

Chemical Engineering

Elixir Chem. Engg. 92 (2016) 39296-39300

Elixir
ISSN: 2229-712X

Textile wastewater treatment using reverse osmosis and SDI

M. Ramesh Kumar¹, C.V. Koushik¹ and K. Saravanan²

¹Department of Fashion Technology, Sona College of Technology, Salem – 636 005, Tamilnadu, India.

²Department of Chemical Engineering, Kongu Engineering College, Erode – 638 052, Tamil Nadu, India.

ARTICLE INFO

Article history:

Received: 19 May 2012;

Received in revised form:

24 March 2016;

Accepted: 29 March 2016;

Keywords

Reverse osmosis,
Textile effluent,
Silica,
Silt density index,
Sulphate,
Treatment.

ABSTRACT

Textile industry is the major source of water consumption and wastewater pollution. There are various treatment techniques to remove textile wastewater pollution. Textile wet processing unit involves a variety of chemicals comprising a various class of dyes along with huge amount of water resulting from wet processing operation. The conservations of chemical become a most important aspect for environment specially in consideration of the pollution phenomenon and increasing cost of chemicals in order to make the industry much more competitive in the globalize context. For that reason, liquid waste management and waste volume reduction by the product recovery are essential. In the case of India many wet processing industries and about 80% of these are woven fabric dyeing industries are needed to feed the fabric in the garments industries. For these reasons, effluent treatment planning is a burning question for a wet processing unit. In order to solve these problems as textile technologist we should define many corrective measures. This paper deals with the effluent standards and different wastages of woven fabric wet processing industries along with reverse osmosis treatment and SDI (Silt Density Index) explained in detail. It also deals with the various advantages, comparison of RO feed and permeates, RO feed and reject parameters of Silica, Sulphate, Free Chlorine, Chlorides, Silicate and S.D.Index. RO feed and permeate parameters Si reduced by – 95.46%, SO₄ reduced by – 99.19%, Cl⁻ reduced by – 94.51%, SiO₂ reduced by – 95.22% and SDI reduced by – 100.00%.

© 2016 Elixir All rights reserved.

Introduction

Drewes (2003) study the Reverse osmosis (RO) membranes are widely used in drinking water, wastewater and industrial applications. The use of RO membranes in advanced wastewater reclamation using secondary treated wastewater effluent to produce water for indirect potable use has also increased over the past few years. However, a major impediment in the application of RO membrane technology for desalination and wastewater reclamation is membrane fouling. Barker (2000) investigate the advanced water reclamation, secondary effluent from wastewater treatment plants contains dissolved organic matter, commonly known as effluent organic matter. When the second wastewater effluent is introduced to the RO membrane processes as feed water, the presence of effluent organic matter contributes to organic fouling.

Amjad (1993) study the membrane – based separation processes like Ultrafiltration (UF) and Reverse Osmosis (RO) have been applied for treating a wide variety of industrial effluents.

Chain (1977) investigate the most of the effluents from different industrial source were used to be discharged directly in the soil or in ground water. But due to stringent environmental restrictions, Central Pollution Control Board (CPCB) has become vigilant and has imposed very stringent measures for recovering pure water from such industrial effluents. However, for the treatment of an effluent by conventional methods like aerobic and non-aerobic digestion, the ratio of biological oxygen demand (BOD) to COD should be >0.6.

Walter (2006) study the membrane processes, namely, reverse osmosis (RO), nanofiltration (NO), ultrafiltration (UF) and microfiltration (MF) are continuing to get more and more

attention world wide for their effectiveness in water treatment. RO got recognition as an alternative option among other conventional treatment processes in the early 1960s when it was successfully used for the first time in the desalination of seawater. As a result of continuous research and development in this field, a new generation of RO membranes which can operate under ultra-low pressure was developed in the beginning of 1995. This new generation of RO and NF were able to produce double the quantity of flux of the conventional RO and NF at low operating pressure without sacrificing the quality of the produced water by keeping the rejection of the organic and inorganic species at the same level.

