Electroflocculation – Constructed Wetland Hybrid for Improved Phosphate Removal In Effluent Reuse

A. Barash, K. Ozer and A. Adin*

Dept. of Soil and Water Sciences, Faculty of Agriculture, Food and Environment, The Hebrew University of Jerusalem, POB 12, Rehovot 76100, Israel

*Corresponding address: adin@vms.huji.ac.il

D. Milstein and A. Gasith

Department of Zoology, Faculty of Life Sciences, Tel-Aviv University, Tel-Aviv 69978, Israel

Abstract
Reusing or recycling wastewater for stream rehabilitation require discharge of high quality effluent complying with strict nutrient standards as well as development of feasible treatment alternatives. Constructed wetland is already a proven technology for efficient polishing wastewater effluent except for phosphorous. We investigated the coupling of Electroflocculation (EF) with constructed wetland (CW) for improved contaminants removal, phosphorous in particular, from secondary effluents. The work consisted of three phases: electro-jar testing, continuous-flow EF-filtration (GF)-CW bench scale experimentation and field, half-industrial piloting. P, turbidity, TSS and TOC were particularly monitored. Laboratory experiments showed that EF-GF effectively removed phosphate (96%), while CW effectively removed organic matter (85%). Therefore, it seemed that the coupling of both unit processes would combine their treating abilities. Field pilot results show that EF-GF removed up to 97% of total phosphorus, resulting in P concentrations of <0.4 mg/L, which are extraordinary results by any comparison**.** In addition to phosphorus removal, the system is capable of meaningfully reducing some of the TOC (53%) and most of the TSS. The hybrid action is explained by combining flocculation and adsorption mechanisms produced by the EF with transport, attachment and biodegradation mechanisms in the CW beds.

Keywords
Phosphate removal; electroflocculation; constructed wetland; water reuse; stream rehabilitation; tertiary treatment

1 Introduction

Discharge of effluent into streams and rivers is a common practice worldwide. In arid lands competition for the freshwater for human use diminishes stream flow and effluents often make much of the base flow. In such situations stream health and rehabilitation highly depend on effluent quality. Strict standards for effluent disposal call for economic and efficient treatment alternatives. Various sources of wastewater contain growing concentrations of phosphorous and nitrogen cause eutrophication of natural water bodies (Feng et al., 2003). One of the consequences of eutrophication is decreasing of dissolved oxygen which adversely affects fish and other aquatic life, diminishing biodiversity.

Constructed wetland (CW) is an environmental friendly technology for treating wastewater or polishing effluent that is becoming increasingly popular in many parts of the world (Haberl, 2003). It is designed and constructed based on natural marshes (Kadlec and Wallace, 2008). CWs are often classified by the pattern of effluent flow in the system (e.g., Brix, 2003). In free-flow (surface flow) systems wastewater flows above the ground through emerged, submerged and floating aquatic vegetation. In subsurface flow systems wastewater moves through a porous medium such as gravel or aggregates, in which rooted hydrophytes grow (USEPA, 2000).Subsurface systems are further classified into horizontal flow (HF), in which anaerobic conditions prevail, or vertical flow (VF) which maintains aerobic conditions. Low flow velocities coupled with the presence of roots and solid substrate, promote settling and filtration of particulate material. Biofilm of diverse microrganisms that develops on the porous medium is responsible for most of the biotransformation and mineralization of pollutants. (e.g, Vymazal, 2003; Kadlec and Wallace, 2008). CWs usually remove organic matter and nitrogen (N) compounds efficiently but are less efficient in removing phosphorous (P) compounds (Kadlec and Wallace, 2008).Retention of P in CWs includes peat/soil accretion (mostly in natural and free flow systems), soil adsorption, precipitation and plant uptake (Vymazal, 2003). In subsurface systems removal by plants is limited and requires plant harvesting annually. The adsorption and chemical precipitation of phosphorus is much more vigorous at the initial operation stage because the process has finite capacity (EPA, 2000). As a result, CW capacity for phosphorous removal is quite limited. For the latter reason we considered coupling CW with physicochemical process that is expected to complement the naturally occurring processes by removing phosphorous efficiently.

