International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 2 Issue 5, May - 2013

Studies On Flyash As An Adsorbent For Removal Of Various Pollutants From Wastewater

Sunil J. Kulkarni[1], Sonali R. Dhokpande[2], Dr. Jayant P. Kaware [3]
[1,2]*Assistant Professor, Department of Chemical Engineering, Datta Meghe College of Engineering ,Airoli, Navi Mumbai,India*
[3]*Professor, Department of Chemical Engineering, College of Engineering and Technology, Akola, Maharashtra*

Abstract

Organic and inorganic pollutants in wastewater are cause of concern in current scenario of rapid industrilization. Flyash as an adsorbent is very good alternative and attracts great application. In the present research, bagasse fly ash is used as an adsorbent for removal of various pollutants like organic matter, phenol, chromium and acetic acid. The effect of parameters like contact time, adsorbent dose, pH and particle size was studied and optimum values of these parameters were reported. The optimum adsorption times for COD, phenol, chromium and acetic acid were found to be 180,250,220 and 150 minutes respectively. It was observed that 3,3.5,1 and 4 grams of flyash is optimum for the 100 ml of effluent sample for the removal of COD, phenol, chromium and acetic acid and the optimum pH values for the adsorption were 6, 6.5, 2 and 6 respectively. The percentage removal remains constant for the particle sizes finer than 72 mesh number particles for these pollutants. It was observed that the adsorption of these pollutants follows Freundlich isotherm reasonably well.

1.Introduction

In recent years, utilization of fly ash has gained much attention in public and industry, which will help to reduce the environmental burden and enhance economic benefit. The technical feasibility of utilization of fly ash as a low-cost adsorbent for various adsorption processes for removal of pollutants in air and water systems has been studied by various researchers. Instead of using commercial activated carbon or zeolites, a lot of researches have been conducted using fly ash for adsorption of nitrogen oxides, oxides of sulphur, organic compounds, and mercury in air, and cations, anions, dyes and other organic matters in waters. It is recognized that fly ash is a promising adsorbent for removal of various pollutants. Chemical treatment of fly ash will make conversion of fly ash into a more efficient adsorbent for gas and water cleaning.

1.1 Organic Matter

Chemical oxygen demand (COD) is the amount of oxygen required for the organic matter for its chemical decomposition. The limit for COD in wastewater to the reservoirs is 250 mg/l. Conventional biological and non biological treatment processes like activated sludge are used for the treatment.

1.2 Phenol

Phenol has its presence in the effluent from major chemical and pharmaceutical industries such as petrochemical industries, petroleum refineries, coal gasification operations, liquefaction process, resin manufacturing industries, dye synthesis units, pulp and paper mills and pharmaceutical industries. It is a highly corrosive and nerve poisoning agent. Phenol causes harmful side effects such as sour mouth, diarrhea, impaired vision, excretion of dark urine. It is also toxic for fishes. The toxic levels usually range between the concentrations of 10-24 mg/L for human and the toxicity level for fish between 9-25 mg/l. Lethal blood concentration of phenol is around 150-mg/100 ml. Various treatment processes used for the removal and/or recovery of phenols are hot gas or steam stripping, adsorption, ion exchange solvent extraction, oxidation, phase transfer catalysis and biological treatment processes. Phenolic waste water is treated using activated carbon in the fixed bed/ moving bed/ fluidized bed.

1.3 Chromium

It is found in the environment in three major states: chromium (0), chromium (III), and chromium (VI).

Chromium (III) occurs naturally in the environment, while chromium (VI) and chromium (0) are generally produced by industrial processes. In the form of the mineral chromite, it is used by the refractory industry to make bricks for metallurgical furnaces. Chromium compounds produced by the chemical industry are used for chrome plating, the manufacture of pigments, leather tanning, wood treatment, and water treatment. The minimum human daily requirement of chromium for optimal health is not known, but a daily ingestion of 50-200 micrograms (µg) per day (0.0007-0.003 milligram of chromium per kilogram of body weight per day) has been estimated to be safe and adequate. Brewer's yeast and fresh foods are good sources of chromium. Long-term exposure of workers to airborne levels of chromium higher than those in the natural environment has been associated with lung cancer. Compounds containing hexavalent chromium-chromium (VI) - is believed to be the major problem when inhaled.

