

Marmara, which is located in the northwestern part of Turkey, consists of 11 cities. Marmara is the largest region in population and in industrial growth. While the population of Marmara makes up 29.9% of the population in Turkey, the medical waste produced in the region makes up 28% of the medical waste produced in Turkey. The details about the amounts of medical wastes produced in the cities of the region and their disposal methods have been provided in Table 1. The data reveal the largest amount of medical wastes is produced in Istanbul, the most populated city of the region as well as of Turkey. The least amount is seen in Yalova. In 2007, the method of disposal used in Istanbul, Kocaeli and Sakarya was incineration; in Bursa it was sanitary landfilling. The method used in the remainder of cities was lime desiccation in special lots. Most of the cities have targeted a transition into the sterilization by 2012. In 2012, Kocaeli will be using incineration as a method of disposal of medical wastes; Tekirdag will be using sanitary landfilling; Bilecik and Yalova will be using lime desiccation in special lots, and the other cities will be using the sterilization method. As of the year 2009, Bursa, Sakarya and Edirne have reached this goal in treating medical wastes.

The Aegean Region

The Aegean Region, located in western Turkey, consists of eight cities. It is the third most populated region in Turkey. While the population of Aegean makes up 13.1% of the population in Turkey, the medical waste produced in the region makes up 13.9 % of the medical waste produced in Turkey. The details about the amounts of medical wastes produced in the cities of the region and their disposal methods have been provided in Table 2. The data indicates the largest amount of medical wastes is in Izmir while the least amount is in Usak. In 2007, the method of disposal that was being used in Izmir was sanitary landfilling while all the other cities of the region employed lime desiccation in special lots. All cities in the region, except Mugla, have targeted a transition to the sterilization method by 2012. Mugla has not set goals concerning this issue. As of the year 2009, Afyon and Aydin have reached this goal in disposing medical wastes.

Table 1. Amount of Medical Waste in Marmara Region.

Cities	Number of Bed	Amount of Medical Waste (kg/year)	A.M.W.P.C* (kg/person × year)	2007 Disposal Method	2012 Disposal Method
Istanbul	29.503	15.519.535	1,3	Incineration	Sterilization
Bursa	5.309	3.037.145	1,3	Sanitary landfilling	Sterilization
Balikesir	2.922	1.360.777	1,0	Lime desiccation in special lots	Sterilization
Kocaeli	2.682	1.330.725	1,3	Incineration	No approach indicated
Edirne	1.748	873.951	1,1	Lime desiccation in special lots	Sterilization
Tekirdag	1.490	624.839	0,9	Lime desiccation in special lots	Sanitary landfilling
Sakarya	1.127	605.734	1,4	Incineration in İZAYDAŞ	Sterilization
Canakkale	1.150	488.153	1,3	Lime desiccation in special lots	Sterilization
Kirklareli	839	319.803	1,0	Lime desiccation in special lots	Sterilization
Bilecik	302	112.618	0,6	Lime desiccation in special lots	No approach indicated
Yalova	237	93.976	0,5	Lime desiccation in special lots	No approach indicated

*Amount of Medical Waste Per Capita.

The Mediterranean Region

The Mediterranean Region, located in southern Turkey, consists of nine cities. The region is fourth largest in population. While the population of the Mediterranean region makes up 12.6% of the population in Turkey, the medical waste produced in the region makes up 11.3% of the medical waste produced in Turkey. The details about the amounts of medical wastes produced in the cities of the region and their disposal methods have been outlined in Table 3. The table illustrates the largest amount of medical wastes is produced in Adana, and the least amount is produced in Kilis in 2007. Lime desiccation in special lots was used to dispose medical wastes in all the cities with the exception of Isparta. The method of disposal used by Isparta was sanitary landfilling. In disposing medical wastes, Hatay and Kahramanmaras have targeted transition to sanitary landfills, while all the other cities, except Burdur, have set sterilization as their goals by 2012. Burdur has not set goals concerning this issue. As of the year 2009, none of the cities have reached this goal in disposing of medical wastes.

The Central Anatolia Region

Located in the midlands of Turkey, this region consists of thirteen cities. It is the second most populated region in Turkey. The population of the Central Anatolia region comprises 16.3% of the population in Turkey, and the medical waste produced in the region makes up 20.7% of the medical waste produced in Turkey. The details about the amounts of medical wastes produced in the cities of the region and their disposal methods have been listed in Table 4. The largest amount of medical wastes is in Ankara, and the least amount in Cankiri. In 2007, lime desiccation in special lots was used to dispose medical wastes in all the cities, except Ankara, and sanitary landfills were used in Ankara. In disposing medical wastes, Yozgat and Nevsehir have targeted transition to sanitary landfilling. The other cities, except Nigde and Cankiri, have set sterilization as their goals by 2012. As of the year 2009, Kayseri and Konya have reached this goal in disposing medical wastes.

The Black Sea Region

Covering the northern parts of Turkey, this region consists of 18 cities. The population of the region makes up 10.3% of the population in Turkey and the medical waste produced in the region is 12.6% of the medical waste produced in Turkey. The details about the amounts of medical wastes produced in the cities of the region and their disposal methods organized in Table 5. The largest amount of medical wastes is produced in Samsun, while the smallest amount is produced in Bayburt. Lime desiccation in special lots was used to dispose medical wastes in all the cities of the region in 2007. The cities of Giresun, Bolu, Bartin and Sinop have not set disposal goals to be set by 2012. Gumushane and Bayburt have set their goals for sanitary landfilling, and the other cities have targeted sterilization by 2012. The cities of Samsun, Trabzon, Rize, Zonguldak and Corum reached this goal for disposing of medical wastes by 2009.

The Eastern and Southeastern Anatolian Regions

The two regions, located in the eastern and southeastern parts of Turkey, consist of 22 cities. The two regions are the least populated in Turkey and are also the least developed regions. The population of the two regions is 17.7% of the population in Turkey, but the medical waste produced in the region is 13.5% of the medical waste produced in Turkey. The details about

Table 2. Amount of Medical Waste in Aegean Region.

Cities	Number of Bed	Amount of Medical Waste (kg/year)	A.M.W.P.C* (kg/person × year)	2007 Disposal Method	2012 Target Method
Izmir	10.686	5.279.430	1,4	Sanitary landfilling	Sterilization
Manisa	2.943	1.661.972	1,3	Lime desiccation in special lots	Sterilization
Aydin	2.091	1.123.777	1,3	Lime desiccation in special lots	Sterilization
Denizli	1.881	1.078.499	1,3	Sanitary landfilling	Sterilization
Afyonkarahisar	2.087	913.020	1,3	Lime desiccation in special lots	Sterilization
Kutahya	1.581	800.598	1,2	Lime desiccation in special lots	Sterilization
Mugla	1.630	718.864	1,3	Lime desiccation in special lots	No approach indicated
Usak	960	474.148	1,5	Lime desiccation in special lots	Sterilization

*Amount of Medical Waste Per Capita.

Table 3. Amount of Medical Waste in Mediterranean Region.

Cities	**Number of Bed**	**Amount of Medical Waste (kg/year)**	**A.M.W.P.C* (kg/person × year)**	**2007 Disposal Method**	**2012 Target Method**
Adana	4.873	1,45	2.815.593	Lime desiccation in special lots	Sterilization
Antalya	3.632	1,15	1.943.809	Lime desiccation in special lots	Sterilization
Icel	3.002	1,18	1.793.150	Lime desiccation in special lots	Sterilization
Isparta	2.280	2,58	1.026.660	Sanitary landfilling	Sterilization
Hatay	1.791	0,61	779.537	Lime desiccation in special lots	Sanitary landfilling
K.Maras	1.320	0,80	751.028	Lime desiccation in special lots	Sanitary landfilling
Osmaniye	655	0,66	287.708	Lime desiccation in special lots	Sterilization
Burdur	613	1,30	306.965	Lime desiccation in special lots	No approach indicated
Kilis	137	0,62	69.654	Lime desiccation in special lots	Sterilization

*Amount of Medical Waste Per Capita.

the amounts of medical wastes produced in the cities of these regions and their disposal methods have been listed in Table 6. The largest amount of medical wastes is produced in Gaziantep, and the least amount is produced in Tunceli. The method of disposal used in Gaziantep, Malatya and Erzincan was sanitary landfilling, and in the other cities of the regions, lime desiccation in special lots was used. In disposing medical wastes, the cities of Malatya, Adiyaman, Erzincan, Mus, Mardin, Hakkari and Ardahan have not set new goals by 2012. The remaining cities of the region have set their goals in sterilization. As of the year 2009, cities of Gaziantep and Erzurum have reached this goal in disposing medical wastes.

The Disposal of Medical Wastes

The methods used in disposal of medical wastes for all cities in Turkey, as well as the projections for 2012, are provided in Tables 1, 2, 3, 4, 5 and 6. The tables indicate a tendency towards the sterilization method for the treatment of medical wastes in Turkey. The changes that have occurred in methods used in the treatment of medical wastes in Turkey in the years 2007, 2009 and 2012 are described in Figure 2.

CONCLUSTIONS

The number of private and government hospitals in Istanbul and throughout Turkey has constantly been increasing. This has led to an increase in the quantity of medical waste generated. The medical waste management in Turkey is executed according to the "The medical waste management legislation" that was prepared by the Ministry of Environment and Forestry in 2005. This legislation was prepared in accordance with the European Union environmental requirements. In addition, the Ministry of Environment and Forestry has prepared the 2008–2012 Solid Waste Management Action Plan in accordance with the EU adaptation pro-

Table 4. Amount of Medical Waste in Central Anatolia Region.

Cities	**Number of Bed**	**Amount of Medical Waste (kg/year)**	**A.M.W.P.C* (kg/person × year)**	**2007 Disposal Method**	**2012 Target Method**
Ankara	15.990	9.104.939	2,06	Sanitary landfilling	Sterilization
Konya	4.748	2.326.346	1,24	Lime desiccation in special lots	Sterilization
Kayseri	2.966	1.719.919	1,53	Lime desiccation in special lots	Sterilization
Eskisehir	3936	1.782.890	2,51	Lime desiccation in special lots	Sterilization
Sivas	2.354	1.252.339	2,07	Lime desiccation in special lots	Sterilization
Yozgat	948	359.192	0,78	Lime desiccation in special lots	Sanitary landfilling
Aksaray	751	253.180	0,74	Lime desiccation in special lots	Sterilization
Nigde	839	240.404	0,79	Lime desiccation in special lots	No approach indicated
Kırıkkale	670	319.803	1,01	Lime desiccation in special lots	Sterilization
Nevsehir	465	134.731	0,52	Lime desiccation in special lots	Sanitary landfilling
Karaman	473	169.466	0,79	Lime desiccation in special lots	Sterilization
Kırsehir	355	190.801	0,90	Lime desiccation in special lots	Sterilization
Cankiri	449	129.813	0,79	Lime desiccation in special lots	No approach indicated

*Amount of Medical Waste Per Capita.

Table 5. Amount of Medical Waste in Black Sea Region.

Cities	Number of Bed	Amount of Medical Waste (kg/year)	A.M.W.P.C* (kg/person × year)	2007 Disposal Method	2012 Target Method
Samsun	3.936	2.238.631	1,9	Lime desiccation in special lots	Sterilization
Trabzon	2.665	1.469.492	2,1	Lime desiccation in special lots	Sterilization
Zonguldak	1.845	1.019.870	1,8	Lime desiccation in special lots	Sterilization
Ordu	1.757	945.188,95	1,4	Lime desiccation in special lots	Sterilization
Tokat	1.441	845.732	1,4	Lime desiccation in special lots	Sterilization
Corum	1.669	817.666	1,5	Lime desiccation in special lots	Sterilization
Giresun	1.281	587.531	1,5	Lime desiccation in special lots	No approach indicated
Kastamonu	1.187	471.008	1,4	Lime desiccation in special lots	Sterilization
Bolu	1.046	454.986	1,7	Lime desiccation in special lots	No approach indicated
Rize	997	392.021	1,3	Lime desiccation in special lots	Sterilization
Amasya	851	383.862	1,2	Lime desiccation in special lots	Sterilization
Karabuk	775	323.501	1,5	Lime desiccation in special lots	Sterilization
Duzce	498	243.778	0,8	Lime desiccation in special lots	Sterilization
Bartin	473	214.756	1,3	Lime desiccation in special lots	No approach indicated
Sinop	559	182.685	0,8	Lime desiccation in special lots	No approach indicated
Artvin	486	148.068	0,9	Lime desiccation in special lots	Sterilization
Gumushane	314	115.259	0,9	Lime desiccation in special lots	Sanitary landfilling
Bayburt	150	89.064	1,2	Lime desiccation in special lots	Sanitary landfilling

*Amount of Medical Waste Per Capita.