Chemical precipitation is widely used for phosphate removal. The common precipitants used are aluminum sulphate and ferric chloride. Chemical treatment involves the addition of high amounts of chemicals resulting in undesirable ions residues and extra salinity being discharged in the treated wastewater (Feng et al., 2003). Electroflocculation (EF) is an electrochemical method that utilizes an electric current to separate and clear solid and dissolved pollutants from wastewater. This method enables water treatment free of additional chemicals, thus offers an alternative to the use of metal salts. EF has been increasingly used in North America for pretreatment of a variety of industrial wastes (Mollah et al., 2001). EF can be considered an alternative process to conventional flocculation, although they are somewhat different. The difference between these processes is manifested in the chemical and physical characteristics of the treated suspension and resulting aggregates (Harif and Adin, 2007). The flocs formed by EF are relatively large and contain less bound water. They are also more stable and therefore amenable to filtration (Abuzaid et al., 2002). The optimum pH for turbidity and phosphate removal is around 5–9 in electroflocculation-electrofloatation by using aluminum and titanium electrodes. In that range the hydrolysis and polymerization of Al^{+3} give rise to the formation of such species as $Al(OH)^{+2}$, $Al_2(OH)_2^{+4}$, $Al(OH)_3$ and charged hydroxo-cationic complexes such as $Al_{13}(OH)_{32}^{+7}$, which are efficient coagulants (Ge et al., 2004). Current density is a major factor in determining the removal rate of phosphate by EF, low initial concentrations of 10–50 mg/l existing in effluents may achieve 90% phosphate removal under low current density values of 5mA/cm^2, duration 7 minutes (Bektas et al., 2004). The overall goal of the investigation was to assess the utility of a tertiary treatment that couples a physicochemical process, i.e., electroflocculation, with natural processes taking place in constructed wetland, to facilitate compliance with stringent standards for river rehabilitation as well as for other uses of treated effluents. Here we examine phosphorous removal applying iron electrodes and vertical flow CW treatment.

2 MATERIALS AND METHODS

The research work consisted of three successive phases, two in the laboratory and one at constructed wetland field site: (a) Jar testing, including development of EF–jar testing batch system, (b) continuous-flow, bench/semi-pilot scale experiments, and (c) field, pilot plant experiments.

Standard (chemical) jar tests with extended settling time of 2 hrs were conducted with secondary effluent, aluminum sulfate (alum) or ferric chloride that served as coagulants. In "modified jar tests" a sample was withdrawn from the jars, immediately after flocculation period, and filtered through a filter paper (Whatman 545). An EF cell was built where various electric current intensities were applied during different time cycles (represents coagulant dose) while rapid mixing 800 ml of secondary effluent, followed by 10 minutes of slow mixing and filtration through a filter paper. 12-cm^2 aluminum or iron strip served as anode.