1.4 Acetic Acid

Environmental effects depend on the concentration and duration of exposure to acetic acid. In high concentrations it can be harmful to plants, animals and aquatic life. Inhalation of acetic acid causes irritation to the nose, throat and lungs. It is a corrosive substance, where inhalation of concentrated vapour may cause serious damage to the linings of these organs and later, breathing difficulties may result. Sensitization may result from repeated exposures. Ingestion of this substance may cause severe corrosion of the mouth and gastrointestinal tract, leading to vomiting, diarrhoea, circulatory collapse, kidney failure and death. Skin contact with concentrated solutions causes skin damage, indicated by pain, redness and blisters. Second degree burns may form after a few minutes of contact. Skin sensitisation is a rare consequence of exposure. Industries reporting acetic acid emissions include those that manufacture paper and paper products, meat and meat products, textile products and chemicals. Metal ore mining can also produce acetic acid.

1.5 Literature Review

Studies carried out by Wang and Wu revealed that unburned carbon component in fly ash plays an important role in adsorption capacity[1]. There are many research reports on work that have been carried out in the field of adsorption techniques for the removal of toxic metal ions, pollutants in air, organic and inorganic compounds, and dye adsorption, in wastewater using fly ash as adsorbent.Treatment of wastewater by using the adsorption derived from agricultural waste was carried out by Mohan et. al.[2]. COD and BOD reduction from coffee processing wastewater using Avacado peel carbon was carried out by Devi et.al.[3]. Treatment of domestic wastewater by using a microaerobic membrane bioreactor was tried by Chu et.al.[4]. Removal of refractory compounds from stabilized landfill leachate using an integrated H_2O_2 oxidation and granular activated carbon (GAC) adsorption treatment carried out by Kurniawan and Lo[5]. Treatment of municipal wastewater using laterite-based constructed soil filter was tried by Kadam et.al.[6].

Various methods have been tried for organic matter removal of wastewater. A review on anaerobic treatments for domestic and industrial was carried out by Chan et.al. According to them high rate anaerobic–aerobic bioreactors have been increasingly employed for wastewaters with high chemical oxygen demand[7]. A bioassay using the luminescent bacterium Vibrio-qinghaiensis associated with solid-phase extraction (SPE) was developed for evaluating the variation of ecotoxicity along with the reduction of organic substances in a domestic wastewater treatment plant employing an oxidation ditch process by Ma and Wang.[8]. Short- and long-term effects of temperature on partial nitrification in a sequencing batch reactor treating domestic wastewater were studied by Guo et.al.[9]. Treatment of municipal solid wastes leachate by means of chemical and electro-coagulation was carried out by Veli et. al.[10]. Reduction of COD and color of dyeing effluent from a cotton textile mill by adsorption onto bamboo-based activated carbon was carried out by Ahmad and Hameed[11].