Table 6. Amount of Medical Waste in East and Southeast Anatolia Regions.

Cities	Number of Bed	Amount of Medical Waste (kg/year)	A.M.W.P.C* (kg/person × year)	2007 Disposal Method	2012 Target Method
Gaziantep	2.295	1.806.611	1,18	Sanitary landfilling	Sterilization
Erzurum	3.208	1.721.736	2,33	Lime desiccation in special lots	Sterilization
Diyarbakir	2.629	1.483.119	1,08	Lime desiccation in special lots	Sterilization
Elazig	2.577	1.344.433	2,59	Lime desiccation in special lots	Sterilization
Malatya	2.079	1.055.448	1,54	Sanitary landfilling	No approach indicated
Van	1.684	984.779	1,08	Lime desiccation in special lots	Sterilization
Sanliurfa	1.519	816.244	0,57	Lime desiccation in special lots	Sterilization
Adiyaman	705	354.292	0,65	Lime desiccation in special lots	No approach indicated
Bingol	653	315.821	1,34	Lime desiccation in special lots	Sterilization
Erzincan	754	284.085	1,43	Sanitary landfilling	No approach indicated
Mus	674	252.403	0,69	Lime desiccation in special lots	No approach indicated
Mardin	407	241.732	0,35	Lime desiccation in special lots	No approach indicated
Agri	441	186.821	0,38	Lime desiccation in special lots	Sterilization
Kars	468	170.621	0,6	Lime desiccation in special lots	Sterilization
Batman	236	139.694	0,31	Lime desiccation in special lots	Sterilization
Bitlis	452	130.474	0,43	Lime desiccation in special lots	Sterilization
Hakkari	214	102.019	0,44	Lime desiccation in special lots	No approach indicated
Siirt	220	98.053	0,36	Lime desiccation in special lots	Sterilization
Sırnak	165	95.852	0,24	Lime desiccation in special lots	Sterilization
Ardahan	191	70.627	0,4	Lime desiccation in special lots	No approach indicated
Igdir	926	68.300	0,4	Lime desiccation in special lots	Sterilization
Tunceli	107	30.449	0,38	Lime desiccation in special lots	Sterilization

*Amount of Medical Waste Per Capita.

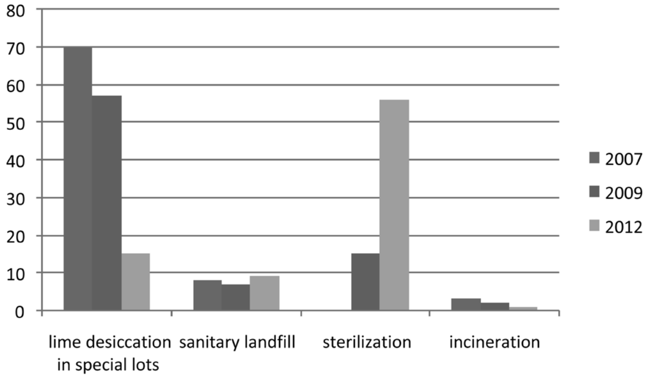

Figure 2. *Disposal method distributions in Turkey during 2007, 2009 and 2012.*

cess. The following conclusions and recommendations can be extracted from this work that was prepared according to the aforementioned legislation and action plan:

- The amount of medical waste produced in Turkey per person is 0.25–2.6 kg yearly. These figures show parallelism with the populations and the hospital bed capacities of the cities. The medical waste production, per person in the cities of the Eastern and Southeastern Anatolian regions, is much lower when compared to the other regions. This might be an indication of the lack of a high quality health service in the regions.
- The most common method used in medical waste disposal in Turkey is lime desiccation in special lots. This method is not suitable in the long term for human health and the environment. This method should be replaced with healthier methods such as incineration or sterilization. There is a tendency towards these methods in Turkey. While the sterilization method was not used in any of the cities in 2007, 15 cities have started using this method as of 2009. The target for the number of cities that use the sterilization method is 56 by 2012.
- Throughout the survey for the country, most of the cities in Turkey are aiming towards using a healthier method in disposing of medical wastes by the year 2012. Some cities have already reached this goal as of 2009. The Ministry of Environment and Forestry should develop new projects for the cities that have not fulfilled their goals, or that have not stated any goals for the year 2012; moreover, it should support these cities in their transition to healthier methods of medical waste disposal.
- Since medical wastes are disposed of separately, they should also be collected separately in their source. The health establishments responsible for the separate collection of the medical wastes in their source should train their personnel about these issues.
- The transportation of the medical wastes from the temporary storage facilities to removal facilities should be done by specially designed vehicles, and the personnel that operate these vehicles should receive the necessary training and orientation.

As the human health is very important, all of these precautions should be taken and all the improvements should be fulfilled as soon as possible. Otherwise, the budget to recover the damages will be very high.

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Comparison of Three Treated Pulp and Paper Sludges as Adsorbents for RB19 Dye Removal

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ABSTRACT: Three types of treated pulp and paper sludge as adsorbents were compared for reactive blue 19 dye removal. Dye removal efficiency was obtained 99.4%, 69.1%, and 24.6% at a natural pH for adsorbents treated using $ZnCl_2$, HCl, and NaOH, respectively. With an increase of initial dye concentration, Q increased and reached maximum values of 47.7, 35.6, and 18.7 mg/g for treated adsorbents, respectively. The adsorption process follows the Freundlich isotherm model and the pseudo-second order kinetic model. For real wastewater, dye removal efficiency was obtained 45.7%, 64.4%, and 20.5% for the treated adsorbents, respectively.

INTRODUCTION

DYES are widely used in industries such as textiles, leather, printing, cosmetics, food, plastics and a variety other applications [1,2]. Various dyes usually have a synthetic origin and complex chemical structure that may be mutagenic and carcinogenic. Therefore, effluents that contain dyes must be treated before discharging into bodies of water, to avoid environmental problems [2].

Many methods are reported to remove dyes from effluents and the technologies can be divided into three categories including [3,4]: (i) physical methods, (ii) chemical methods, and (iii) biological degradation. Among the various available technologies, the adsorption process is considered preferable because of convenience, ease of operation and the simplicity of design [5]. Adsorption on various activated carbons is widely used for removal of dyes, but is considered to be expensive adsorbents [1].

Some investigations have been reported using nonconventional, low-cost adsorbents for dye removal such as pistachio nut shell [6], almond shell [7], metal hydroxide sludge [8], sewage sludge [9], and wood waste [10]. Additionally, various agents including different acids, bases and salts such as NaOH, HCl, and $ZnCl_2$ were used for the treatment of different adsorbents to increase dye removal efficiency [11,12].

Management of pulp and paper sludge in recent years has become a significant environmental issue due to the quantity of sludge generated and its disposal. Some investigations have proposed different applications of this sludge, such as a soil improver, fertilizer, or building material [13]. In our previous study, performance of pulp and paper sludge on reactive blue 19 (RB19) dye adsorption was tested [14].

The aim of this study is to compare potential of the three types of treated pulp and paper sludge as alternative adsorbents for removal of RB19 dye. Effects of contact time, initial pH, adsorbent dose and initial dye concentration on performance of the adsorption process were studied. Isotherm and kinetic studies were performed in addition. Treatment of real textile wastewater was then examined for all adsorbents. More investigation regarding negative and positive effects and economics' discussion are needed.

MATERIALS AND METHODS

Preparation of Synthetic Wastewater

RB19 (Ariazol Brill. Blue R-SP) was provided by the Alvan Sabet Company in Iran and is used for preparation of synthetic wastewater. General properties for RB19 are: empirical formula = $C_{22}H_{16}N_2Na_2S_3$, mo-

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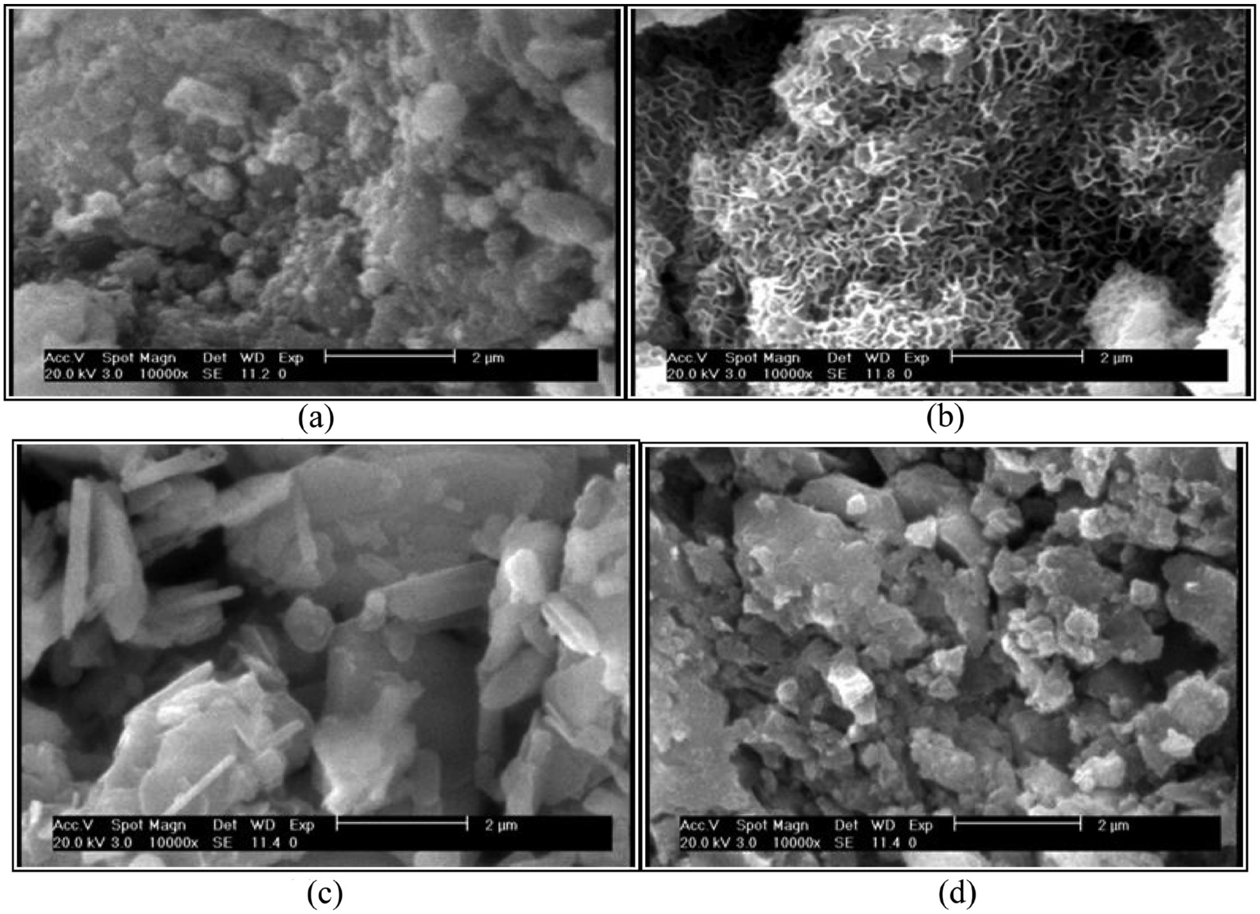
lecular weight (MW) = 626.54, and λ_{max} = 594 nm. This dye is widely used in textile industries in Iran. A Stock dye solution of 1000 mg/L was prepared in double distilled water and then diluted to obtain desired concentration.

Real textile wastewater containing RB19 was collected from Negin-Nakhe-Beshel Company, in Mazandaran, which is North of Iran. This real wastewater has some additives including NaCl, Na_2CO_3, caustic NaOH, cationic ion exchange, detergent (ABS), cationic softener, antifoam, and other chemical agents. Characteristics for the real textile wastewater are: RB19 concentration = 500 mg/L, pH = 10, COD (chemical oxygen demand) = 1000 mg/L, and NTU (nephelometric turbidity unit) = 7.9.