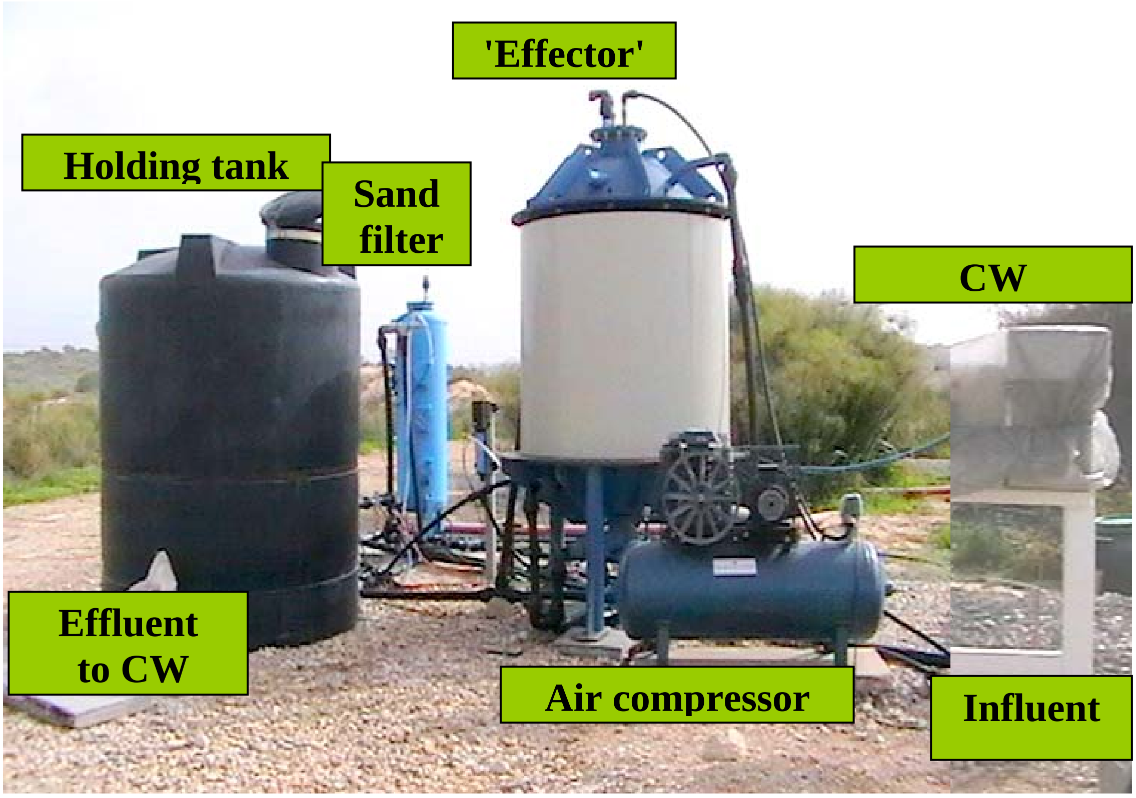
The continuous flow bench-scale experiments were conducted using 1-liter cell equipped with two perforated iron electrodes with an area of 114.22 cm^2, preceding a filter of 39 cm bed depth and 1 mm grain size. Artificial wastewater was prepared as described elsewhere (Egozy, 1996) with additional phosphate stock solution containing 2.865 g/l KH_2PO_4. Wastewater flow rate was 130 ml/min, implying contaminant injection flow rate of 0.65 ml/minute for a dilution ratio of 1:200. A bench-scale, horizontal-flow CW consisting of two units (basalt and dolomite beds) with a total area of 0.216m^2 followed. Filter backwash was activated when a pre-set time/turbidity/ΔP was reached. pH was adjusted, turbidity, particle count, TOC, DOC, phosphate, aluminum and iron were analyzed (specific on analytical equipment may be obtained from the authors).

A pilot EF–CW system (Fig.1) was built at the Shafdan municipal, activated sludge wastewater treatment plant, comprising of the following components: (a) pre-strainer, (b) up-flow EF generator (EFector, TreaTec21 Industries Ltd.), 1.4 m^3 in volume, 1.25 m in diameter, containing 12 pairs of perforated iron electrodes, (c) granular filter, 1m bed depth and 0.6mm effective grain size, (d) 4 m^3 filtered water tank, used also for system backwash and flushing, and (e) a complex of CW ponds were constructed in the Shafdan WWTP (Tel-Aviv – Dan metropolitan area; Constructor Ofra Aqua Plants, modified by Moran consulting, design, & construction of aquatic ecosystem). The system included several series of three successive wetland ponds (ca. 35m^2 each), vertical or horizontal subsurface flow and one free flow. The results reported here relate to a treatment by a single VF pond. The VF ponds were packed from top to bottom with an 8cm layer of basalt (20-30mm); 9 cm of basalt (2-3mm); 8 cm basalt (5-10mm); 8 cm dolomite (8mm); 15 cm basalt (3-6 mm) and 20 cm of dolomite (50-60mm) at the bottom. *Cyperus papyrus*, *Canna sp.*, *Iris pseudoacorus*, *Phragmites australis* and *Juncus ensifolius* were planted, but by the third year *Cyperus papyrus* dominated the system. 'Shafdan' secondary effluents characteristics (annual average): turbidity–6.4 NTU, phosphate–2.7 mg/l as P, BOD–12 mg/l, COD–51 mg/l, nitrogen–9.2 mg/l as N, pH 7.35, Fe<0.1 mg/l.

3 RESULTS AND DISCUSSION

3.1 Jar tests

The effect of pH levels on phosphate removal by chemical flocculation and EF is shown in Figs. 2, 3. Fe:PO_4^{-3} molar ratio was similar for both experiments (1.6 and 1.95, correspondingly). For EF treatment, PO_4^{-3} removal was improved as pH increased, up to 85% removal at pH 8. In contrast, chemical flocculation showed a stable removal at all pH ranges (up to 69%). Those results indicate that the neutral pH ranges are optimized for phosphate



removal by EF technology with iron electrodes.