The work on new adsorbent from coconut husk has been carried out by Krishna and Yenkee[12]. The activated carbon adsorption has also been used for coke effluents by Prasad and Singh[13]. The principle of adsorption, types of adsorption and its the isotherms are described by Treybal[14]. A batch study for phenol adsorption using leaf litter has been carried out by Mishra and Bhattacharya[15]. The treatment of phenolic wastewater in a multistage bubble column adsorber has been tried by Kumar et.al.[16]. These studies have shown that metals removal is most effcient when the loading rates are low. Removal of chromium from electro-plating wastewater by simple chemical treatment and ion exchange has been studied by Barbooti et al.[17]. The elecrocoagulation was tried for removal of metals by Christoforidis and Valsamidou.[18]. They carried out experiments for studying the performance of electrocoagulation with aluminum electrodes for simultaneous removal of nickel, copper, zinc and chromium from synthetic aqueous aliquot solutions and actual electroplating wastewater . Stasinakis et al have studied the effects of chromium (vi) addition on the activated sludge process [19,20] . Ion exchange resins were used for removal of chromium from water and wastewater by Rengaraj et al.[21] .The ion exchange resins investigated in this study showed reversible uptake of chromium and, thus, have good application potential for the removal/recovery of chromium from aqueous solutions. Liquid−liquid extraction of chromium(VI) with Tricaprylmethylammonium Chloride using isoamylalcohol as the diluent was carried out by Kalidhasan et al.[22] . Cellulose-clay composite biosorbent was tried for removal of chromium from industrial wastewater by Kumar et al.[23]. Reverse osmosis membrane for chromium Removal from aqueous solution was reported by Red et al. [24] .The reasearch on removal of acetic acid from wastewater by liquid surfactant memebrane was carried out by Van et.al.[25]. Nawle and Patil have carried out investigation on acetic acid removal from waste water using fly ash[26]. They observed that the adsorption process reasonably agrees with Freundlich adsorption isotherm. The equilibrium established between concentration of acetic acid in solution and fly ash on surface within first 20 minutes of agitation and there after no appreciable change in acetic acid adsorption was observed.

2. Methodology

The flyash from the sugar industries was activated by heating in oven at about 350°C. Then it was screened and used for adsorption. The batch experiments were carried out in 300 ml conical flasks with 100 ml of the effluent sample. For COD, the distillery effluent containing 6000 mg/l of COD was used. For phenol, the sample was prepared in the laboratory with 1000 mg/l of phenol. The sample for chromium contained 100 mg/l of chromium and the acetic acid sample was containing 2000 mg/l of acetic acid. The COD was determined using COD digestion apparatus (make-spectralab). The concentrations of phenol and chromium were determined by using UV spectrophotometer(make-Elico). The acetic acid concentration was determined by titrating the sample against 0.01N sodium hydroxide. To the wastewater sample, the adsorbent was added in suitable amount according to the requirement of the batch. These samples were kept on shaker for sufficient time so as to reach the equilibrium. Then the samples were filtered and the filtrate was analyzed for the various pollutants i.e. COD, phenol, chromium and acetic acid. For deciding initial concentration, studies were carried out by taking different initial concentration of these pollutant for fixed adsorbent dose and it was allowed to reach the equilibrium. The initial concentration giving the maximum removal percentage was selected for the batch studies. The equilibrium relationship between solute concentration in the fluid phase and its concentrationon the solid resembles somewhat the equilibrium solubility of a gas in a liquid.The concentration in the solid phase is expressed as q, mass of adsorbate per mass of adsorbent, and in the liquid phase as C, concentration of adsorbate in solution. The Langmuir Isotherm is expressed as $q = \frac{q_0 C}{K+C}$ where q_0 is mass of adsorbate per mass of solid, K the constant. The Freundlich isotherm equation, which is impirical, often approximates data for many physical adsorption systems and is perticulerly useful for liquids.According to Freundlich, $q = KC^n$, Here K and n are constants. The logarithmic plot of q verces C gives slope n and intercept K.

3. Results and discussion

3.1 Effect of contact time on percentage removal

Batch experiments were carried out in 100 ml conical flasks for the samples with known initial concentration. The samples kept on shaker for different contact times ranging from 30 minutes to 350 minutes. Then sample were filtered and analyzed for the pollutants. Fig.1 shows the effect of contact time on percentage removal of various pollutants. It was observed that percentage removal increases with contact time up to certain period and thereafter it remains constant. This is because of attainment of equilibrium between the adsorbate in the solution and the one adsorbed on the solid. The optimum adsorption times for COD, phenol, chromium and acetic acid were observed to be 180,250,220 and 150 minutes respectively. Flyash adsorption shows the percentage removal of 88 to 92 percent at optimum adsorbent time.

