Removal of Ions from Water with Electrosorption Technology

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ABSTRACT

Electrosorption is defined as potential-induced adsorption of ions onto the surface of charged electrode. When an electrical potential was applied to electrode, charged ions migrated to the electrode and are held in the electric double layer. Once external field is removed, the ions are quickly released back to bulk solution. Compared to conventional desalination technologies, electrosorption is an energy-efficient desalination process due to it operates at lower electrode potential (about 1–1.5 V) at which no electrolysis reactions occur. In addition, this process is environmentally attractive because it requires no chemicals for regeneration. Activated carbon is an effective electrode material for electrosorption. The material is inert, conductive, inexpensive, abundant and has high surface area to provide sufficient adsorption sites. Applications of electrosorption on ions removal for various kinds of water streams are introduced in this study.

INTRODUCTION

Water shortage is widely experienced in the whole world. It is particularly severe in China, which could even cause security problem in the world [1]. The water treatment market is enormous in China. This has naturally brought fierce competition for all major water companies all over the world. It is also the place where new technology has to be developed to meet all market challenges.

China has been experiencing high economic growth rate. However, water shortage is getting worse with the industrialization and the expansion of cities. China has over 600 cities (population above half million per city) in shortage of water. The amount in shortage is about 40 billion metric tons in 2006. In the rural area, more than 60 million farmers are drinking water with fluorine contents exceeding the limits and about 37 million farmers are drinking brackish water. The water needs to be treated for their drinking exceeds 15 billion metric tons per year [2, 3].

The World Bank has estimated that the population of China will reach 1.6 billion in 2030. The water demand will be 3 times of that in 1980. The water pollution problems in China are getting worse recently. Water shortage and water pollution have been identified as a serious threat to the public safety by the government. Many policies are made. These policies will promote the development of the water business continuously.

According to the governmental statistics, the water treatment market in China grows from $300 billion RMB in 2007 to $2,000 billion RMB in 2010. The annual growth rate is estimated at 15% for the next 30 years. This enormous market has brought competition from major companies all over the world.

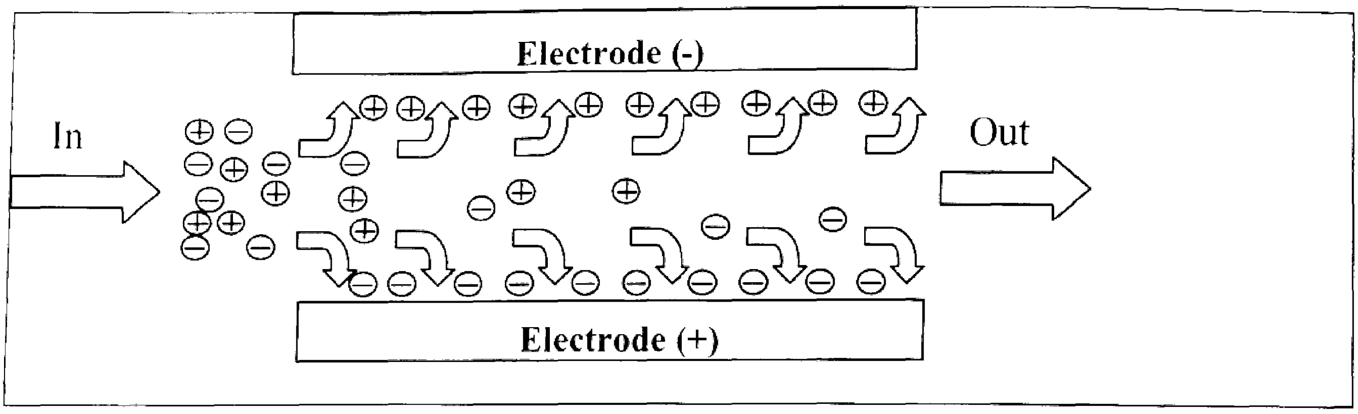

Figure 1. Capacitive deionization

Technologies are the fundamental for all the competitions. There have been many water treatment technologies developed. Depending on the applications, there are different advantages and disadvantages for different technologies. In general, there are various sedimentation, flotation and filtering technologies for the removal of suspended solids and oil droplets. Organics are frequently digested through various biological systems or removed with adsorbents. The removal of ions (desalination) is only considered when necessary due to its high cost.