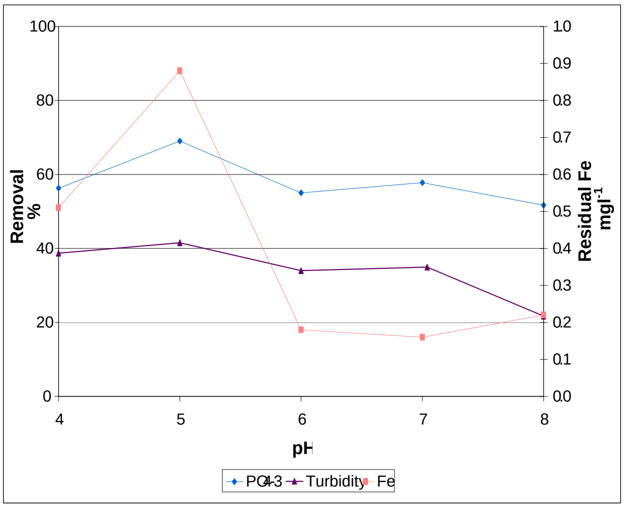
Figure 1: The EF–CW pilot system

A similar picture appears for residual Fe concentration. Chemical flocculation showed a relatively stable level of residual Fe (0.9–0.2 mg/l at pH 4-6 and a constant 0.2 mg/l at pH 6–8) while residual Fe levels for EF decreased as pH was neutralized. Those results may explain why turbidity levels worsened by hundreds percents in the EF treatment case, except for a 38% removal measured at pH 8, in contrast to chemical flocculation, where turbidity removal varied between 41–22% as pH increased.

3.2 Laboratory scale coupled unit

Phosphate removal with CW bedding alone was low, resulting between 18% removal to 12% contribution to the initial level (Table 1). The most beneficial in this configuration was organic matter removal, ranging 25–85% dependently of initial concentration and time. In addition, it lowered turbidity to values of 0.3–0.6 NTU.

At the first 20 days, turbidity was reduced by 20–72% of 2–6.9 NTU initial values. Beyond that period, the wetland contributed up to 27% to the turbidity. When EF-GF preceded the CW gravel beds,, this combined treatment was very effective in turbidity and iron elimination, which could be attributed to efficient transport and attachment mechanisms of the colloids, provided by the flow and surfaces of the wetland porous media. Phosphate removal by EF–GF was up to 92% (lower detection limit was 0.4 mg/l PO_4^{-3}). Turbidity breakthrough correlated with high residual ferric concentrations, which could be explained by overdosing when raw turbidity was low (0.5 NTU). That EF-GF-CW configuration encouraged green algae development in the CW bed, enriching the water with oxygen by average of 13%. The development of green algae added organic matter particularly when initial concentration was low. Oxygenated water creates a defensive layer over the sediment, reducing phosphate release to the water, caused by anaerobic conditions (Braskerud et al., 2003, Ahn & Mitsch, 2002). As time passes, biofilm layer grows thicker and oxygen diffusion to the substrate is prevented. With time, microorganism mortality grows and leads to the release of biofilm segments to the water (Egozy, 1996). That could be the reason for organic mater addition to the effluent by the CW and also for the depletion of turbidity removal with time. Another possibility for that variability was the lack of vegetation in the CW bed, an important building block in its stabilization (Braskerud et al., 2005).



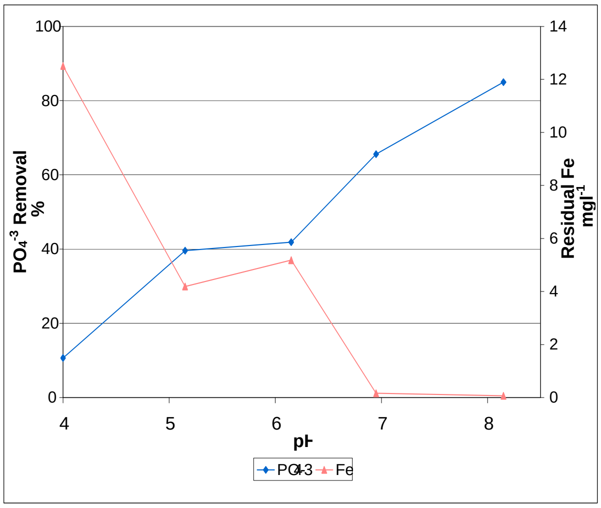


Figure2: Phosphate removal by a modified
modified jar-test as a function of pH
of pH

Figure.3: Phosphate removal by a
EF jar-test as a function

When considering reverse flow (CW–EF–GF), the combined treatment lost its advantages. Filtrate turbidity deteriorated despite considerable reduction in coagulant dose, until the filter bed has been replaced with finer one. The new bed showed better turbidity removal efficiency, while the coarse grain showed a moderate head-loss development. Organic matter removal by the CW was divided: the first cell (basalt bed) removed 12–40% of DOC while the second cell (dolomite bed) added organic matter. The EF-GF treatment abilities varied between 12–85% in DOC removal.