Schwinge (2004) study the membranes are manufactured in different shapes and configurations, the most popular are spiral wound membrane (SWM), hollow fibre, tubular and frame and plate module with the target to reach an optimal performance for both operating conditions and configuring modules. Studying how different variables in the process change along the membrane play an important role in the optimization process and it was the issue for most of the researches both numerically and experimentally. Previous studies reported that across the longitudinal direction of the SWMs a fall in the permeate flow rate and a rise in the permeate and concentrate concentrations always took place.

Brian (1965) study the finite difference method was used by Brian to calculate the salt concentration polarization over the length of the membrane for the case of permeate surface. The results obtained were compared with a constant flux model across the membrane length.

Bhattacharyya (1990) investigate in used a finite element method to predict flux behaviour and concentration polarization

throughout various configurations of RO membranes. The results obtained from this study were in total agreement with previous work regarding increase in concentration and decrease in permeate flux along the membrane length.

Fletcher (2004) In another numerical study, the effect of gravity on the permeation velocity and salt mass fraction through out the membrane were investigated. Their results showed that the effect of gravity cannot be overlooked along the channel with the adverse gravity conditions giving the highest salt concentrations and lowest flux at the membrane surface.

Drewes (2006) investigate the RO process is gaining wider use for contaminant removal in advanced water and wastewater treatment and desalination. Advancements in membrane developments result in the production of better and more economical membranes. These are yielding the desired result of being adopted as an efficient water treatment technology. However, membrane fouling is still a great hindrance for operation and cost efficiency. Fouling phenomena could severely limit membrane process efficiency as they lead to several deleterious effects including flux decline, possible permeate quality decrease and a gradual membrane degradation. An uneconomical increase in applied pressure and the need for frequent cleaning (shortening membrane life) or replacement become the necessary options if the rate of water production is to be maintained constant. The effect of fouling has been investigated extensively by numerous researchers.

Machenbach (1998) study the membrane process the increasing cost of water and its wasteful consumption have now induced a treatment process which is integrated in in-plant water circuits rather than as a subsequent treatment. From this standpoint, membrane filtration offers potential applications. Processes using membranes provide very interesting possibilities of separating hydrolyzed dyestuffs and dyeing auxiliaries, thus simultaneously reducing coloration and the BOD/COD of the wastewater.

Tinghui (1983) investigate the Reverse osmosis membranes have a retention rate of 90% or more for most types of ionic compounds and produce a high quality of permeate. Decoloration and the elimination of chemical auxiliaries in dye house wastewater can be carried out in a single step. Reverse osmosis permeates the removal of all mineral salts, hydrolyzed reactive dyes and chemical auxiliaries. The problem involved is that the higher the concentration of salts, the more important the osmotic pressure becomes and therefore the greater the energy required.

Erswell (1988) study the Nanofiltration membranes retain organic compounds of low molecular weight, divalent ions or large monovalent ions, such as hydrolyzed reactive dyes as well as dyeing auxiliaries. (Tang, 2002) investigate the effect of the concentration of dyes has been frequently reported in dye house effluents as well as the concentration of salt and the pressure. In most published studies concerning dye house effluents, the concentration of mineral salts does not exceed 20 g L^{-1} and the concentration of dyestuff 1.5 g L^{-1} . (Abari, 2002) study the effluents are reconstituted with generally only one dye and the volume studied is low. (Freger, 2000) study the treatment of wastewater after dyeing by nanofiltration thus represents one of the rate applications possible for the treatment of solutions with highly concentrated and complex solution.