The common desalination technologies include distillation, ion exchange, electrodialysis, and reverse osmosis [4–11]. High purity water can be obtained when these technologies are applied. However, there are in many cases we do not need to remove all the salts to generate the high purity water. For different applications, such as the drinking water, tap water, cooling water, irrigation water, paper mill water, steel mill water, petrochemical plant water, and electronic plant water, etc., different purities are required. There is definitely a need of a technology that is capable to adjust the amount of salt removed at will.

ELECTROSORB TECHNOLOGY

The electrosorb technology (EST) is developed based on the capacitive deionization (CDI) technology. The CDI technology was first patented by Becker in 1957 [12]. The fundamental theory is based on the electric double layer phenomenon in water. On a charged surface, counter ions are adsorbed preferably in the Helmholtz layer and the Diffuse layer on the surface. Therefore, a pair of electrodes will be able to adsorb both the cations and anions, as shown in Figure 1. When the charge is removed, cations and anions will be released from the electrodes. This mechanism allows one to design and engineering the apparatus capable to separate ions from water. Since the adsorption of ions is related to the voltages applied, the gap between the electrodes, the surface area of electrodes, the flow velocity, the retention time, etc., there are plenty parameters to adjust the amount of ions adsorbed during the process. Hence this technology has the potential to meet the needs on adjusting effluent salt contents at will.

There have been many developments on the CDI technology [13–21]. A good review can be found in a recent article by Marc Anderson [15]. Most of the developments are related to the electrode materials, which include graphite, activated carbon, carbon aerogels, carbon nanotubes, carbon cloth, etc.

Most developments of the CDI technology ended in the laboratory, with only a few making the effort to commercialize. Among those commercial developments, there is only one reached the full commercial stage with mass production capability, while the rests are still in the pilot to small capacity unit stages.

Figure 2. EST manufactured electrode modules

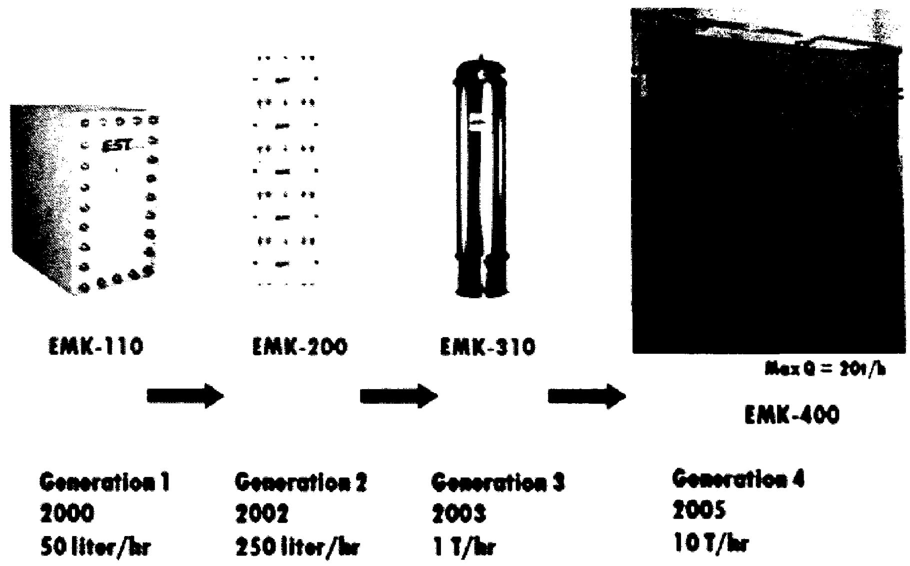

Figure 3. Advancement of EST treatment module

EST Water and Technologies Co., Ltd., is the company that so far has advanced the CDI technology to the arena that can compete commercially with all other technologies. The company is headquartered in Changzhou, China, where its manufacturing facility (Figure 2) is also located. Its marketing division and R&D Center are located in Beijing.