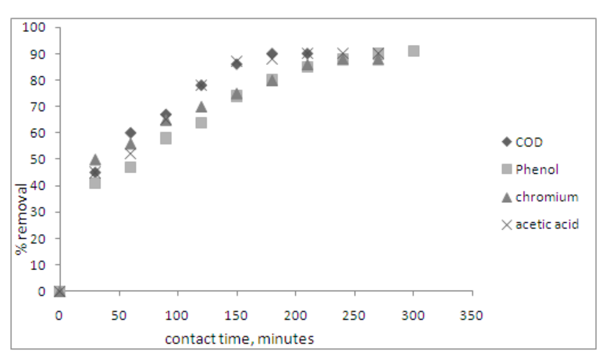

Fig.1 Effect of contact time on percentage removal

3.2Effect of adsorbent dose on percentage removal

International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 2 Issue 5, May - 2013

Effect of adsorbent dose on percentage removal of adsorbate is indicated in Fig.2. For this, experiments were carried out in the conical flasks with 100 ml of effluent with known initial concentration. To the 100 ml of effluent, various quantities of adsorbents were added and kept on shaker. The effluent was filtered and sample was analysed for the pollutant. It was observed that, as shown in the figure, 3,3.5,1 and 4 grams of flyash is optimum for the 100 ml of effluent sample for the removal of COD, phenol, chromium and acetic acid respectively.

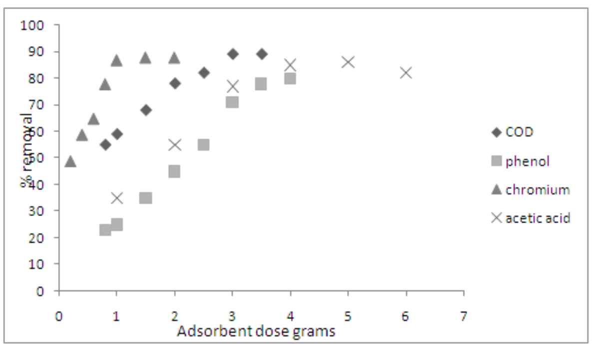

Fig.2 Effect of adsorbent dose on percentage removal

3.3 Effect of pH on percentage removal

Adsorption phenomenon is analogous to ion exchange process. The pH of the aqueous solution has significant effect on adsorption by the adsorbent. The pH of the solution also influences the actives sites and therefore, the solution chemistry. Effect of variation of pH on percentage removal of Phenol is presented in Fig.3. It is observed from figure that percentage phenol removal increases with increase in pH upto certain value and decreases further with increase in pH.The percentage removal rate of phenol is observed to be very slow upto pH value of 4.0, increases rapidly at pH 6.5.After increase in pH, percentage removal of phenol decreases sharply.It is also seen from present study that percentage removal of phenol observed to be maximum at corresponding pH value of 6.5.Figure also depicts the effect of pH on the chromium adsorption for flyash. Decreasing pH results in the formation of more polymerised chromium oxide species. On the other hand, under acidic conditions, the surface of the adsorbent becomes highly protonated and favours the uptake of Cr (VI) in the anionic form. With increase in pH, the degree of protonation of the surface reduces gradually and hence adsorption is decreased. The net positive surface potential of sorbent decreases, resulting in the weakening of electrostatic forces between sorbent and sorbate, which ultimately leads to reduced sorption capacity. The optimum pH for flyash was observed to be 2 . In case of acetic acid and COD the pH value of 6 was found to be optimum .