Watters (1991) study the Ultrafiltration enables the elimination of macromolecules and particles but the elimination of polluting substances, such as color is never complete (between 31% and 76%). (Rott, 1999) study the even in the best

of cases, the quality of the treated wastewater does not permit its reuse for feeding sensitive processes, such as the dyeing of textile. Ciardelli (2001) study Ultrafiltration can only be used as a pretreatment for reverse osmosis or in combination with a biological reactor. (Mignani, 1999)

Al-Malack, (1997) study the Microfiltration is suitable for treating dye baths containing pigment dyes as well as subsequent rinsing baths. Sadr Ghayeni (1998) investigate the auxiliaries remain in the retentant. Microfiltration can be used as a pretreatment for nanofiltration or reverse osmosis

Hitendra Bhuptawat (2007) investigates the water extract of Moringa. Oleifera seed was applied to a treatment sequence comprising coagulation-flocculation-sedimentation-sand filtration. Model waters (kaolinite suspensions) of turbidities 10, 100, 300 and 700 NTU were prepared. For the 10 NTU water, the optimum dose was only evident when sand filtration was incorporated into the treatment.

Zhi Lin Li, Wei Liu, Xin Fang. Chen (2010) study the feasibility of using laccase to treat oily wastewater was examined. When only laccase was added to the synthetic oily wastewater, the suitable technological conditions were laccase at 3 U/ml, pH at 6.0, a temperature of 30°C , and a reaction time of 6 h for the initial oil concentration of 120 mg/L. Under those conditions, the rate of oil removal was as high as 69%. The effects of Mg^{2+} , Mn^{2+} , Cu^{2+} , and Fe^{2+} ions in wastewater on the rate of oil removal using laccase were investigated. The results showed that Cu^{2+} and Fe^{2+} ions obviously inhibited the catalytic performance of laccase under the studied concentration. On the other hand, Mg^{2+} and Mn^{2+} ions only had slight effects on the rate of oil removal for the range of concentrations studied. A 95% oil removal rate could be obtained when actual wastewaters were treated using laccase with the additive chitosan under the suitable technological conditions.

Fons Moi. Pang, Sheau Ping. Teng, Tjoon Tow. Teng (2009) investigates the hydroxide precipitation and coagulation-flocculation methods were used to treat wastewater containing lead, zinc, copper, and iron. The concentrations of heavy metals in the synthetic wastewater range from 1 to 14 mg/L for lead, 5 to 90 mg/L for zinc, 3 to 90 mg/L for copper and 5 to 45 mg/L for iron. Individual Zn(II) and Cu(II) with concentrations below 90 mg/L and Fe(III) with concentrations below 45 mg/L were removed up to 99% by the precipitation method in the pH range of 8.7 to 9.6, 8.1 to 11.1, and 6.2 to 7.1, respectively.

Daniel Babineau, Dominique Chartray, Roland Leduc (2009) investigates the treatment of municipal wastewaters by physical-chemical methods normally requires the use of a metallic salt coagulant and a synthetic coagulant aid. Integrating the sustainable development concept in the treatment of waters favours the use of renewable resources such as natural biopolymers. In order to better understand the peculiarities of using a product of natural origin in municipal wastewater treatment, laboratory testing (jar tests) was achieved with chitosan as a coagulant aid, as well as full-scale testing in a medium size physical-chemical wastewater treatment plant. The full-scale test was performed in two parallel, identical systems treating the same wastewater under the same conditions. The one using a combination of alum with a synthetic polymer (AL/SP) was compared with the other which used alum and chitosan (AL/CH). Removals for COD, SS, and total phosphorus reached 87%, 95% and 93%, respectively, for the AL/CH combination. These results are similar to those obtained for COD and SS with the AL/SP combination. Some results show a coagulant dosage (alum) up to 24.8% lower with chitosan as the

usual coagulant aid. For total phosphorus, however, the results show that removals.

Methodology

One of the leading woven fabric-dyeing units, SIPCOT, Perundurai, Erode, visited for manufacturing process and wastewater quantity were collected. Effluent samples collected from Reverse Osmosis feed, permeate and reject parameters. Following parameters were tested

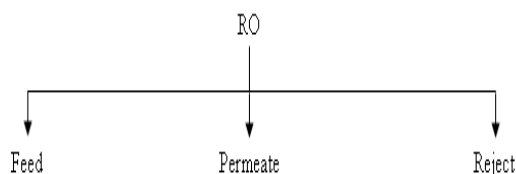
1. Silica
2. Sulphate
3. Free Chlorine
4. Chlorides
5. Silicate
6. S.D. Index

Then comparison between the results of RO feed and Permeate, RO feed and rejects parameters.