3.3 Field pilot stage

3.3.1 CW performance.

Wetland performance was evaluated after three years of operation (mature system). The following average removal efficiencies (n= 6, Table 2) were recorded after treatment in the first VF pond. Relative to inflow concentrations BOD and TSS removal was high (>60%) resulting in concentration suitable for stream rehabilitation. Excellent ammonia removal (>90%) was achieved following efficient nitrification in the first VF pond. As a result the effluent of the first VF pond was enriched with nitrate. Nitrate removal was attained in the last, free-flow pond (final concentration 0.8±0.8 mg/l nitrate-N) and overall total nitrogen removal was >50% (final concentration 2.1±1.1 mg/l). No removal of phosphate occurred in the wetland mature system

Table 1: Continuous flow, bench-scale constructed wetland performance as a function of operation period treating artificial wastewater.

Operation period (day)	Inlet TOC concentration (mg/l)	TOC removal (%)	Inlet DOC, (mg/l)	DOC removal (%)	Inlet PO_4^{-3} (mg/l)	PO_4^{-3} removal (%)
10	31.7	86			5.94	9
18	18.3	59			6.21	13
26	21.3	46			6.10	-2
35	15.9	69	12.4	85	4.50	5
43			9.8	50	4.60	-12
50			11.1	25	4.77	18

Table 2: Average removal efficiency and effluent concentration of selected water quality variables after treatment of Shafdan secondary effluent in vertical subsurface flow constructed wetland

Parameter	Removal (%)	Final concentration (mg/l)
BOD	63±16	2.3±1
TSS	67±20	1.5±0.9
NH4-N	93.2±5.5	0.15±0.12
NO3-N	-211.2±237.9	1.9±1.45
PO4-P	-11.3±49.3	1.3±0.6

3.3.2 Phosphorous removal by EF-CW systems.

Total phosphorous (TP) removal by different treatment configurations is depicted in Fig. 4. CW alone removed up to 20% of TP, while EF alone removed 10–-40% of TP regardless of Fe concentration. Filtration improved TP removal to an average of 90% when Fe concentration exceeds 5 mg/l, with optimum 97% TP removal reaching TP concentration <0.3 mg/l. For Fe<5 mg/l TP removal by EF–GF–CW ranged 75–89% resulting in TP concentration <0.7 mg/l at all times. Laboratory experiments presented earlier had shown similar results. When EF-GF preceded CW treatment, TP removal depleted to a maximum of 83% removal for Fe>5 mg/l, with TP concentration of 0.3-0.7mg/l. Comparing the later with the above mentioned results indicate that CW consistently contributed additional phosphorous to the effluent; that could be explained by formation of a phosphorous 'reservoir' supplied by (a) Shafdan's secondary effluent between EF treatments, and (2) plants decay, and released by water of lesser concentration.

CW–EF–GF configuration showed similar results to the EF–GF treatment, reaching an average of 90% TP removal, re-convincing that CW did not affect the TP level after granular filtration. Those results indicate that the latter is the best configuration for TP removal from wastewater. Still, it is possible that a long term flow of low phosphorous wastewater through the CW would have eliminated the phosphorous reserve and so would improve on the EF–GF–CW results. This long term operation could not have been carried out under current conditions for technical limitations. When observing residual Fe concentration after EF–GF, results show that only for initial Fe concentration >12 mg/l there is a 95% Fe removal by granular filtration and only for initial Fe concentration >15 mg/l there's less then 0.5 mg/l Fe in the filtrate. This indicates that raising coagulant does effect both phosphorous removal and residual coagulant concentration. Raising coagulant dosage, with the enhanced conveying streams, induced by the increased current intensity, creates more opportunities for successful particle collisions and flocs formations, which can be further removed by the sand filter.