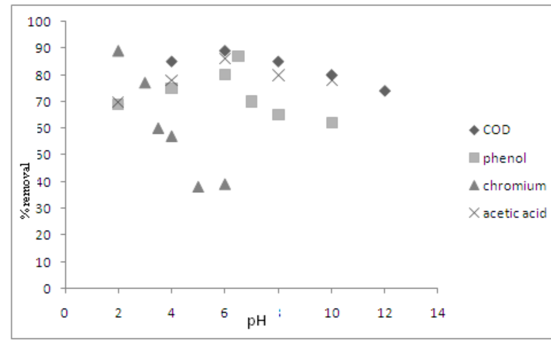

Fig.3. Effect of pH on percentage removal

3.4Effect of particle size on percentage removal

Experiments were carried out at optimum values of the three parameters i.e. contact time, adsorbent dose and pH, by using different sizes of particles. The particles with different mesh numbers (-36,-50,-60,-72,-100,-200) were used for experiments. As shown in fig.4, it was observed that as particle size decreases from mesh number 36 to 72, the percentage removal increases. This is because of the increase in the surface area available for adsorption. After that that the percentage removal remains constant. The percentage removal remains constant for the particle sizes finer than 72 mesh no. particles. The adsorbate is not able to utilize the extra surface area. This may be because of due to lack of contact with adsorbent.

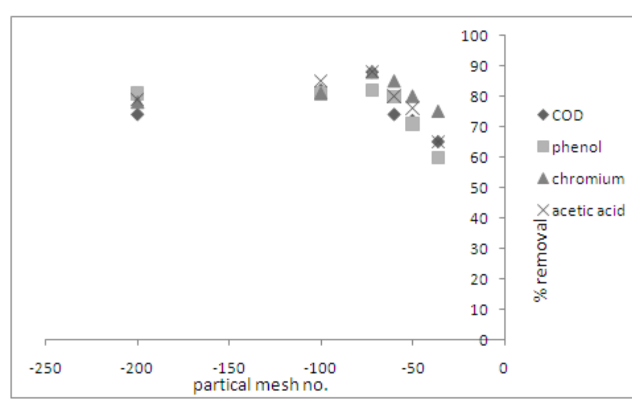

Fig.4 Effect of particle size on percentage removal

3.5 Freundlich Adsorption isotherm

Fig.5 shows freundlich adsorption isotherm for COD, phenol, chromium and acetic acid respectively.

Adsorption operation for all four adsorbates on flyash fits in the isotherm.

Freundlich isotherm is presented in following empirical equation ,

$$\frac{X}{M}=b\,X^{m} \quad (1)$$

$$\ln X/M = \ln b + m \ln C^{*} \quad (2)$$

Here X/M is the catalyst loading , C* is the equilibrium concentration of organic matter, b and m are constants.The values of b and m for COD were found to be 0.025 and 1.653 respectively. For the phenol these values were found to be 2.06 x 10^{-9} and 4.038 respectively. In case of chromium , the values of b and m were estimated to be 0.133 and 1.673 respectively. These values for acetic acid were 1.19 and 1.067 respectively.

3.6 Regeneration

Generally regeneration methods other than thermal will not be effective if a mixture of organics has been adsorbed. Only a portion of sorbed materials will be removed by a given solvant, hot gas, chemical or biologic regeneration procedure.Therefore performance of adsorbent will consistently decrease on successive regenerations, and after few regenerations, the adsorbent usually has to be discarded. Thermal regeneration is most versatile, and because most granular carbon treatment systems remove a complex mixture of organics, it is far the most widely used. Disposal of flyash is a universal problem. Flyash that is obtained after using in effluent treatment plant for removal of organic matter is obviously rich in organic content. At present flyash is disposed in the form of slurry in flyash ponds. The major environmental concern from flyash discharge and disposal is organic pollution of surface and ground water. Even dumping of flyash creates similar problem.

Flyash precipitated from air by rain finds their way to the surface water unless flyash ponds are properly sealed. These efforts are made to utilize flyash in productive methods as pozzolona in making of cement, raw materials for making bricks, treatment of sewage and polluted water, fire resistant materials, insulation materials, raw material for glass etc. There is scope for development of effective disposal systems for flyash. Controlled disposal of flyash in stack and its disposal on ground is recommended.