Results and Discussion

The present work focus on the process and treatment methodology adopted in woven fabric dyeing industry. Four numbers of soft flow reactor (batch process), two numbers of beam dyeing machine and three numbers of padding are used for dyeing.

Three stages of treatment water tested like, RO feed, RO Permeate and RO reject. Each stage tested in following parameters of Silica, Sulphate, Free Chlorine, Chlorides, Silicate and Silt Density Index (S.D. Index).



Reverse Osmosis (10 Lack liters capacity)

- Membrane: Polyamide
Spiral wound
5 Micron size
Membrane diameter 8"
- Dosing:
Dosing for pH correction - HCl
Dosing for Dechlorination - Sodium Metta Bi Sulphite (SMBS)
Dosing for Anti sculentent - Phospanic Acid Base
- RO – I; 1st stage feed: 6 Vessel & 4 Vessel (2nd stage feed)
[6 X 6: 4 X 6]
[6 Vessel X6 Membrane: 4 Vessel X 6 Membrane]
(10 X 6 = 60 Membrane)
- RO – II; 1st stage 2 Vessel & 1 Vessel (2nd stage)
[2 X 6: 1 X 6]
[2 Vessel X6 Membrane: 1 Vessel X 6 Membrane]
(3 X 6 = 18 Membrane)
(Vessel length 6 meters, Sprial wound membrane 6 numbers, each membrane length1M)
- Flow Rate
Feed water 50 m³/hour
Permeate 45 m³/hour
Reject to evaporator 5 m³/hour

Table 1, Reverse Osmosis feed parameters

| Days | Si ppm | SO4 ppm | Free Cl2 ppm | Cl ⁻ ppm | SiO2 Ppm | SD Index |
|------|--------|---------|--------------|---------------------|----------|----------|
| 1. | 5.47 | 284 | Nil | 1276 | 11.76 | 4.2 |
| 2. | 5.31 | 253 | Nil | 1270 | 11.40 | 3.0 |
| 3. | 5.75 | 242 | Nil | 1150 | 12.36 | 4.0 |
| 4. | 5.90 | 236 | Nil | 1092 | 11.88 | 4.4 |
| 5. | 4.90 | 222 | Nil | 1040 | 10.29 | 3.5 |
| 6. | 5.5 | 272 | Nil | 1190 | 10.98 | 4.0 |
| 7. | 6.17 | 266 | Nil | 1210 | 12.02 | 4.4 |
| 8. | 5.22 | 240 | Nil | 1160 | 11.06 | 3.0 |
| 9. | 5.30 | 234 | Nil | 1210 | 10.96 | 3.2 |
| 10. | 5.42 | 246 | Nil | 1226 | 10.84 | 3.4 |

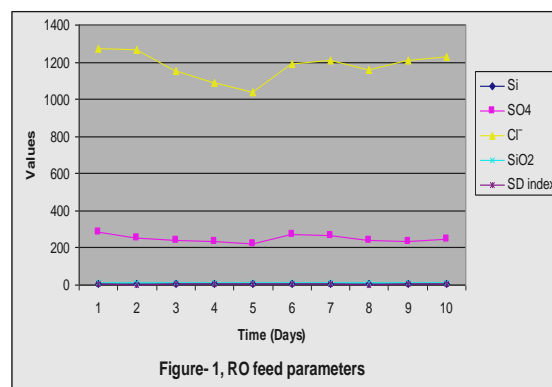


Table 1 and figure 1, show the characteristics of RO feed parameters in the frequency of ten days.