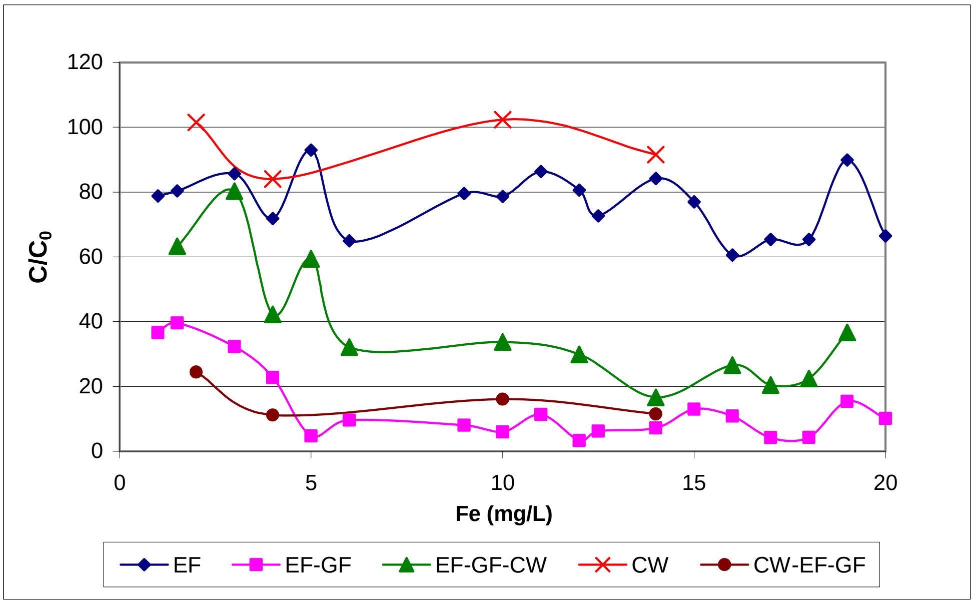


Figure 4: Residual phosphorus in 'Shafdan' secondary effluent for different treatments. C_0=1-3 mg/l TP. Flow rate 1.5 m^3/hr.

3.3.3 Turbidity, TSS and TOC removal by EF-CW systems.

Table 3 summarizes the field pilot results of the different system configurations experimented in this work. Extra turbidity is formed within the system by the ferrous/ferric addition. It is possible that the extra turbidity is a result of a delayed oxidation of bivalent to trivalent iron. That mechanism has to be further investigated. Turbidity removal is optimized only with enhanced sand filtration. The wetland constantly reduced residual Fe concentration by at least one order of magnitude but not less then levels of 0.2–0.5 mg/l Fe. Some amount of Fe passes through the sand filter and the CW bed causing lowest residual turbidity of 0.88 NTU. Results for carbon load removal showed a similar picture with EF–GF capability of reducing about 20–30% of the TOC in the system, depending on coagulant dose, as shown in the bench scale study. Again, adding the CW improved organic matter removal and when CW preceded the electroflocculation unit, TOC removal was 53% at best.

Table 3: Field pilot results of different configurations

	Influent	**Outlet EF-GF**	**Outlet CW**	**Outlet EF-GF-CW**	**Outlet CW-EF-GF**	**No. of exp.**
TP, mg/l	1.40±0.54	0.22±0.18	1.10±0.15	0.53±0.33	0.17±0.04	35
Turbidity,NTU	3.3±0.8	3.2±1.7	09±0.3	2.4±0.9	12±0.38	30
TOC, mg/l	12.2±2.3	10.8±1.4	8.0±0.8	9.4±1.4	6.4±0.6	20
TSS, mg/l	4.9±2.6	4.8±2.1	1.4±1.0	2.5±1.3	0.6±0.2	25

Practically thinking, the EF unit (EFector) – constructed wetland hybrid system implies shorter residence time and better water quality, thus reduces land, construction and maintenance costs of the constructed wetlands as well as water loss. Overall, the different configuration has different advantages in contaminates removal from the wastewater. The combination of the two treatments (electroflocculation and constructed wetland) contributed to the removal of contaminates in every inspected aspect. Contaminants removal was at best when the constructed wetland preceded the electroflocculation unit, but a good sand filtration is needed in order to remove turbidity. A full scale system may be in use both for river and lake rehabilitation and tertiary wastewater purposes. It can be modular, with relative small footprint and automatically controlled according to pre-set currents and backwash sequence.