Preparation and Characterization of Adsorbents

Pulp and paper sludge used in this study was collected from Mazandaran wood and paper industries (MWPI) in Mazandaran. This factory is the largest paper manufacture in Iran, and produces 100–120 tons of air-dried sludge daily. Collected sludge was dried at room temperature for 48 hours in a laboratory, then ground, and then sieved by 150 µm sieve. Sludge particles less than the 150 µm sieve soaked in solutions of 3M $ZnCl_2$, H_2SO_4, and NaOH and were kept at room temperature for 24 hours. Resulting materials were washed with double distilled water, dried in an oven at 50°C overnight, ground, and sieved by a 150 µm sieve. The Three types of treated sludge less than the 150 µm sieve were used as adsorbents for further experiments. Treated pulp and paper sludge with $ZnCl_2$, H_2SO_4, and NaOH are termed ZTPPS, ATPPS, and BTPPS, respectively.

As determined by XRF, using a X"Uniqe model XRF analyzer (Philips, Netherlands), chemical composition of dried pulp and paper sludge was 9.7% Al_2O_3, 0.27% Fe_2O_3, 16.4% CaO, 1.46% MgO, 3.8% SiO_2, 3.52% SO_3, 0.11% Na_2O, 0.12% K_2O, and 0.2% P_2O_5. The loss on ignition (LOI) of pulp and paper sludge was found to be 64.25% by weight. A scanning electron microscope (SEM) was also used to characterize the samples for the morphological information using a XL-C model SEM analyzer (Philips, Netherlands). SEM images (Figure 1) show porous morphology of



(a) (b)

(c) (d)

Figure 1. SEM images of the pulp and paper sludge (a) before and after treated using (b) $ZnCl_2$, (c) H_2SO_4, and (d) NaOH.

Table 1. Textural Properties Obtained by N_2 Adsorption/Desorption Studies.

Parameters		ZTPPS	ATPPS	BTPPS
BET surface area (m^2/g)	BET[a]	3.94	12.76	10.31
Pore volume (cm^3/g)	BJH adsorption[b]	0.0568	0.0396	0.0562
Pore diameter (Å)	BJH adsorption	24.98	27.85	24.94

[a] Computed in the P/P_0 range 0.05–0.30.

[b] BJH (Barrett Joyner Halenda) cumulative adsorption pore volume for pores in range of 0 and 5000Å diameter.

the three treated adsorbents, as well as dried sludge (without any treatment) with pores of different sizes and shapes. The textural properties of adsorbents were also carried out by N_2 adsorption/desorption isotherms at 77K using an Autosorb 1 analyzer (Quantachrome Corporation, USA). The specific surface area was calculated by Brunauer–Emmett–Teller (BET) method that is termed S_{BET}. The textural Characteristics of the adsorbents are presented in Table 1.

Adsorption Batch Experiments

The dye solutions and adsorbents were agitated by a jar test at 150 rpm agitation speed. A Six beaker jar test apparatus from Zag-Chemi Company in Iran was used to simulate the adsorption process. All samples were centrifuged at 5000 rpm for 10 minutes prior to analysis. The dye concentration of the synthetic wastewater and the real textile wastewater were measured using a HACH spectrophotometer DR/4000 (USA) at a wavelength corresponding to the maximum absorbance 594 nm (λ_{max}) for RB19. The pH measurement was carried out using a 340i/SET pH meter (WTW-Germany). The initial solution pH was adjusted with dilute HCl and NaOH. All experiments, except the study of pH effect, were performed at natural pH of solutions, which are about 7, 3, and 10 for the experiments of ZTPPS, ATPPS, and BTPPS, respectively. Additionally, effectiveness of different pH (2–12) on stability and dye adsorption of RB19 were also investigated. Quite stable in this range of pH was observed for RB19 dye. A Similar result has been reported by Mahmoud et al. (2007) for RB 19 dye [15]. The observed dye removal is a result of adsorption process. The sorption studies were carried out at 23±1°C. Percentage of dye removal was calculated by the following equation:

$$\text{Dye removal (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \qquad (1)$$

where, C_0 and C_t (mg/L) are the initial dye concentration and concentration at equilibrium time t (min), respectively.

RESULTS AND DISCUSSIONS

Effect of Contact Time on Dye Adsorption

Contact time is one of the most important parameters in the design of economical dye wastewater treatment systems. As shown from the Figure 2, the adsorption efficiency increased with the increase of contact time in the first minutes rapidly. The rate of adsorption was found to be slow and then became approximately constant, Similar trends were also presented by our research group for wood waste [10] and dried pulp and paper sludge [14] as well as other researcher for different types of dyes using activated carbon from orange peel [16]. As seen from the Figure 2, the percentage of RB19 removal was obtained 99.4%, 70.2%, and 24.2% at 30 minutes of contact time for ZTPPS, ATPPS, and BTPPS, respectively. Regarding the obtained results, 30 minutes of contact time was selected for the further experiments.

Effect of Adsorbents Dose on Dye Adsorption

The effect of the adsorbents dose on RB19 adsorption is presented in Figure 3. Figure 3 data indicates the percentage of the dye removal increased with the increase of the adsorbents dose. Increases in the percentage of the dye removal with adsorbents dose could be attributed to increases in the adsorbent surface areas, augmenting the number of adsorption sites available for adsorption [17]. Increases in the percentage of the dye removal efficiency for the removal of acid violet 17 dye with activated carbon prepared from pistachio

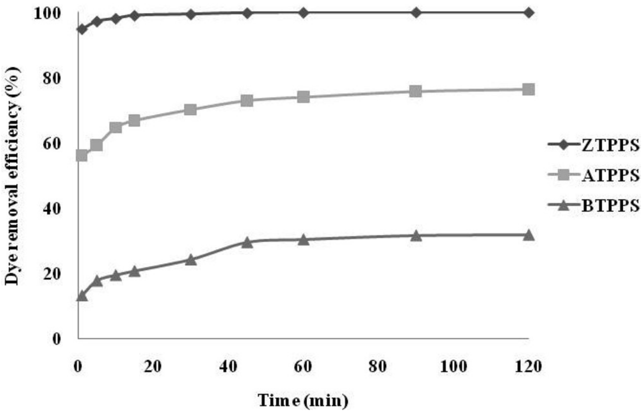


Figure 2. Effect of contact time on RB19 adsorption (Initial dye concentration = 100 mg/L, Adsorbent dose = 6 g/L, pH = natural).

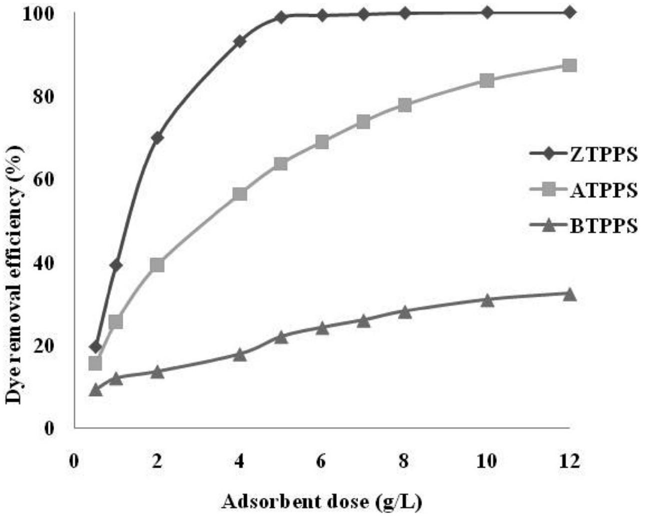


Figure 3. Effect of adsorbents dose on RB19 adsorption (Initial dye concentration = 100 mg/L, Contact time = 30 min, pH = natural).

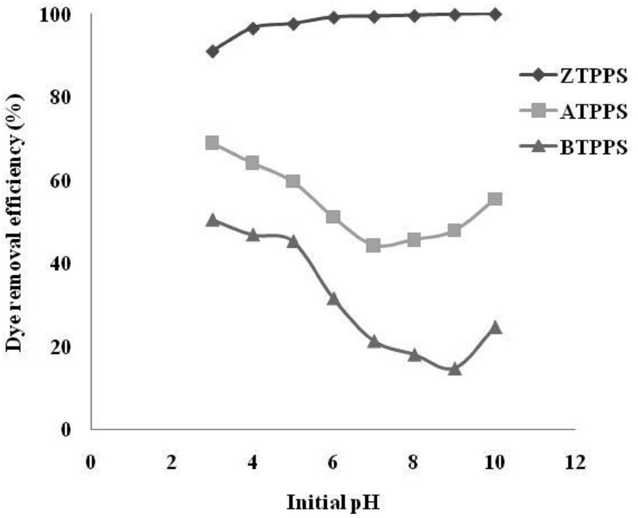


Figure 4. Effect of initial pH on RB19 adsorption (Initial dye concentration = 100 mg/L, Adsorbent dose = 6 g/L, Contact time = 30 min).

nut shell [18], and for the removal of brilliant green dye with homemade activated carbons [19], were reported. Similar trends have also been reported using classical [14] and statistical [20] methods in our previous papers. Maximum removal efficiency was obtained 100%, 87.3%, and 32.4% at a 12g/L dose of ZTPPS, ATPPS, and BTPPS, respectively. For this study, 6g/L dose of adsorbents was chosen as adsorbent dose for the experiments.

Effect of Initial pH on Dye Adsorption

The pH of the solution plays an important role in the adsorption process. Figure 4 illustrates the behavior of ZTPPS under the effect of pH was different than ATPPS and BTPPS. The highest adsorption efficiency of ZTPPS may be due to the reaction between the negative charge in the dye molecule and Zn^{2+} charged adsorbent's surface. Under alkaline, neutral, and acidity conditions, the change of initial pH had no significant effect on the adsorption for RB19 onto ZTPPS and only about 8% difference between the minimum and the maximum adsorption was observed. For ATPPS and BTPPS, at low pH, maximum observed adsorption capacity may be due to the electrostatic attractions between negatively charged $-SO_3^-$ groups in the dye molecule and positively charged adsorbent's surface [21]. Lower adsorption at alkaline pH than acidity pH may be due to the presence of excess of OH^- ions competing with the dye anions for the adsorption sites [22]. Similar results were observed by our research group as well as other researcher for the removal of different types of dyes [10,14,23]. The dye removal efficiency was obtained 99.4%, 69.1%, and 24.6% at natural pH for ZTPPS, ATPPS, and BTPPS, respectively. In our previous study, the maximum and the minimum percentage of RB19 dye removal using pulp and paper sludge were observed 92.3% and 15.1% at optimum pH (pH = 3) and natural pH (pH = 8), respectively [14].

Effect of Initial Dye Concentration on Dye Removal

As displayed in Figure 5 for ZTPPS and ATPPS, removal efficiency decreased with an increase of initial dye concentration. This may be due to saturation of surface area and active sites on adsorbents [24]. Similar results were observed by other researchers for the removal of different types of dyes [24,25]. Compara-

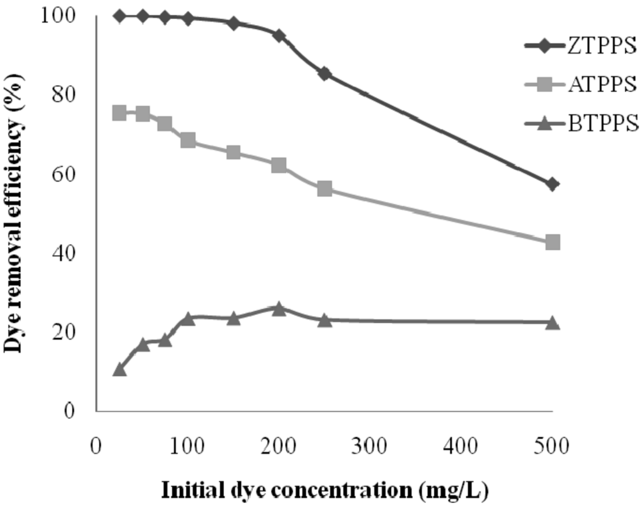


Figure 5. Effect of initial dye concentration on RB19 adsorption (Adsorbent dose = 6 g/L, Contact time = 30 min, pH = natural).

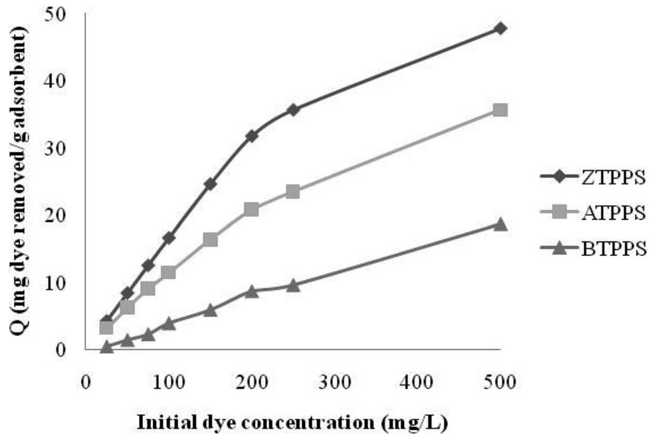


Figure 6. *Effect of initial dye concentration on Q (Adsorbent dose = 6 g/L, Contact time = 30 min, pH = natural).*

tively, removal efficiency increased with the increase of the initial dye concentration from 25 mg/L to 200 mg/L and then decreased for BTPPS. At lower initial dye concentration, sufficient adsorption sites with the maximum adsorption potential are available for sorption of dye molecules. During higher concentrations the ratio of number of dye molecules to available adsorption sites is high and consequently removal efficiency of dye decreases [26]. Similar results were also observed in previous works as well as for other researchers regarding removal of different types of dyes [10,14,27].