Si maximum value of - 6.17 ppm,
SO4 maximum value of – 284 ppm,
Free Cl2 value is Nil,
Cl⁻ maximum value of – 1276 ppm,
SiO2 maximum value of – 12.36 ppm and
SDI maximum value of – 4.4

Table 2, Reverse Osmosis permeate parameters

| Days | Si ppm | SO4 ppm | Free Cl2 ppm | Cl ⁻ ppm | SiO2 ppm | SD Index |
|------|--------|---------|--------------|---------------------|----------|----------|
| 1. | 0.34 | 4 | Nil | 74 | 0.72 | Nil |
| 2. | 0.32 | 3 | Nil | 80 | 0.67 | Nil |
| 3. | 0.36 | 2 | Nil | 82 | 0.75 | Nil |
| 4. | 0.36 | 3 | Nil | 70 | 0.76 | Nil |
| 5. | 0.32 | 2 | Nil | 85 | 0.67 | Nil |
| 6. | 0.35 | 3 | Nil | 72 | 0.74 | Nil |
| 7. | 0.36 | 4 | Nil | 76 | 0.76 | Nil |
| 8. | 0.28 | 3 | Nil | 70 | 0.59 | Nil |
| 9. | 0.29 | 3 | Nil | 74 | 0.61 | Nil |
| 10. | 0.31 | 4 | Nil | 78 | 0.65 | Nil |

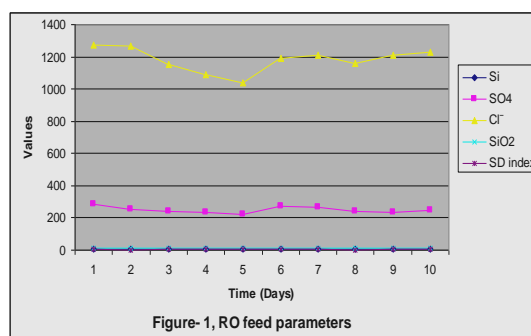


Table 1 and figure 1, show the characteristics of RO feed parameters in the frequency of ten days.

Si maximum value of - 6.17 ppm,
 SO₄ maximum value of - 284 ppm,
 Free Cl₂ value is Nil,
 Cl⁻ maximum value of - 1276 ppm,
 SiO₂ maximum value of - 12.36 ppm and
 SDI maximum value of - 4.4

Table 2, Reverse Osmosis permeate parameters

| Days | Si ppm | SO ₄ ppm | Free Cl ₂ ppm | Cl ⁻ ppm | SiO ₂ ppm | SD Index |
|------|--------|---------------------|--------------------------|---------------------|----------------------|----------|
| 1. | 0.34 | 4 | Nil | 74 | 0.72 | Nil |
| 2. | 0.32 | 3 | Nil | 80 | 0.67 | Nil |
| 3. | 0.36 | 2 | Nil | 82 | 0.75 | Nil |
| 4. | 0.36 | 3 | Nil | 70 | 0.76 | Nil |
| 5. | 0.32 | 2 | Nil | 85 | 0.67 | Nil |
| 6. | 0.35 | 3 | Nil | 72 | 0.74 | Nil |
| 7. | 0.36 | 4 | Nil | 76 | 0.76 | Nil |
| 8. | 0.28 | 3 | Nil | 70 | 0.59 | Nil |
| 9. | 0.29 | 3 | Nil | 74 | 0.61 | Nil |
| 10. | 0.31 | 4 | Nil | 78 | 0.65 | Nil |

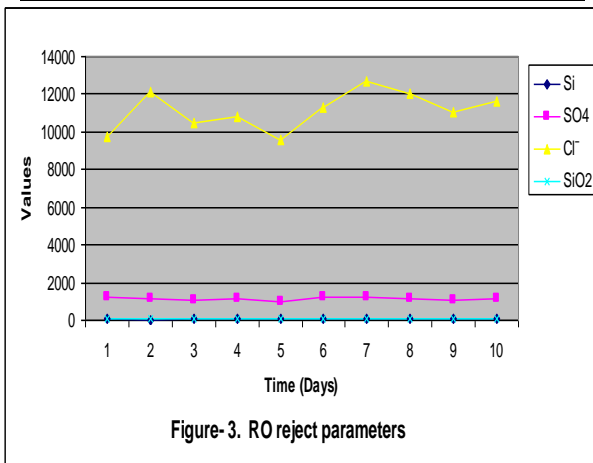


Table - 3 and figure - 3, show that the RO reject parameters. The comparison between RO feed and reject parameters was given below.