The company was established in 2000. Its R&D has made tremendous effort to refine the technology on both the electrodes and the systems to scale up the capability. As shown in Figure 3, the company took a module manufacturing approach. Its first generation product is only capable to treat 50 liter per hour. The capacity per module has been increased to 250 liter per hour in 2002, 1 ton per hour (1 cubic meter per hour or 6,341 gallons per day) in 2003, and 10 ton per hour in 2005. With the capability to mass produce the 10 ton per hour module, the company is able to compete with other technologies for large scale industrial water market by using multiple modules.

Activated carbon is utilized to make the electrodes. Activated carbon has high surface area, excellent permeability, good conductivity, and is inert to the reaction. It is abundant and is not too expensive. These characteristics made it an ideal electrode material.

Each module contains multiple pairs of electrodes. The gap between the electrodes is about 1 to 2 millimeters so that ions do not have to travel far distance. Figure 4 shows the schematics of the EST water treatment system. Mechanical filters are placed before the EST modules to prevent the entrance of large particles which may cause the blocking of the electrodes. Water is pumped into the EST modules from the bottom of the module. Conductivity is measured continuously for both the influent and the effluent. Voltage, flow velocity and retention time are the parameters utilized to ensure the effluent meeting the water salinity specifications. When the conductivity exceeds the specifications, the valve to the clean effluent is closed. Voltage is then turned off to release ions from the electrodes. A small amount of water is fed into the module to flush the ions out, which is collected as the concentrate. When disinfection is required, UV, ozone, or chlorination can be installed after the desalination.

APPLICATIONS

The EST system has been widely applied in a variety of industries in China. Its robustness and cost effectiveness have been demonstrated. Examples include applications in municipals, groundwater, petrochemicals, steel mills, thermoelectric powers, coal chemicals, paper mills, fertilizers, and high fluorine and high arsenic brackish water, etc. Some of the examples are presented here.

Figure 5 shows the picture of a desalination plant treating 80,000 tons per day (21 MGD) wastewater from the municipal sewage and coal chemical plant in Taiyuan, China. Taiyuan is the coal capital in China with 3 million populations. Its water supply is in extremely shortage. The Taiyuan Chemicals, a coal chemical company, has to look for alternative resources to meet its water demand.

The plan to use alternative water is shown in Figure 6. With cooperation from the city government, the company is able to obtain the city sewage water. Together with the wastewater from the coal company, the water is treated with conventional primary and secondary process and then feed to the EST modules.

Many technologies have been evaluated for this application. After a series of round robin pilot testing, the EST technology is determined as the only one that meets the challenges from both the technical and economic points. The organics from both the sewage and chemical plants are too hazardous to the membrane technologies, which causes the quick fouling of the membranes of reverse osmosis and other membrane based approaches.

The plant was built in 2007 and has been operating smoothly. Technical results of the operation are shown in Table 1. It is designed to remove 75% salts at 75% water yields. This has been easily achieved. The conductivity is reduced from 1174 μS/cm to 197 μS/cm, equivalent to 83% salt removal. The COD is reduced from 20 mg/L to 8 mg mg/L. Color is reduced from 26 degree to 9 degree. Elements such as chloride, sulfate, nitrogen, calcium, iron etc., are all removed at satisfactory level. This plant is planned to be expanded later to 8 times bigger to treat the whole city's wastewater.

In another example, the wastewater from the cold rolling mill of Bao Steel in Shanghai, China was recycled. The water contains oils and has been treated with catalytic oxidation and Membrane Bioreactor (MBR). The effluent of MBR is rich in salt, with conductivity around 3200 μS/cm. This water needs to be desalinated before it can be reutilized. The specification is to reduce the conductivity to less than 1500 μS/cm at a yield of 75%.