Variations of amount of removed dye per unit mass of adsorbent (Q) versus initial dye concentration are displayed in Figure 6. Q increased with an increase of dye concentration. A similar result was presented by other researcher for Remazol Black B dye removal using cotton plant wastes [28]. Maximum Q was obtained 47.7, 35.6, and 18.7 mg removed dye/g for ZTPPS, ATPPS, and BTPPS, respectively.

Adsorption capacity for three adsorbents in this study regarding RB19 dye removal in comparison with adsorption capacity of activated carbon from bagasse pith using KOH (21.5 mg/g) [29], modified silk cotton hull waste by H_3PO_4 (12.9 mg/g) [30], and activated carbon prepared from bamboo waste (39.02 mg/g) [31] is acceptable. It is clear that treatment of pulp and paper sludge effected size and shape of pores and textural properties. As demonstrated in this paper, treated adsorbent with $ZnCl_2$ had maximum dye removal efficiency and adsorption capacity for synthetic wastewater. More investigation (i.e., economics related discussion) is needed in full scale and for optimum condition based on chemical agent consumption.

Adsorption Isotherms Study

In this study, three important isotherms, Langmuir, Freundlich, and Temkin isotherms are applied. The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface. Employing the Langmuir theory, the basic assumption is that sorption takes place at specific homogeneous sites within the adsorbent [32]. The Temkin isotherm assumes that (1) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent/adsorbate interactions, and that (2), the adsorption is characterized by a uniform distribution of binding energies, up to a maximum binding energy [33]. The isotherms parameters are explained in Table 2 [34].

In order to obtain an interaction between the adsorbent and adsorbate, adsorption isotherm studies were conducted with the different adsorbent doses that ranging from 0.5 to 12 g/L at natural pH. Isotherms constants and correlation coefficient (R^2) are presented in Table 3. Results are shown that the Freundlich adsorption isotherm was the best model for the dye adsorption on ZTPPS, ATPPS, and BTPPS with R^2 of 0.991, 0.993, and 0.993, respectively.

Table 2. Isotherm Equations.

Isotherm Name	Isotherm Equation	Parameters
Langmuir isotherm	$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m}$ (2)	C_e = concentration of dye at equilibrium (mg/L) q_e = amount of dye adsorbed per amount of adsorbent at equilibrium (mg/g) K_L = Langmuir adsorption constant (L/mg) Q_m = theoretical maximum adsorption capacity (mg/g)
Freundlich isotherm	$\log q_e = \log K_F + \frac{1}{n}\log C_e$ (3)	C_e = concentration of dye at equilibrium (mg/L) q_e = amount of dye adsorbed per amount of adsorbent at equilibrium (mg/g) K_F = an indicator of the adsorption capacity (L/mg) n = adsorption intensity
Temkin isotherm	$q_e = B_1 \ln K_T + B_1 \ln C_e$ (4)	C_e = concentration of dye at equilibrium (mg/L) q_e = amount of dye adsorbed per amount of adsorbent at equilibrium (mg/g) K_T = equilibrium binding constant (L/mg) B_1 = heat of adsorption

Table 3. Adsorption Isotherm Constants.

	Adsorbents		
Isotherm Type	**ZTPPS**	**ATPPS**	**BTPPS**
Langmuir			
K_L (L/mg)	0.19	0.006	–0.05
Q_m (mg/g)	66.7	83.3	–28.8
R^2	0.954	0.864	0.940
Freundlich			
K_F (L/mg)	14.8	0.8	0.02
n	2.9	1.3	0.7
R^2	0.991	0.993	0.993
Temkin			
K_T (L/mg)	4.7	0.09	0.03
B_1	9.9	12.7	12.6
R^2	0.927	0.960	0.969

Adsorption Kinetics Study

Several kinetic models are available to understand the behavior of the adsorbents and examine the controlling mechanism of the adsorption process [35]. In this investigation four different kinetic models, namely the pseudo-first order, pseudo-second order, the Elovich models, and Intra-particle diffusion model were tested. The kinetics parameters are explained in Table 4 [34]. In order to investigate the mechanism of sorption, the kinetics parameters for the adsorption process were also studied for contact time ranging from 1 to 120 minutes. Kinetics constants and correlation coefficient (R^2) are presented in Table 5. Results show the adsorption process follows a pseudo-second order model with R^2 of 1, 0.999, and 0.994 for ZTPPS, ATPPS, and BTPPS, respectively. As seen from Table 5, if *I* is equal to zero, the only controlling step is intraparticle diffusion. If *I* ≠ 0, this indicates adsorption process is rather complex and involves more than one diffusive resistance [36].

Treatment of Real Textile Wastewater Using ZTPPS, ATPPS, and BTPPS

The experiments of the real textile wastewater containing RB19 dye were also performed under the obtained experimental conditions including contact time (30 min), and adsorbent dose (6 gr/L), initial pH (natural) while, the initial dye concentration of the real textile wastewater was 500 mg/L. The dye removal efficiency of the real wastewater was obtained 45.7%, 64.4%, and 20.5% for ZTPPS, ATPPS, and BTPPS, respectively. In addition, Q (the adsorption capacity) was obtained 38, 53.6, and 17.1 mg/g for ZTPPS, ATPPS, and BTPPS, respectively.

CONCLUSIONS

In this study, the effect of contact time, pH, adsorbent dose and initial dye concentration on the performance of the adsorption process using the three treated pulp and paper sludge were studied. Results from this study show rapid adsorption was observed in the first minutes of contact time and then became constant. Dye removal efficiency was observed 99.4%, 69.1%, and 24.6% at natural pH for ZTPPS, ATPPS, and BTPPS, respectively. Dye removal efficiency increased at the higher dose of adsorbents and the maximum removal efficiency was obtained 100%, 87.3%, and 32.4% at 12 g/L dose of ZTPPS, ATPPS, and BTPPS, respectively. Q increased with the increase of initial dye concentration and reached 47.7, 35.6, and 18.7 mg removed dye/g ZTPPS, ATPPS, and BTPPS, respectively.

The adsorption isotherm and the adsorption kinetic were found to follow Freundlich adsorption isotherm and pseudo-second-order rate kinetic model. For the real textile wastewater containing RB 19, the dye removal efficiency was obtained 45.7%, 64.4%, and 20.5% for ZTPPS, ATPPS, and BTPPS, respectively.

Table 4. Kinetics Equations.

Kinetic Name	Kinetic Equation	Parameters
Pseudo-first order	$\log(q_e - q_t) = \log(q_e) - \frac{K_t}{2.303}t$ (5)	q_t = amount of dye adsorbed per amount of adsorbent at t (min) (mg/g) q_e = amount of dye adsorbed per amount of adsorbent at equilibrium (mg/g) K_1 = rate constant (1/min)
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t$ (6)	q_t = amount of dye adsorbed per amount of adsorbent at t (min) (mg/g) q_e = amount of dye adsorbed per amount of adsorbent at equilibrium (mg/g) K_2 = rate constant (g/mg.min)
Elovich model	$q_t = a + b\ln t$ (7)	q_t = amount of dye adsorbed per amount of adsorbent at t (min) (mg/g) a,b = constants
Intra-particle diffusion model	$q_t = K_i t^{0.5} + I$ (8)	q_t = amount of dye adsorbed per amount of adsorbent at t (min) (mg/g) K_i = intra-particle diffusion rate constant (mg/g.min(1/2)) I = the intercept

Table 5. Adsorption Kinetic Constants.

Kinetic Type	Adsorbents		
	ZTPPS	**ATPPS**	**BTPPS**
Pseudo-first order model			
K_1 (1/min)	0.018	0.037	0.014
R^2	0.98	0.99	0.955
Pseudo-second order model			
K_2 (g/mg.min)	0.33	0.04	0.02
R^2	1	0.999	0.994
Elovich model			
a	16.2	8.7	2.4
b	0.08	0.89	0.87
R^2	0.951	0.984	0.959
Intra-particle diffusion model			
K_i (mg/g.min$^{(1/2)}$)	0.04	0.38	0.34
I	16.3	9.2	2.8
R^2	0.971	0.873	0.961

In addition, Q was obtained 38, 53.6, and 17.1mg/g for ZTPPS, ATPPS, and BTPPS, respectively for the removal of real wastewater.

Three types of treated pulp and paper sludge obtained in this study showed acceptable adsorption capacities for the RB19. It can be concluded that the different types of treated pulp and paper sludge can be considered as appropriate alternative and effective adsorbents for the dye removal as well as removal of real textile wastewater.

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LIST OF SYMBOLS

ATPPS: acid treated pulp and paper sludge
BET: Brunauer–Emmett–Teller
BJH: Barrett Joyner Halenda
BTPPS: basic treated pulp and paper sludge
LOI: loss on ignition
MW: molecular weight
MWPI: Mazandaran wood and paper industries
NTU: nephelometric turbidity unit
RB19: reactive blue 19
SEM: scanning electron microscope
XRF: X-ray fluorescence spectrometry
ZTPPS: $ZnCl_2$ treated pulp and paper sludge

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Simultaneous Determination of Residues of Chloramphenicol and Florfenicol in Animal Feed by Liquid Chromatography Tandem Mass Spectrometry

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ABSTRACT: A LC/MS/MS method was developed for determining florfenicol and chloramphenicol in animal feed. The analytes were extracted with ethyl acetate, and the extracts were evaporated to dryness. The residue was dissolved in acetone-hexane mixture and passed through a silica cartridge and a SPE cartridge. The collected eluant was evaporated and the residue was dissolved in acetonitrile-water mixture for injecting LC/MS/MS. The LC separation was performed on a Shim-pack XR-ODS II column with a gradient mobile phase system of ammonium formate-acetonitrile. The recoveries of florfenicol and chloramphenicol were 94.7–114%. The limits of detection were 0.5 ng/g for both compounds.

INTRODUCTION

FLORFENICOL (FF) and chloramphenicol (CAP) are broad spectrum antibiotics belonging to a group of phenicol antibiotics, which have been approved for use in domestic animals in many countries. Since FF is rapidly metabolized to a dominant metabolite, florfenicol amine, the sum of FF and florfenicol anime is used as the marker residue for animal species in the EU, United States, Australia, and New Zealand. On the other hand, FF is used as the marker residue in Taiwan, Japan, and Canada. In Japan, the maximum residue limits (MRLs) of FF are 0.03–3 ppm in food, while CAP is listed as one of the substances that is stipulated to be "not detected" in foods [1]. Both FF and CAP are stipulated to be "not detected" in animal feed [2]. Dried skim milk and dried whey for feed imported from Ukraine were found to be contaminated with CAP in September 2008. This caused shutdown of shipments and recall of the contaminated materials and compound feed containing them. This kind of contamination could happen in FF.

Various methods have been reported for determination of CAP and/or FF in materials of animal origin, such as capillary electrophoresis [3], micellar electrokinetic chromatography [4], liquid chromatography (LC) [5-9], LC/mass spectrometry (LC/MS) [10], LC/MS/MS [11], gas chromatography (GC) [12, 13], and GC/MS [14]. However, there is no method for simultaneous analysis of chloramphenicol and florfenicol in animal feed. Since animal feed may contain materials which are inhibiters of analysis, we cannot simply apply the existing methods to feed. For example, one of the feed ingredients, dried skim milk, is easily clamped by acetonitrile, which inhibits extraction. Ono *et al.* indicated LC determination of FF in animal feed is susceptible to feed derived inhibitors, since the chromatogram was fluctuated [8]. Some of the existing methods using reagents, such as dichloromethane, should preferably not be used according to "Green Sustainable Chemistry" and a relevant law in Japan [15].

The purpose of the present study was to develop a rapid, routine, and efficient method for the simultaneous determination of residues of FF and CAP in animal feed by LC/MS/MS, without using any harmful reagents.