Si reduced by - 88.08%
 SO₄ reduced by -76.72%
 Cl⁻ reduced by -89.94%
 SiO₂ reduced by -88.86%



Figure 4 Reverse Osmosis plant 10 Lack liters capacity

Figure 4,5,6 shows the RO 10 lack liters capacity, RO stage I, stage II and RO dosing tank. Figure 7 show the soft flow dyeing machine 1000 KLD capacity and Figure 8 show the Beam dyeing machine 500 KLD capacities.



Figure 5 Reverse Osmosis Plant Stage I and II



Figure 6 Reverse Osmosis dosing tanks



Figure 7 Soft flow dyeing machine



Figure 8 Beam dyeing machine

Silt Density Index (SDI)

$$SDI = (1 - t_1 / t_2) \times 100 / T_{15}$$

Where,

t_1 = initial time taken (for 500 ml sample)

t_2 = final time taken (for 500 ml sample)

T_{15} = time duration 15 minutes

Example :

t_1 = 44 sec (2 kg pressure)

t_2 = 80 sec (2 kg pressure)

$$SDI = [1 - (44/80)] \times 100 / 15$$

$$SDI = 3.0$$

Standard value of SDI < 5.

[SDI paper: cellulose nitrate

Paper dia = 47 mm

Pore size = 0.45 micron

- colloidal silica

- silt (fine particals)

- living(or) non living organism i.e, >0.45 micron]

Conclusion

▪ The recycling of treated wastewater and zero wastewater discharge concept are found technically feasible and economically viable in the textile dyeing industries located in the area of Erode.

▪ Reduction percentage between RO feed and permeate Si – 95.46%,
SO₄ reduced by – 99.19%, Cl⁻ reduced by – 94.51%,
SiO₂ reduced by – 95.22% and SDI reduced by – 100.00%.

▪ The most attracting part of water recovered from these membranes is its extremely low hardness, which is always demanded in textile sector for an improved finish and better quality of dyeing.

▪ Reverse osmosis membrane technologies are of the most importance several advantages are given below:

○ Separation does not require addition of chemicals as may be the case in the water clarification, by means of coagulation-flocculation process

○ Decreased the production cost

○ High permeability to water

○ High efficiency of the membranes in selective mineral rejection

Nomenclature

Cl⁻ - Chlorides

Free Cl₂ – Free Chlorine

SO₄ – Sulphate

SO₃ – Sulphide

Si – Silica

ppm – Parts Per Million

RO – Reverse Osmosis

SiO₂ – Silicate

SDI - Silt Density Index

References

[1] Amjad. Z (Ed.), 1993. Reverse Osmosis: Membrane Technology, Water chemistry and industrial applications. Van Nostrand Reinhold, New York.

[2] Abari, A., Remigy, J.C., Aptel, P., 2002. Treatment of textile dye effluent using a polyamide-based nonofiltration membrane, Chemical engineering production, 41, 601 – 609.

[3] Al-Malack, M.H., Anderson, G.K., 1997. Use of crossflow microfiltration in wastewater treatment, Water Research, 31, 3064 – 3072.

[4] Barker, D.J., Salvi, S.M.L., Langenhoff, A.A.M. and Stuckey, D.C. (2000). "Solubel microbial products in ABR treating low – strength wastewater", Journal of Environmental Engineering, 126, 239 – 249.

[5] Brian, P.L.T., 1965. "Concentration polarization in reverse osmosis desalination with variable flux and incomplete salt rejection", Indian Engineering Chemical Fund. 4, 439 – 445.

[6] Bhattacharyya, D., Back, S.L., Kermode, R.I., 1990. "Prediction of concentration polarization and flux behavior in reverse osmosis by numerical analysis", Journal of membrane science, 48, 231 – 262.

[7] Chain, E.S.K., Dewalle, F.B., 1977. "Treatment of high strength acidic wastewater with completely mixed anaerobic filter", Water Res. 11, 295.