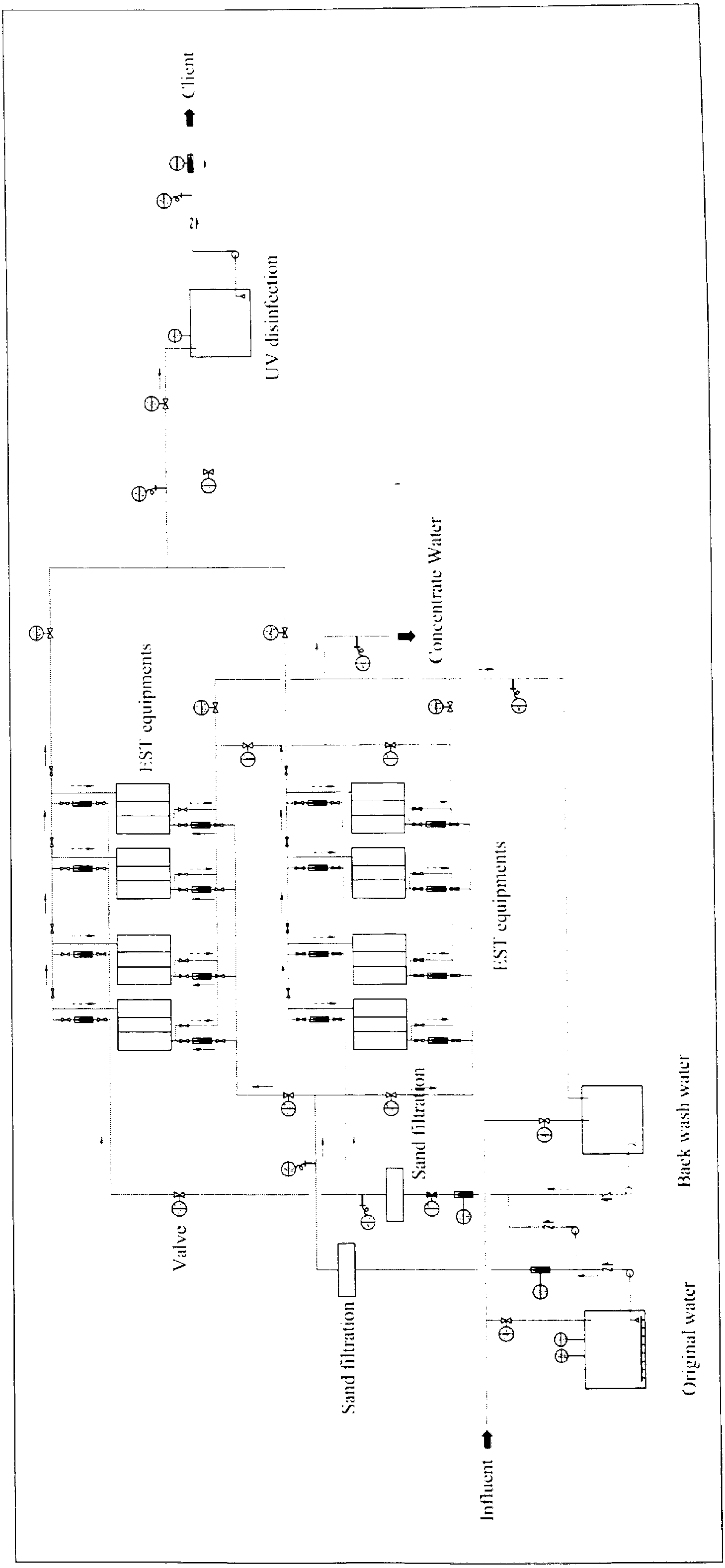

Figure 4. EST desalination process

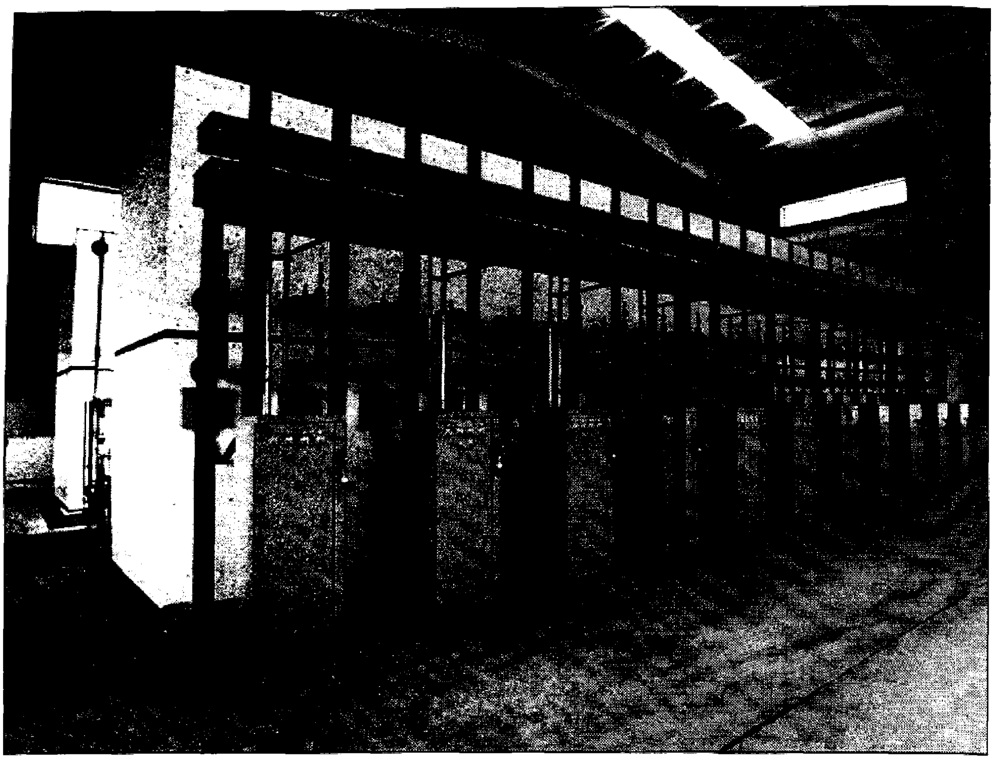

Figure 5. An EST plant at 80,000-TPD (21-MGD) capacity

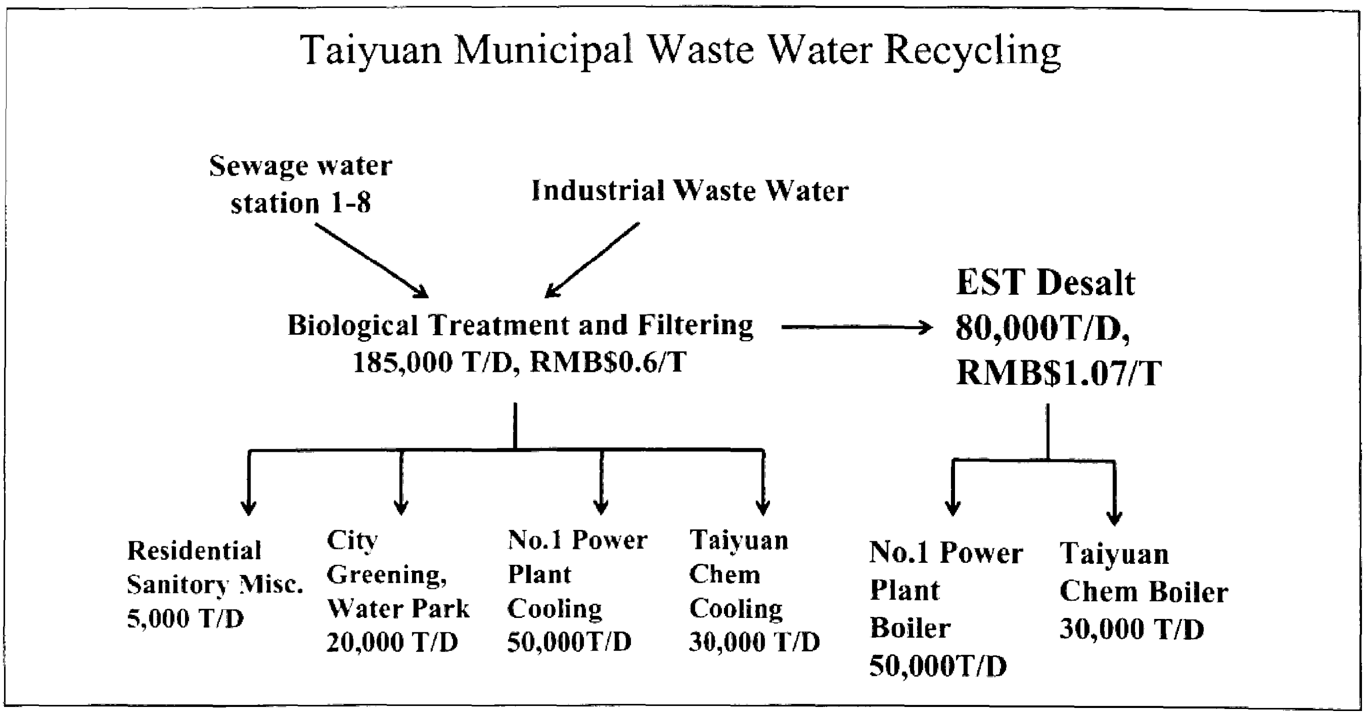

Figure 6. Treatment plan to recycle municipal wastewater

Figure 7 shows the EST plant operation data of the water for 16 days. During the operation, the water comes into the EST module has conductivity ranging from 2980 μS/cm to 3490 μS/cm. The average is 3213 μS/cm. After the EST