MATERIALS AND METHODS

List of Experimental Apparatus

1. Shaker—SR-2DW (Taitec, Saitama, Japan).
2. Filter funnel—Kiriyama Rohto Model S-60 (Kiriyama, Tokyo, Japan)
3. Rotary evaporator—R-200 (Büchi, Flawil, Switzerland).
4. Macroporous diatomaceous earth column—Extube

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Extraction Columns Chem Elut (Varian, Palo Alto, CA).
5. Silica cartridge—Sep-Pak Plus Silica Cartridge (Waters, Milford, MA) .
6. SPE cartridge.—Supelclean ENVI-Carb SPE Tubes (Sigma-Aldrich, St. Louis, MO).
7. HPLC column—Shim-pack XR-ODS II, 150 × 2 mm id, 2.1 µm particle size (Shimadzu, Kyoto, Japan).
8. HPLC system—Agilent 1200 Series LC system (Agilent, Santa Clara, CA).
9. MS/MS system—Agilent 6410 Triple Quad LC/MS system (Agilent, Santa Clara, CA).

List of Chemicals and Solutions

1. Water—HPLC grade, purified using Milli-Q Integral 5 water purification system.
2. Acetonitrile, ethyl acetate, hexane, and acetone—HPLC grade (Kanto chemical, Tokyo, Japan).
3. Analytical standards—FF and CAP (Wako, Osaka, Japan)
4. Internal standard—100 µg/mL CAP-d_5 (Wako, Osaka, Japan)
5. Stock solutions of analytical standards—100 µg/mL. Prepare individual stock standards by dissolving 20 mg FF and CAP in acetonitrile, and dilute to volume in separate 200 mL volumetric flasks. Keep refrigerated.
6. Mixed standards—0.5 µg/mL. Dilute 1.0 mL of each stock solution to volume with acetonitrile in a 200 mL volumetric flask.
7. Working internal standard—Internal standard solution A: 100 ng/mL. Dilute internal standard with acetonitrile. Internal standard solution B: 10 ng/mL. Dilute internal standard solution A with ethyl acetale.
8. Standard curve solutions—0.5, 2, 5, 10, and 20 ng/mL of standards, each standard solution containing 5 ng CAP-d5. Mix a certain amount of mixed standards and internal standard A, and dilute with acetonitrile–water (3 + 7).
9. HPLC mobile phase—Solvent A: 10 mmol/L ammonium formate solution; Solvent B: acetonitrile.

Animal Feed and Feed Material

Formula feed, fish meal, and dried skim milk were obtained from feed manufacturers. Each composition of the formula feed samples is shown in Table 1. These samples were ground to particles less than 1 mm in diameter with an ultracentrifugal mill (ZM200, Retsch, Haan, Germany).

Sample Preparation

Extraction

Weigh 2 g sample into a 100 mL erlenmeyer flask. Add 1 mL internal standard solution B and 50 mL ethyl acetate to the flask, and extract by shaking vigorously for 30 min. Place a 200 mL recovery flask under a filter funnel and filter the mixture by suction filtration

Table 1. Compositions of Frmula Feeds Used in this Study.

Types	Ingredient Types	Ingredients	Proportion (%)
Formula feed for suckling pig	Animal by-products	Dried skimmilk, Dried whey, fish meal, Whey protein concentrate Plasma protein concentrate	38
	Grains	Extruded wheat, Extruded corn, Wheat flour, Corn starch	36
	Oil meal	Soybean meal, Soybean protein concentrate	7
	Others	Glucose, Animal fat, Sugar, Vegetable oil, Yeast extract, Calcium phosphate, Fossil shells powder, Salt, Calcium carbonate, Hawthorn powder, diatomite, fructo-oligosaccharide syrup, Lactic acid, Green tea extract, Garlic powder, Citric acid, Desugared sugarcane extract, Fermented soybean, Buckwheat flour, Enzyme-treated feed yeast, Feed yeast, Fermented milk powder, Fatty acid calcium, Grass bacillus, Bifidus cell powder, Feed additives	19
Formula feed for fish (porgy)	Animal by-products	Fish meal	50
	Grains	Wheat flour, Lupine	32
	Oil meal	Defatted rice bran, Corn gluten meal, Soybean meal	11
	Others	Fish oil, Calcium phosphate, Liquorice extract, Garlic powder, Sea weed meal, Betaine, Feed yeast, Feed additives	7

Table 2. MS/MS Parameters.

Substance	Precursor (m/z)	Product (m/z)	Qualifier (m/z)	Collision (eV)
FF	356	185	121	20
CAP	321	152	119	20
CAP-d_5	326	157	–	15

through a filter paper (No. 5B). Wash the Erlenmeyer flask with 50 mL ethyl acetate, and filter the wash into the into the recovery flask. Evaporate sample solution to dryness at 40°C in a water bath and dry with nitrogen. Dissolve the residue with 5 mL hexane–acetone (17 + 3).

Cleanup

Add the solution to a silica cartridge washed with 5 mL hexane–acetone (17 + 3) beforehand. Wash the recovery flask the sample residue was in with 2 successive 5 mL hexane–acetone (17 + 3) portions, each successive ethyl acetate being added to the silica cartridge as the previous one drained through. Connect a SPE cartridge that has been washed with 5 mL hexane–acetone (7 + 3) beforehand under the silica cartridge. Place a 50 mL recovery flask under the column and add 20 mL hexane–acetone (7 + 3) to the column. Evaporate to dryness at 40°C in a water bath and dry with nitrogen. Dissolve the residue with 2 mL acetonitrile–water (3 + 7), centrifuge at 5,000 ×g for 5 min, and analyze the supernatant by LC/MS/MS.

Operating Conditions

LC was performed using an Agilent 1100 series LC system, and mass detection was performed with LC/MS/MS in negative ion mode. A 20 µL sample was loaded onto a Shim-pack XR-ODS II column (150 × 2 mm id, 2.1 µm) at 40°C. Linear gradient was constructed as follows at a flow rate of 0.18 mL/min: 30% Solvent B for 1 min; to 95% Solvent B in 10 min; to 30% Solvent B in 0.1 min; equilibrate for 10 min.

The nebulizer gas of the mass detector interface was nitrogen at 60 psi, the drying gas was nitrogen at 10 L/min at 350°C, and the capillary voltage and fragmenter voltage were set to 4.0 kV and 100 V, respectively. The mass spectrometer was used in selected reaction monitoring (SRM) mode. Precursor ions, product ions, and qualifier ions collision energies are presented in Table 2.

RESULTS AND DISCUSSION

Extraction and Operating Parameters

We tried to use 50 mL acetonitrile, 10 min swelling pretreatment by water (5, 10, 15, or 20 mL) and 50 mL acetonitrile, and 50 mL methanol-1%metaphosphoric acid (3 + 2). All of them were failed to use for dried skim milk extraction because of lumps.

Precursor ions, product ions, and qualifier ions were determined by scan mode of LC/MS/MS. Collision energies were determined by changing the parameter as follows, FF: 15, 20, 25; CAP: 15, 20, 25; CAP-d5: 10, 15, 20. The most sensitive parameters were adopted.

Native FF and CAP contaminated samples could not be acquired so far. We plan to acquire them and confirm applicability of this method.

Linearity of Standard

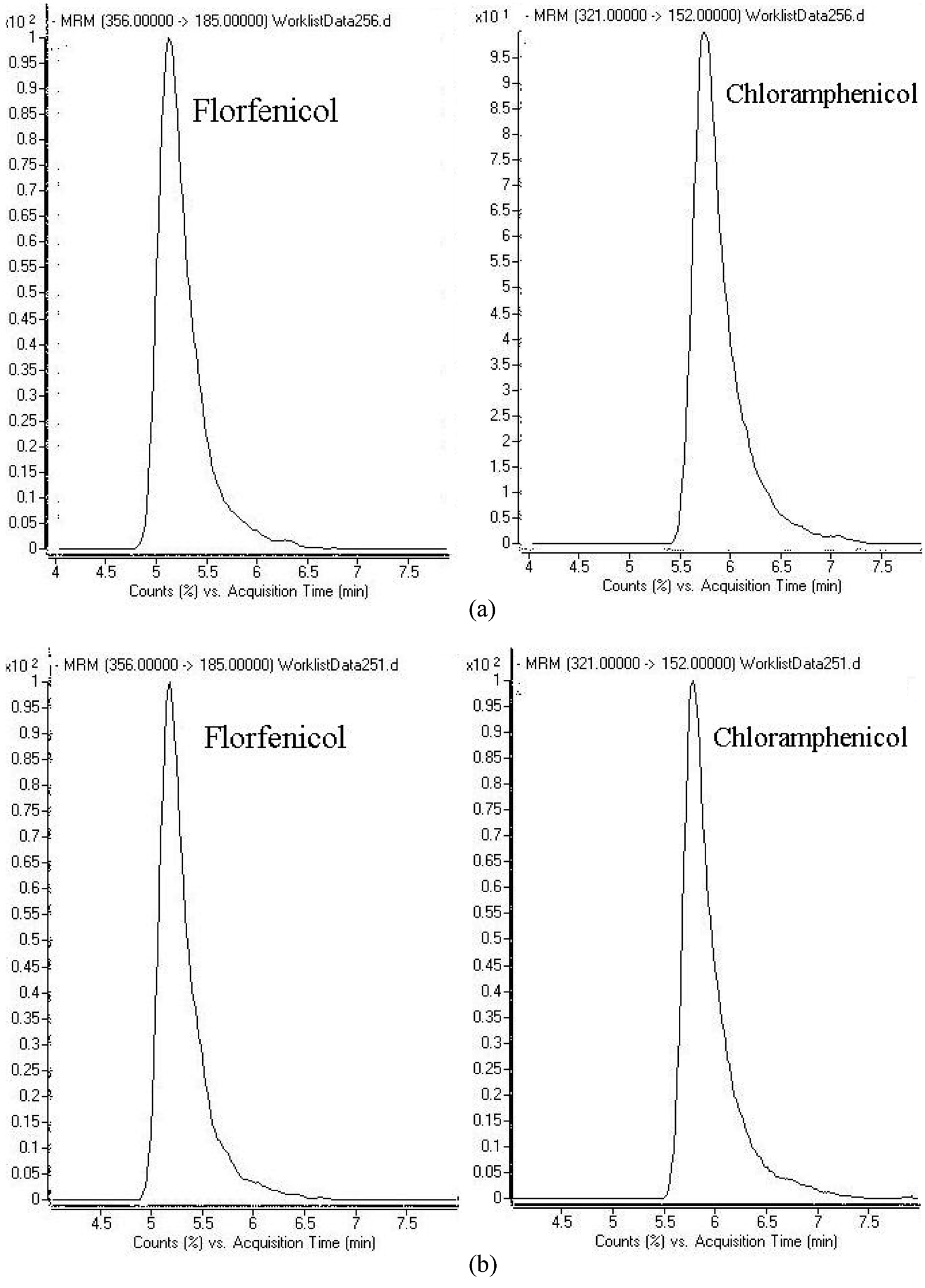
FF and CAP are easily separated from one another and eluted from the HPLC column in < 6 min (Figure 1). Quantitations were based on peak areas. Calibration curves were linear between 0.5 and 20 ng/mL. Correlation coefficients of the standard curves were in the 0.999 range for both FF and CAP.

Precision and Recoveries

Results from replicated analyses of feed samples spiked at levels of 0.5–20 ng/g are shown in Table 3. Following the developed conditions, the recoveries for FF and CAP by LC/MS/MS were 94.7–114% and 97.4–113%, the RSDs were <14% and <10%, respectively. According to the signal-to-noise ratio (S/N), the limit of detection was 0.5 ng/g (S/N ≈ 3), and the limit of quantitation was 1 ng/g (S/N ≈ 10) for both FF and CAP. Since the recoveries without internal standard correction were 55.2–110% (especially low for dried skim milk), the use of internal standards was essential in order to correct the recovery at low levels.

CONCLUSION

This simple and rapid method is valuable for simultaneous measurement of FF and CAP. The method has been tested with formula feed, fish meal and dried skim milk with similar results.



(a)

(b)

Figure 1. *Chromatograms of standard solution and sample solution. (a) Standard solution spiked FF and CAP at each 20 ng/mL. (b) Sample solution of formula feed for fish (porgy) spiked FF and CAP at each 20 ng/g.*

Table 3. Compositions of Frmula Feeds Used in this Study.