[8] Ciardelli, G., Ranieri, N., 2001. "The treatment and reuse of wastewater in the textile industry by means of ozonation and electroflocculation", Water research, 35, 567 – 572.

[9] Drewes, J.E., Reinhard, M. and Fox, P., 2003. "Comparing microfiltration – reverse osmosis and soil – aquifer treatment for indirect potable reuse of water", Water Res. 37, 3612 – 3621.

[10] Drewes, P.Xu. J.E., Kim, T.U., Bellona, C., Amy, G. 2006. "Effect of membrane fouling on transport of organic contaminants in NF/RO membrane applications", journal of membrane science, 279, 165 – 175.

[11] Daniel Babineau, Dominique Chartray, Roland Leduc, 2009. "Comparative study of two flocculants in the physical-chemical treatment of municipal wastewater, chitosan and a synthetic polymer", Water quality research journal of Canada, Vol. 43 (2/3), pp 219 – 229.

[12] Erswell, A., Brouchaert, C.J., Buckley, C.A., 1988. The reuse of reactive dyes liquors using charged ultrafiltration membrane technology, Desalination 70, 157 – 167.

[13] Fletcher, D.F., Wiley, D.E., 2004. A computational fluids dynamics study of buoyancy effect in reverse osmosis, journal of membrane science, 245, 175 – 181.

[14] Freger, V., Arnot, T.C., Howell, J.A., 2000. "Separation of concentrated organic/inorganic salt mixtures by nanofiltration", Journal of membrane science, 178, 185 – 193.

[15] Fons Moi. Pang, Sheau Ping. Teng, Tjoon Tow. Teng, A.K. Mohd. Omar, 2009. "Heavy metals removal by hydroxide precipitation and coagulation-flocculation methods from aqueous solutions", Water Quality Research Journal of Canada, Vol. 44 (2):pp 174 – 182.

[16] Hitendra Bhuptawat, G.K. Folkard, Sanjeev Chaudhari, 2007. "Laboratory evaluation of a water-treatment sequence using Moringa oleifera seed coagulant", International Journal of Water, Vol. 3, No.3 pp. 299 - 315.

[17] Machenbach, I., 1998. Membrane technology for dyehouse effluent treatment, Membrane Technology, 7 – 10.

[18] Mignani, M., Nosenzo, G., Gualdi, A., 1999. Innovative ultrafiltration for wastewater reuse, Desalination 124, 287 – 292.

[19] Rott, U., Minke, R., 1999. Overview of wastewater treatment and recycling in the textile processing industry, Water Science Technology, 40, 37 – 144.

[20] Schwinge, J., Neal, P.R., Wiley, D.E., Fletcher, D.F., Fane, A.G., 2004. Spiral wound modules and spacers review and analysis, Journal of membrane science, 242, 129 – 153.

[21] Sadr Ghayeni, S.B., Beatson, P.J., Schneider, R.P., Fane, A.G., 1998. Water reclamation from municipal wastewater using combined microfiltration – reverse osmosis, preliminary performance data and microbiological aspects of system operation, Desalination 116, 65 – 80.

[22] Tinghui, T., Matsuura, T., Sourirajan, S., 1983. Effect of membrane materials and average pore size on reverse osmosis separation of dyes, Industrial engineering chemical production research division, 22, 77 – 85.

[23] Tang, C., Chen, V., 2002. Nanofiltration of textile wastewater for water reuse, Desalination 143, 11 – 20.

[24] Walter, I.R., Van der Meer, G.V., 2006. Mathematical modeling of NF and RO, in <http://www.gezondheidstechniek.tudelft.nl/meer.htm>, [accessed in 2006].

[25] Watters, J.C., Biagtan, E., Senlar, O., 1991. Ultrafiltration of a textile plant effluent, Separation science and Technology, 26, 1295 – 1313.

[26] Zhi Lin Li, Wei Liu, Xin Fang. Chen, He Sheng. Li, Yun Miao. Tian, 2010, "Research on the application of Laccase to the treatment of oily wastewater", Water quality research journal of Canada, Vol. 45 (1), pp 91 – 98.