treatment, the conductivity of the water is reduced to about 1100 μS/cm, with a range of 910 to 1254 μS/cm. This is well below the 1500 μS/cm specification. The 75% yield requirement is also exceeded.

Arsenic is an element that has troubled many water operations. This element has been linked to cancer of the bladder, lungs, skin, kidney, nasal passages, liver, and prostate. Non-cancer effects can include thickening and discoloration of the skin, stomach pain, nausea, vomiting; diarrhea; numbness in hands and feet; partial paralysis; and blindness. EPA has

Table 1. Taiyuan municipal wastewater treatment results

No.	Item	Unit	Influent	Effluent	Removal (%)
1	Conductivity	μS/cm	1174	197	83.2
2	COD_{Cr}	mg/L	20	8	60.0
3	Color	degree	26	9	65.4
4	Turbidity	NTU	6	1	81.4
5	Nitrogen	mg/L	10.1	3.7	63.8
6	Hardness	mg/L($CaCO_3$)	336.7	44.9	86.7
7	Alkalinity	mg/L($CaCO_3$)	248.4	77.3	68.9
8	Chloride	mg/L	132.2	7.1	94.6
9	Sulfate	mg/L	144.5	36.4	74.8
10	Total iron	mg/L	0.130	0.053	58.9
11	TDS	mg/L	882	224	76.3