		Recovery[a] (RSD[b]) (%)		
			CAP	
Sample	**Spiked Level (µg/kg)**	**FF**		**Without Internal Standard Correction[c]**
Fish meal	20	114 (11)	110(8.7)	–
	5	111 (9.1)	102 (9.2)	–
	1	94.7 (13)	98.3 (6.3)	70.2
	0.5	99.0 (33)	93.0 (2.5)	68.4
Dried skimmilk	20	109 (5.0)	111 (10)	–
	5	110 (1.9)	113 (9.1)	–
	1	110 (3.7)	97.4 (4.2)	59.8
	0.5	115 (23)	98.1 (4.4)	55.2
Formula feed for suckling pig	20	108 (4.0)	108 (2.7)	–
	5	109 (2.8)	109 (6.2)	110
	1	110 (3.8)	95.5 (5.2)	101
	0.5	73.8 (12)	93.1 (10)	89.2
Formula feed for fish (porgy)	20	108 (3.4)	106 (9.0)	–
	5	103 (2.5)	99.5 (2.4)	–
	1	95.1 (14)	109 (9.2)	77.2
	0.5	82.3 (14)	74.2 (15)	70.1

[a] Mean recovery (n = 3).

[b] Relative standard deviation (RSD).

[c] n = 1.

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Use of Solid Wastes from the Leather Industry as an Adsorbent

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ABSTRACT: Utilization of solid wastes from the leather industry as a potential alternative adsorbent for removal of Cr (VI), phenol and dyes from aqueous solution is the objective of this study. Chromium shaving and activated waste sludge from the tannery industry were used as an adsorbent. Although both shavings and waste sludge showed low removal efficiency for phenol, they had high adsorption capacity for Acid Red 111. Due to presence of excess positive charge on its surface, shavings had low affinity to both Basic Red 18 and chromate. However, their adsorption on activated sludge compared well with other low-cost adsorbents.

INTRODUCTION

LEATHER and the leather industry have been in existence for a long time. Leatherworking is claimed to be the second oldest profession in the world. Globally, approximately 6.0 million tonnes of raw hides on a wet salted basis were processed to yield about 522,600 tonnes of heavy leather and about 12,759 million square feet of light leather including split leather [1].

Developing countries now produce over 60% of the world's leather, and this proportion is growing. Leather processing has emerged as an important economic activity in several developing countries. In Turkey, the leather industry has a significant place in Turkish economy concerning its weight in production, employment, and export. Turkey is one of the leading countries of the leather and leather products in both production and export. On the other hand, a large amount of waste, in particular organic waste, is inherent to production in tanneries. The industry is strongly regulated regarding emissions such as wastewater, solid wastes and air emissions. These regulations, which limit leather industrial activity, claim alternative methods for disposal of residue. Due to the regulations, treatment of waste products from leather tanning becomes more important day by day. Therefore, leather industry has started to consider recycle and utilization of wastes for both environmental and economical concerns. Approximately 0.2 kg of waste sludge (on a dry basis) per kilogram of wet salted hides/skins is generated as a result of wastewater treatment [1]. On the other hand, the equivalent of approximately 10 % of the weight of raw hides is removed as shavings and trimmings which is considered as a solid waste [2]. It was reported that about 0.8 million tonnes of chrome shavings could be generated annually worldwide [3]. The most common way to manage solid wastes is by disposing of them on land sites, since profitable disposal of chrome shavings and waste sludge from wastewater treatment is difficult. Since the chromium metal is the most important tanning agent, the shavings from chromium (III)-tanned leather require special attention because of the legislative restrictions. In literature, there are many studies on the treatment of chromium tanned wastes. Most of these studies concern the extraction of chromium from wastes to re-use in the tanning process [4], isolation of protein fractions [5], gasification to obtain syngas [6], and production of activated carbon [7,8].

The removal of heavy metals and dyes from contaminated waters has greatly increased because of the ecological awareness of their role in the environment. Chromium (VI) is used in various industries including metallurgy, leather tanning, and electroplating. Therefore, it is a major pollutant of the wastewaters rejected by these industries. It is toxic, carcinogenic and mutagenic in nature. On the other hand, in textile dyeing processes, a large volume of dye-contaminated effluent is discharged. Dyes, even in low concentrations, affect the aquatic life and the food web. Some dyes are carcinogenic and mutagenic. Restrictions on discharge concentrations of heavy metals and dyes have become

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more stringent as a result. Several treatment technologies have been developed to remove chromium and dyes from wastewater. Adsorption has been recognized as an effective method for the removal of this type of pollutants from wastewaters in terms of simplicity of design, ease of operation and insensitivity to toxic substances. In general, activated carbons are widely used effective adsorbents for wastewater treatment. But the large-scale application of activated carbon is restricted due to its higher price of both fabrication and regeneration. Recently, many non-conventional adsorbents, including natural materials and waste materials from industry and agriculture [9–13] have been considered as alternate of activated carbon. The waste materials have little or no economic value and often present a disposal problem. Therefore, there is a need to valorize these low-cost wastes. So, their conversion into activated carbon would add economic value and help reduce the cost of waste disposal. For example, waste sludge from waste water treatment is carbonaceous in nature and rich in organic materials and it can be converted into activated carbon after chemical treatment. This could reduce the volume of sludge and produce a lower cost adsorbent. Recently several studies have been made. Since a drying step is always necessary in the production of commercial activated carbon by chemical activation, high water content (up to 60%) in sludge does not considerably affect the cost of process.

One of the approaches in this study is the utilization of tannery wastes as adsorbent. Besides chromium, shaving is mainly consisted of collagen containing amino, carboxyl and other hydrophilic/hydrophobic functionalities which provide adequate sites for adsorption of transition metal cations and organic molecules. Few studies about use of tannery wastes as adsorbent exist in literature. These studies highlighted the ability of these wastes to adsorb oil [14], aromatic organic acids [15], dyes [16, 17], tannins [18], surfactants [19], As(V) and Cr(VI) [20]. In these studies, the adsorption properties of native collagen varied according to the treatment of collagen. For example, in the case of cationic dye adsorption, it was observed that the adsorption capacity increases in the order, natural leather < leather waste after chromium extraction < chromium-containing leather waste. The small adsorption capacity for the cationic dye was probably related to the presence of chromium in the chromium-containing leather and leather waste after chromium extraction (remaining chromium) [16]. On the other hand, for anionic dye adsorption, the adsorption intensity was higher on chrome shavings in comparison with buffing dusts, since chrome shaving has more positive surface charge than buffing dusts [17].

In this work, utilization of the solid wastes from the leather industry as potential alternative adsorbent for the removal of Cr (VI), phenol and dyes from aqueous solution were aimed. The chromium shaving and activated carbon obtained from waste sludge of tannery industry were used as adsorbent. Optimum adsorption conditions were found and equilibrium isotherms were determined for each adsorbate. The applicability of the Langmuir and Freundlich models to the adsorption processes was also examined.

MATERIALS AND METHODS

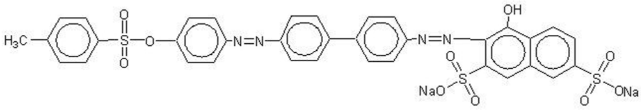
Materials

The chromium tanned shaving (CS) and waste sludge (WS) were supplied Sepiciler Caybasi Leather Ind. Inc, Izmir, Turkey. The waste sludge was a mixture of chemical and biological sludge obtained from wastewater treatment plant. CS was crushed until a particle size less than 1 mm in a cryogenic mill. Proximate and ultimate analyses of CS and WS are given in Table 1.

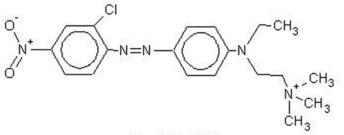
The preparation of activated carbon involved the chemical activation of sludge by using of $ZnCl_2$ at 600°C. Thus, the sludge was impregnated with $ZnCl_2$ solution at a 1 $ZnCl_2$/sludge ratio and dried at 105°C overnight. The dried and impregnated sludge was carbonized at 600°C under nitrogen flow for 2 h. Before utilization, the activated sludge was treated with 10% HCl solution for the removal of impregnating salt followed by washing with hot distilled water for the removal of chlorides and acidity. BET surface area and ash content of the obtained activated carbon were found to be 737 m^2g^{-1} and 35.6 %, respectively.

Table 1. Properties of Waste Sludge and Chromium Tanned Shavings.

	Waste Sludge	Chromium Tanned Shaving
Proximate Analysis, wt %		
Moisture	4.0	15.4
Ash	33.1	4.7
Ultimate analysis, wt %		
C	34.2	37.20
H	4.4	6.40
N	5.2	13.6
S	1.5	1.79
Cr	2.4	4.35
Cl	–	4.11



Acid Red 111



Basic Red 18

Figure 1. *Chemical structure of investigated dyes.*

Commercial-grade Basic Red 18 and Acid Red 111 (FGN) were used as received (Bayer). Their chemical structures are given in Figure 1. The Cr (VI) solutions were prepared by dissolving potassium dichromate in distilled water. Phenol and potassium dichromate were purchased from Merck as analytical reagent grade.

Characterization of Adsorbent

Fourier transform infrared (FTIR) spectra of shavings before and after adsorption was obtained using a spectrophotometer (Spectrum 100, Perkin Elmer) in order to qualitatively identify the chemical functionality of shaving. Pellets were prepared by mixing 1 mg of dried sample with 500 mg of KBr (Merck, for spectroscopy). The Scanning Electron Microscope (SEM) analyses were recorded by JSM–6060 JEOL instrument.

Aqueous AdsorptionCharacteristics

The ability of the activated carbons to remove two dyes from different classes, phenol and Cr (VI) from aqueous solutions was determined under batch-mode conditions. 0.1 g of adsorbent was added to 100 ml of the test solutions. The pH of solutions was adjusted with HCl or NaOH solutions after the addition of the adsorbent. The pH values below 3 were not tested due to the possible degradation of collagen. The suspensions were shaken for a desired time. The concentration of test solutions were 200 mg l^{-1} for dyes and 50 mg l^{-1} for phenol and Cr(VI). At the end of each experiment, the filtrates were analyzed for residual Acid Red 111, MB, Basic Red 18 and phenol concentration using the UV-visible spectrophotometer (UV-160A, Shimadzu) at 504 nm, 665 nm, 484 nm and 269 nm, respectively. For residual Cr (VI) concentration, the filtrates were analyzed by reaction with 1,5-diphenylcarbazide followed by absorbance measurement at 540 nm using the UV-visible spectrophotometer.

The adsorbate uptake onto shavings was calculated from the difference between the adsorbate concentration before and after adsorption onto the shavings.

For adsorption isotherm, test solutions (100 ml) of various concentrations were added to the adsorbent (0.1 g) in flasks and after pH adjusting, suspensions were shaken for an equilibrium time determined with preliminary studies. The selected pH values and equilibrium times are presented in Table 2. The equilibrium adsorption data was described in terms of either a Langmuir-type or Freundlich-type isotherm.

RESULTS AND DISCUSSION

The adsorption of the three adsorbates (Cr (VI), acidic and basic dyes) depends on the surface chemistry as well surface area and porosity. On the other hand, the adsorption of phenol depends on the surface area and microporosity of adsorbent. In the following sections, potential of adsorbents for the removal of adsorbates from aqueous solution are discussed.

Chromium Adsorption

The influence of pH on the removal of Cr (VI) was studied over a pH range of 3.0–6.5 at different contact times. Cr (VI) adsorption depends on pH from the point of charge of both adsorbate and adsorbent surface. At pH ranging from 1 to 14, there are four soluble Cr (VI) species, which are CrO_4^{2-}, $Cr_2O_7^{2-}$, $HCrO_4^-$, and H_2CrO_4. From pH 1 to pH 6, most chromium species exist in solution in the form $HCrO_4^-$.

The adsorption capacity of shaving and activated carbon for Cr (VI) decreases significantly with increasing pH. Similar behaviour has also been reported by other researchers [20,21]. The variation in adsorption of chromium ions can be explained by taking the surface charge of the adsorbents and the existing forms of chromium species at different pH values into account.

Table 2. pH and Equilibrium Time in Adsorption Isotherms.

Dye/adsorbent	pH	Equilibrium time, hour
Cr(VI) /shaving	3	4
Cr(VI) /activated carbon	3	24
Acid Red 111/shaving	neutral	6
Acid Red 111/activated carbon	neutral	6
Basic Red 18/ activated carbon	8	24
Phenol/ activated carbon	neutral	4

Under acidic conditions, the surface of the activated carbon becomes highly protonated and favours the uptake of Cr (VI) in the anionic form.