4 CONCLUSIONS

1. Complementing CW treatment with a physicochemical process of electroflocculation can provide a tertiary treatment that effectively polishes secondary municipal effluent. While EF effectively reduces phosphate in both soluble and particulate forms CW treatment provides a transport-attachment trap to turbidity that escapes the electro-physico-chemical process and removes organic matter and N compounds.
2. Laboratory tests showed that electroflocculation coupled with sand filtration effectively removed phosphate and suspended particles in contrary to the wetland gravel performance. The wetland gravel removed effectively organic matter, possibly by microbial degradation, as opposed to the EF-GF configuration.
3. Field pilot results show that the EFector is capable of removing up to 97% of the total phosphorus, getting final concentrations smaller than 0.4 mg/l. Former electro-jar tests followed by continuous-flow, bench-scale results showed similar capabilities of up to 96% removal. The system is optimized for phosphorous removal by controlling current intensity, which represents coagulant dose and by controlling flow rate, which controls reactor residence time and turbulence.
4. The hybrid process also enhances suspended solids (87%) and organics removal (53%) in addition to phosphorus removal. A well designed sand filtration following the EFector is highly recommended.

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Reference

Abuzaid N.S., Bukhari A. and Al-Hamouz Z.M., 2002. Ground water coagulation using soluble stainless steel. *Adv. Environm. Res.*, **6,** 325-333.

Ahn, C. & Mitsch, W.J., 2002. Scaling concicderations of mesocosm wetlands in simulating large created freshwater marshes. *Ecological Eng*, **8,** 327-342.

Bektas, N., Akbulut, H., Inan, H., Dimoglo, A., 2004. Removal of phosphate from aqueous solutions by electro-coagulation. *J. Hazardous Materials*, **B106,** 101-105.

Braskerud, B.C., Hartnik, T., & Lovstad, O., 2003. The effect of the redox-potential on the retention of the phosphorus in a small constructed wetland. Diffuse pollution conference Dublin, 170-175.

Braskerud, B.C., Tonderski, K.S., Wedding, R.B., Blankenberg, A-G.B., Ulen, B. & Koskiaho, J., 2005. Can constructed wetlands reduce the diffuse phosphorus loads to eutrophic water in cold temperate regions? J. Env. Quality, **34,** 2145-2155.

Brix, H., 2003. Plant use in constructed wetland and their function. In Dias, V. and J. Vymazal (Eds.). The 1st international seminar on the use of aquatic macrophytes for wastewater treatment in constructed wetland, Portugal. 81-109

Egozy, Y., 1996. Water recirculation through biological filter for coastal streams rehabilitation in Israel. MSc thesis, The Hebrew University of Israel and Tel-Aviv University (in Hebrew).

EPA, 2000. Constructed wetlands treatment of municipal wastewater. EPA/625/R/99/010.

Feng, C., Sugiura, N., Shimada, S. (2003. Development of a high performance electrochemical wastewater treatment system. *J. Hazardous Materials,* **B103,** 65- 78.

Ge, J., Qu, J., Lei, P., Liu, H., 2004. New bipolar electrocoagulation-electrofloatation process for the treatment of laundry wastewater. *Separation and Purification Techn.,* **36,** 33-39.

Haberl, R., 2003. History of the use of constructed wetland. In Dias, V. and J. Vymazal (Eds.). The 1st international seminar on the use of aquatic macrophytes for wastewater treatment in constructed wetland, Portugal.
Harif, T. and Adin, A., 2007.Characteristics of aggregates formed by electroflocculation of a colloidal suspension. *Water Research,* **41:13,** 2951-2961
Kadlec, R.H. and Wallace, S.D., 2008. Treatment wetland, Second edition. CRC Press. INC, U.S.A.
Mollah, M.Y.A., Schennach, R., Parga, J.R. & Cocke, D.L., 2001. Electrocoagulation (EC)-science and applications. *J. Hazardous Materials*, **B84,** 29-41.
USEPA, 2000. Constructed wetlands treatment of municipal wastewater. EPA-625-R-99-010
Vymazal, J., 2003. Removal mechanisms in constructed wetland. In Dias, V. and J. Vymazal (Eds)..The 1st international seminar on the use of aquatic macrophytes for wastewater treatment in constructed wetland, Portugal. 219-263.