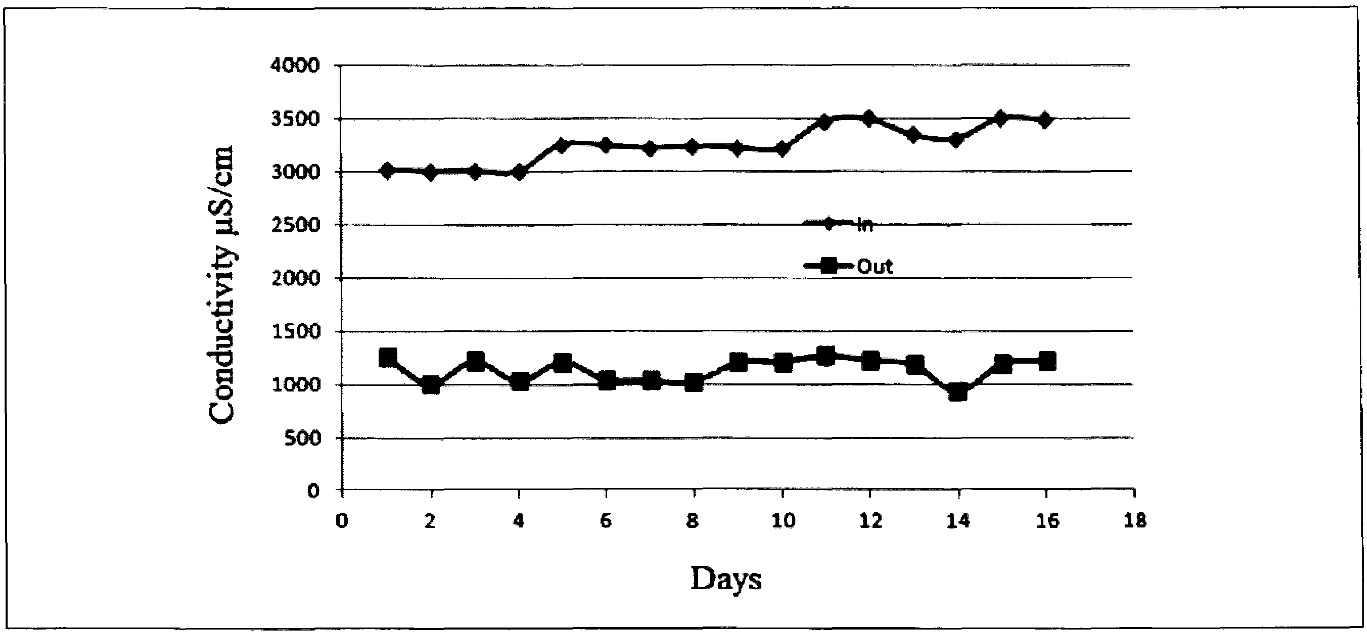

Figure 7. Desalination results at Bao Steel cold rolling mill

set the arsenic standard for drinking water at 0.010 parts per million (10 parts per billion) to protect consumers.

EST system has been installed for arsenic removal from the spring water by a bottling company. Except the arsenic, this water is rich in trace elements which is considered beneficial to the client's health. The conductivity of the water is about 450 μS/cm. The goal of this company is to reduce the arsenic to below the 10 ppb level.

Table 2 shows the operation data for this plant. The goal of arsenic reduction to below 10 ppb is well achieved. In addition, the conductivity is reduced to a level of about 90 μS/cm. This level gives the best taste of water. The system is still in good condition after 8 years operation.

CONCLUSIONS

EST has established its position in the water and wastewater treatment businesses. It has demonstrated the following technical advantages:

Table 2. Plant data on arsenic removal

No.	Arsenic (mg/L)		Conductivity (μS/cm)		pH	
	Influent	Effluent	Influent	Effluent	Influent	Effluent
1	0.06	<0.01	450	90	7.2	6.5
2	0.06	<0.01	446	90	7.4	6.5
3	0.06	<0.01	447	92	7.5	6.5
4	0.07	<0.01	447	93	7.2	6.5
5	0.07	<0.01	446	95	7.2	6.5

1. It consumes less energy than other desalination technologies. The low pressure drop nature of the process requires only low pumping energy. The flow path design is simple and is independent of the other structure factors. It does not require thermal energy.
2. The technology offers flexible and adjustable salt removal. The adjustment can be achieved by adjusting operation parameters such as voltage applied, flow velocity, and retention time, etc.
3. The EST technology is quite robust. It needs low maintenance. The EST module is very sturdy and can last for more than 5 years. The fouling problem associated with the membranes is not involved.
4. Little restrictions on influent water quality are involved. Unlike many other technologies, water containing COD, oils, chlorine, hardness, solvents, etc., can all be tolerated to some extents in the EST system.
5. No chemical additions are necessary. This is a physical process and does not require chemicals such as chelating agents or salt exchangers in the process.
6. It works in a broad temperature range. The variation of water temperature does not change the function of the equipment or the mechanism of the process.
7. The yield of water is typically above 75%. This is higher than the others and is quite important for areas where water is in shortage.

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