In the case of chromium shaving, at pH ≤ 3, the amino group is present in the protonated form, while the carboxylic groups are in the –COOH form. But at pH > 3, carboxylic acid groups are partly dissociated to carboxylate anion leading to increase in negative surface charge [22]. The adsorption mechanisms of Cr (VI) on activated carbon and shaving may be considered as electrostatic interaction between the protonated groups of activated carbon or $-NH_3^+$ groups of shaving and $HCrO_4^-$. With the increasing pH, the number of negatively charged sites on shavings increases and the number of positively charged sites decreases. A negatively charged surface site on the shavings does not favour the adsorption of $HCrO_4^-$ anions due to the electrostatic repulsion. Since the activated carbon is probably highly protonated under acidic conditions and has a higher surface area, it showed higher chromium adsorption capacity than shaving.

Phenol Adsorption

The influence of pH on the removal of phenol was studied over a pH range 4.0–8.0 at different contact times (between 2 and 24 h). In case of shaving, the uptake of phenol was almost independent of the pH within 4.0 to 8.0 for all tested contact times. Adsorption of polyphenols (eg. vegetable tannins) on collagen is well known [18]. Their phenolic hydroxyl groups are capable of reacting with collagen, at the basic group of side chains and at partially charged peptide links via hydrogen bonding. Because of their large molecular weights containing high numbers of hydroxyl groups, polyphenols can be bound via multi hydrogen linkages to C=O groups of the backbone and to the protonated $-NH_3^+$ groups on the side chains of collagen leading to a stable adsorption. This reaction usually takes place at relatively lower pH values (3.5–4), however, the main hydrogen bonding with C=O has lower dependency on pH. In our case, since phenol is a small molecule (having only one hydroxide group), hydrogen bonding capacity of it was not enough to keep it stable on collagen during adsorption and even the change of pH did not have any affect on the adsorption of phenol on chromium tanned shavings.

In the case of activated carbon, the relative affinity of the phenol toward the carbon surface was related to the donor-acceptor complexes formed between the basic sites on the adsorbent surface and the organic ring of the phenol as well as the surface area and the porosity [23]. The effect of basic surface oxygen groups of activated carbon on the adsorption of phenol was reported in the literature [24]. As in the case of shaving, the adsorption of phenol is independent of the tested solution pH. The percentage adsorption increased by contact time, reaching a maximum at 4 h and then slightly decreased because of desorption

Basic Dye Adsorption

The influence of pH on the removal of Basic Red 18 (cationic dye) by shaving was studied over a pH range 4.0–10.0 for different contact times. Under all tested adsorption conditions, shaving showed poor affinity to basic red (results are not presented here). Similar result was also obtained by Oliveira *et al.* [16] They tested three leather types (a natural non-tanned leather, a chromium-containing leather waste and a leather waste after being passed through a chromium extraction process) for methylene blue (basic dye) adsorption. The chromium-containing leather waste had the lowest adsorption capacity (3 mg methylene blue g^{-1} leather). They mentioned that the small adsorption capacity of chromium-containing leather for the cationic dye, methylene blue, was probably related to the presence of chromium in the solid matrix of the leather. The basic dyes carry a net positive charge due to their cationic amino substituents and react electrostatically with ionized carboxyl groups on collagen through these amino groups. However, since most of the anionic sites of chromium tanned leather are occupied by chromium complexes, basic dyes have very low affinity to the chromium tanned leather and, accordingly, were poorly adsorbed on the chromium shavings in our study also.

In contrast to shaving, activated carbon was more effective for removal of basic dye. The adsorption of basic dye on activated carbon increased with increasing pH from 6.5 to 10.0 and contact time from 2 to 24 h. This may be attributed to the increase of negative surface charge of activated carbon with increasing pH that resulted in the enhancement of cationic dye adsorption due to stronger electrostatical force of attraction. Similar results of pH effect were also reported for the adsorption of methylene blue onto jute fibre carbon [25] and the adsorption of basic blue 9 from aqueous solution by dried activated sludge [26].

Acidic Dye Adsorption

It is well known that chromium leather has affinity towards the acidic dyes. Because of their anionic character, acid dyes predominantly react electrostatically with protonated amino groups of collagen through their sulfonate groups. However, they also may react with auxochrome groups via hydrogen bonding. In addition, some of acid dyes may bind with chrome in chrome tanned leather [27].

It was reported that the adsorption of acidic dyes on chrome shavings under highly acidic conditions (pH < 3) could be explained by the protonated amino groups [17]. It is also known that chromium tannage increases the isoelectric point (I.P.) of leather to 6–7 [22]. This means that at the pH values below the I.P. (pH < 7), the leather has tendency to have more dissociated cationic groups which may easily react with anionic groups. This also explains the high uptake of acid dyes independent from the pH values between 3 and 7.

To study the influence of pH on the removal of acidic dyes, the pH of the solution was varied from 3 to7. The uptake of acidic dye was independent of the pH within 3 to 7. This shows that chromium in the shaving played the main role in uptake of acidic dye as well as quaternizated amino groups. The time required to attain the equilibrium was 6 h.

In the case of activated carbon, the influence of pH was also investigated at different pH ranging from 3 to 7. The adsorption of acidic dye by activated carbon was independent of the tested solution pH. On the other hand, the percentage adsorption increased by the contact time and reached the equilibrium within the 6 h.

Adsorbent Characterization

The FT-IR spectra of chrome shaving before and after Cr (VI) and acidic dye adsorption (Figure 2) display a typical protein structure of the leather with the stretching of carbonyl group (C=O) at 1567 cm^{-1} and the N-H at 1601 cm^{-1} [16]. The FT-IR spectrum is complex and peak areas are too large due to the nature of leather. Although there is an appearance of a peak at 1157 cm^{-1} after adsorption, it is not easy to assign it.

Figure 3 shows micrographs of chrome shaving before and after adsorption. As seen from Figure 3(a) and (b), morphological features of the fibre bundles of shavings did not show any difference before and after Cr (VI) adsorption. However, after dye adsorption, the fibre bundles were coated by dye molecules, where the edges of the fibre bundles are not clearly visible (Figure 3(c).

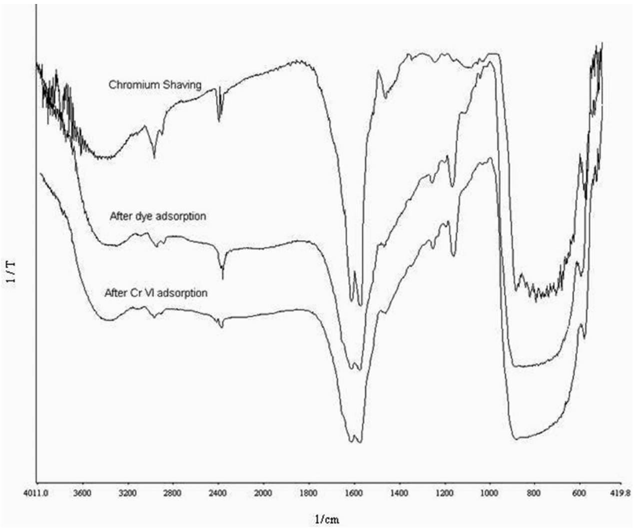


Figure 2. *FT-IR spectras of chromium shaving, Cr(VI) adsorbed shaving and FGN adsorbed shaving.*

Adsorption Isotherms

Adsorption is usually described through isotherms, that is, the amount of adsorbate on the adsorbent as a function of its concentration at constant temperature. The quantity adsorbed is nearly always normalized by the mass of the adsorbent to allow comparison of different materials. The distribution of adsorbates between the liquid phase and the solid phase can be described by several isotherm models. Two most common isotherm equations, namely Langmuir and Freundlich were tested in this study. The Langmuir model assumes that the uptake of adsorbate occurs on a homogenous surface by monolayer adsorption, without any interaction between adsorbed ions. However, the Freundlich model assumes that the uptake of adsorbate occurs on a heterogeneous surface and that the adsorption depends on the energy of the adsorption sites [9]. The obtained isotherm parameters and correlation coefficients (R^2) are presented in Table 3.

Langmuir model was found to fit the experimental data for all adsorbates well as indicated by the high values of the correlation coefficients (Figures 4–9).

However, Freundlich isotherms provided the better correlations for phenol and Cr (VI). S_M and K_L are Langmuir constants related to the maximum adsorption capacity and the energy of adsorption, respectively. The different K_L values indicate different adsorption mechanism. K_F (mg g^{-1}) and n are Freundlich constants related to the adsorption capacity and adsorption intensity. Generally, KF increases as the adsorption capacity of the adsorbent increases and 1/n decreases as the adsorption strength increases.

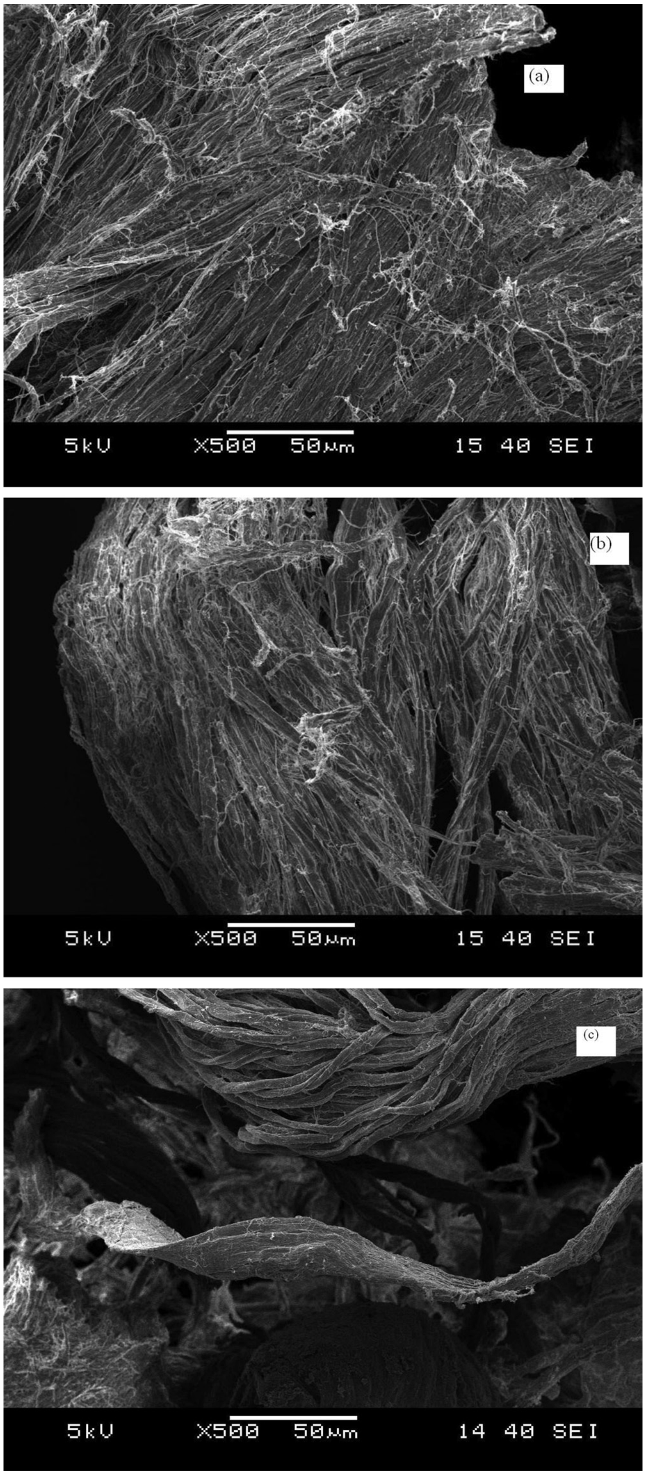


Figure 3. *Micrograph of chrome shaving (a), Cr(VI) adsorbed shaving (b), FGN adsorbed shaving (c).*

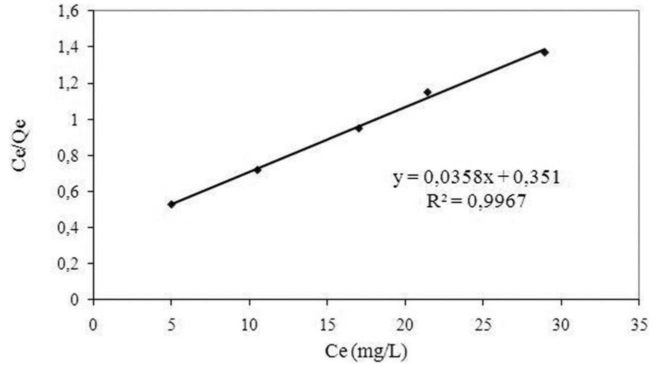


Figure 4. *Langmuir Adsorption isotherm for Cr (VI) on shavings (initial Cr (VI) concentrations: 20–50 mg/L).*

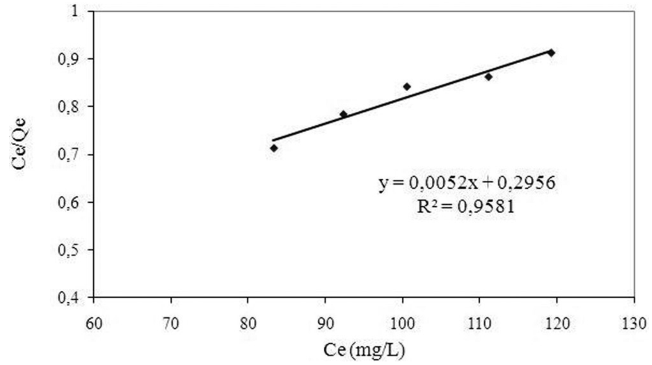


Figure 5. *Langmuir Adsorption isotherm for Acid Red 111 on shavings (initial dye concentrations: 200–250 mg/L).*

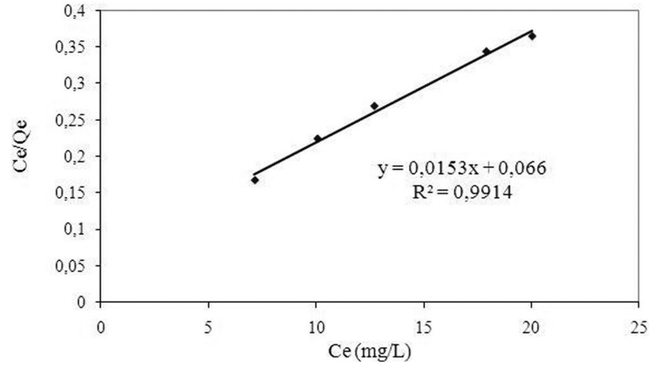


Figure 6. *Langmuir Adsorption isotherm for Cr (VI) on activated carbon (initial Cr (VI) concentrations: 50–75 mg/L).*

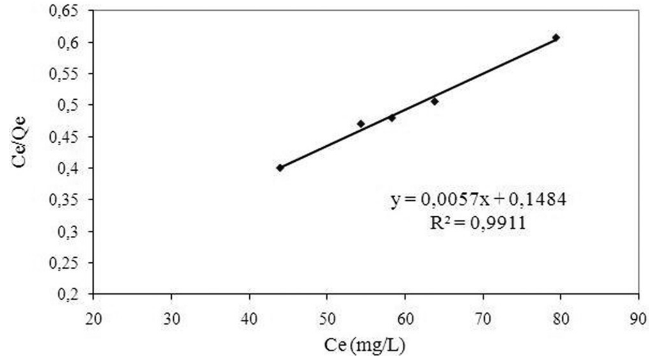


Figure 7. *Langmuir Adsorption isotherm for Acid Red 111 on activated carbon (initial dye concentrations: 150–210 mg/L).*

As seen from Table 3, activated carbon derived from waste sludge adsorbed larger amounts of Cr (VI) ions compared to shaving. This may be partly attributed to the high surface area of activated carbon which provides larger amounts of the acidic surface groups having affinity towards to $HCrO_4^-$. In contrast, for acidic

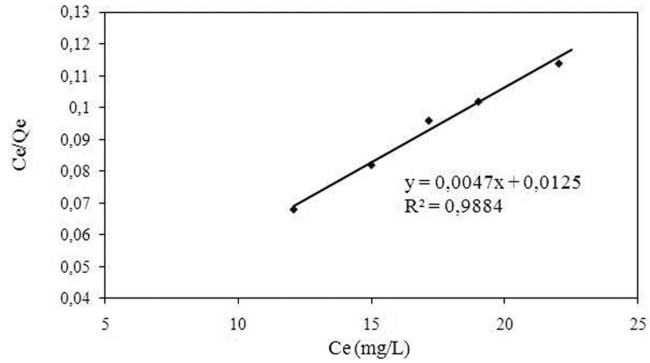


Figure 8. *Langmuir Adsorption isotherm for Basic Red 18 on activated carbon (initial dye concentrations: 190–215 mg/L).*

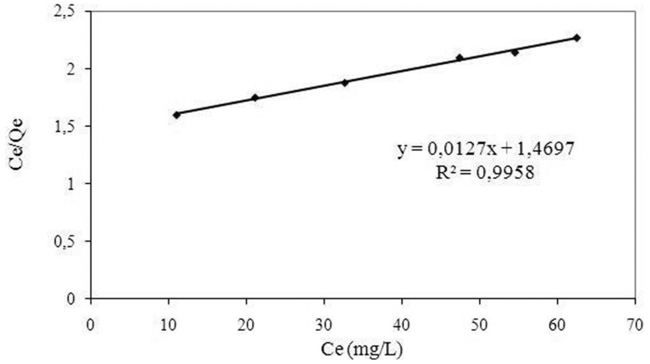


Figure 9. *Langmuir Adsorption isotherm for phenol on activated carbon (initial phenol concentrations: 20–90 mg/L).*

dye, the sorption capacity of shaving was more than that of activated carbon. This may be due to the high amount of functional groups in shaving which provide adequate sites for adsorption of anionic dye molecules.

Comparison of Adsorption Capacity of Solid Wastes from Tannery Industry with Other Adsorbents

Cr (VI) adsorption capacity of chrome shaving was lower [10, 28, 29] or higher [11, 30, 31] than the adsorption capacities reported for lignocellulosic materials in the literature. In a previous study carried out by the wet blue leather waste [20], it was reported that a high amount of Cr (VI) (133 mg g^{-1}) was adsorbed on the wet blue leather waste. This adsorption performance may be due to the nature of waste. On the other hand, activated carbon obtained in this study showed higher Cr (VI) adsorption capacity than some of the waste tyre and lignocellulosic material-derived activated carbons and commercial activated carbons found in literature [32–35].

Although, adsorption of phenol on chrome shaving was less favorable, phenol adsorption on activated carbon derived from sludge compares well with the sewage sludge-based adsorbents which were reviewed by Smith *et al.* [36]. In this review, it was noted that the phenol adsorption capacity of sewage sludge-based activated carbons varied generally between 20–81.6 mg g^{-1}. Only one sludge-based adsorbent had a phenol adsorption capacity of 182 mg g^{-1}, which is higher than that of the activated carbon used in this study, but this adsorbent was produced from limed activated sludge [37]. On the other hand, activated carbon obtained in this study has lower phenol adsorption capacity than the activated carbons derived from lignocellulosic materials [38–40].

For dye adsorption, direct comparison of adsorbents used in this study with other adsorbent materials is difficult, owing to the variety in the molecular structure of dyes. For example, in adsorption of two acidic dyes (JK2R and VK2RL), the adsorption capacities of chrome shaving were found as 400 and 600 mg g^{-1}, respectively, although both the adsorbent and the class of dye used were same [17]. But it can be generalized that basic dye adsorption is less favourable on chromium containing leather waste. On the other hand, the leather waste can present much greater adsorption capacities for acidic dyes than that of lignocellulosic materials and activated carbons due to its surface charge. It should be noted that basic dye uptake of activated carbon derived from sludge was higher than acidic dye

Table 3. Parameters of the Langmuir and Freundlich adsorption models of phenol, dyes and Cr(VI).

		Langmuir Model			Freundlich Model		
Adsorbates	**Adsorbents**	**S_M (mg g^{-1})**	**K_L (l mg^{-1})**	**R^2**	**1/n**	**K_F**	**R^2**
Phenol	AC	78.740	0.009	0.95	0.721	1.411	1.00
Basic Red 18	AC	212.76	0.376	0.98	0.115	131.67	0.56
Acid Red 111	AC	175.43	0.038	0.98	0.298	35.381	0.88
	shaving	192.30	0.018	0.96	0.351	24.344	0.89
Cr(VI)	AC	65.359	0.232	0.99	0.240	26.230	0.97
	shaving	27.33	0.102	0.99	0.357	6.343	0.98

uptake. This result is agreement with the literatures [41–43] reviewed by Smith [37].

CONCLUSION

Use of solid wastes from leather industry as adsorbent to remove organic and inorganic contaminants from aqueous-medium was investigated in this study. Chromium tanned shavings and waste sludge obtained from a wastewater treatment plant was used for this purpose. For use as adsorbent, waste sludge was activated by $ZnCl_2$ impregnation following carbonization, whereas shaving was used as received. Acid Red 111, Basic Red 18, phenol and Cr (VI) were tested as adsorbate. Although both shaving and waste sludge derived activated carbon showed low removal efficiency for phenol, they had high adsorption capacity for Acid Red 111 (192.30 and 175.43 mg g^{-1}, respectively). Due to presence of excess positive charge on its surface, shaving had low affinity to both basic dye and chromate. In contrast, basic dye and chromate adsorption on sludge derived activated compared well with the other low-cost adsorbents. Experimental data provided best fit with Langmuir equation, indicating monolayer sorption on a homogenous surface.

The study showed that solid wastes from the tannery industry can be effectively used as an adsorbent for removal of dyes and Cr (VI) from aqueous streams. But further studies on spent adsorbents are needed, such as desorption and reuse which are important for possible utilization of tested adsorbents in continuous systems in industrial processes. In addition, efforts need to be made to carry out a cost comparison between conventional and non-conventional adsorbents. Moreover, undoubtedly, utilization of wastes as adsorbent seems to be a promising solution for wastes from an environmental and economics' point of view.

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BOOK REVIEW

Industrial Composting: Environmental Engineering and Facilities Management, by Eliot Epstein. CRC Press, 2011, 334 pp., ISBN 978-1-4398-4531-8

THE author of this book, Dr. Eliot Epstein, is an internationally known expert in composting and waste management. He has served as a project leader for the United States Environmental Protection Agency (USEPA) on the project to revise the 40 CFR Part 503 document as well as a consultant to the World Bank, the USEPA, and the United Nations Development Programs. Years after the success of his first book on composting, The Science of Composting (CRC Press, 1997), Dr. Epstein published this book, Industrial Composting.

The purpose of this book is to "provide the reader with the principles related to the design of facilities; considerations for siting; planning; elements of economics and cost; major management issues such as odors, pathogens, and bioaerosols; public relations; and product utilization and marketing" (page 1). This purpose is well accomplished.

This book consists of sixteen chapters. The first four chapters briefly cover the history and fundamentals of composting. Chapters 5 through 7 describe various composting technologies, facility planning, and design. The economics of composting are presented in Chapter 8. Three chapters, 9 through 11, are dedicated to odor control systems and management. Chapters 12 and 13 discuss potential hazards during composting from pathogens and bioaerosols.

Each chapter starts with an "introduction" section giving an overview of the chapter and ends with a "conclusion" section that summarizes key points. Regarding readers who find it difficult to find time to read the entire book and for reference purposes, browsing through conclusions may help guide them to chapter specifics.

One of the great features of this book is its comprehensiveness. It covers almost every aspect of composting from mass balance to pathogen and vector reduction and from facility planning to product marketing. The book incorporates many pictures of composting facilities including processing equipment, which makes the understanding of the composting process and its applications much easier. It also provides many additional references for readers interested in specific topics and wanting to explore more.

This book is not an encyclopedia or design manual for composting facilities. Rather, it is a "tour guide" covering key points in just enough detail. It does not teach chemistry, microbiology, and mathematics necessary to design an Aerated Static Pile (ASP) system or a biofilter odor control system. In fact, the scientific basics of composting are covered very briefly in less than 60 pages. The rest of the book focuses on a pragmatic approach to explaining principles and rules of thumb to be considered, and pitfalls that should be avoided during planning, design, and operation of composting facilities.

Odors, pathogens, and other public health concerns are major issues faced by many composting facilities and legislators. A considerable portion of this book addresses how these issues can be mitigated or eliminated by proper planning, design, and operation of composting facilities. Readers from North America may find this book more useful than readers from other parts of the world because most case studies and discussions about regulatory issues are based on examples from the United States and Canada.

As experienced in many first edition publications, there are a few editorial errors in this book such as inconsistency in fonts and misspelling of abbreviations. This will most likely be corrected in the second edition or in following editions.

Written by an expert who has 40 years of experience in composting, this book is a must have for composting advocates and facility operators. It is also a valuable reference for engineers and regulators. Researchers and students might not find this book as useful because of its practical orientation. However, anyone who has recently begun investigating composting will undoubtedly benefit from this book.

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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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