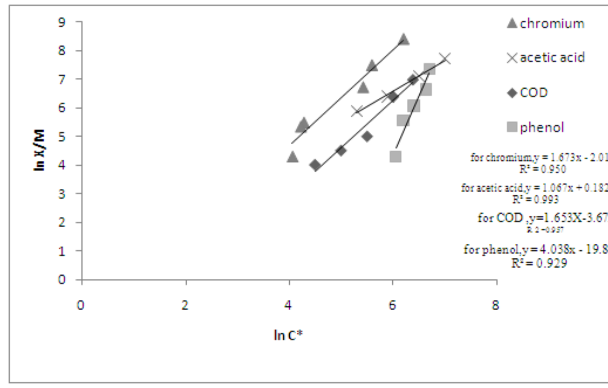

Fig.5 Freundlich adsorption isotherms

4. Conclusion

In the present investigation it is observed that flyash is promising alternative to the conventional adsorbents. Adsorption is an effective method for removing organic and inorganic impurities from the wastewater. The bagasse flyash is found to be very effective adsorbent. The percentage removal obtained was 88 to 95 for various pollutants.. The adsorbent dosage, pH, contact time and initial concentration of organic matter have significant effect on the removal. The optimum adsorbent doses for COD, phenol, chromium and acetic acid removal were observed to be 3, 3.5,1 and 4 grams. The optimum contact times for these pollutants were 180,250,220 and 150 minutes respectively. The optimum pH values for the adsorption were 6, 6.5, 2 and 6 respectively for COD, phenol, chromium and acetic acid. The flyash can be regenerated by thermal regeneration in multi hearth or rotary furnace in presence of steam to volatize and carbonize organic matter. Other chemical and biological methods are also available. Regeneration and disposal depends on the amount and the availability of the adsorbent

References

1]Shaobin Wang, and Hongwei Wu, “Environmental-benign utilisation of fly ash as low-cost adsorbents”, *Journal of Hazardous Materials*, Vol. 136(3), pages 482-501, (2006).

[2]Dinesh Mohan, Kunwar P. Singh, Vinod K. Singh “ Wastewater treatment using low cost activated carbons derived from agricultural byproducts—A case study,” *Journal of Hazardous Materials*, Volume 152, Issue 3, Pages 1045-1053(2008).

[3]Rani Devi,Vijender Singh, Ashok Kumar “COD and BOD reduction from coffee processing wastewater using Avacado peel carbon ”, *Bioresource Technology*, Volume 99, Issue 6, Pages 1853-1860(2008).

[4]Libing Chu, Xingwen Zhang, Fenglin Yang, Xiaohui Li “Treatment of domestic wastewater by using a microaerobic

membrane bioreactor" ,*Desalination*, Volume 189, Issues 1-3, Pages 181-192(2006).

[5]Tonni Agustiono Kurniawan, Wai-hung Lo "Removal of refractory compounds from stabilized landfill leachate using an integrated H_2O_2 oxidation and granular activated carbon (GAC) adsorption treatment", *Water Research*, Volume 43, Issue 16, Pages 4079-4091.(2009)

[6]Avinash M. Kadam, Pravin D. Nemade, G.H. Oza, H.S. Shankar "Treatment of municipal wastewater using laterite-based constructed soil filter", *Ecological Engineering*, Volume 35, Issue 7, Pages 1051-1061(2009).

[7]Yi Jing Chan, Mei Fong Chong, Chung Lim Law, D.G. Hassell "A review on anaerobic–aerobic treatment of industrial and municipal wastewater", *Chemical Engineering Journal*, Volume 155, Issues 1–2, Pages 1-18(2008).

[8]Xiaoyan Y. Ma, Xiaochang C. Wang, Yongjun J. Liu "Study of the variation of ecotoxicity at different stages of domestic wastewater treatment using Vibrioqinghaiensis p.Q67",*Journal of Hazardous Materials*, Volume 190, Issues 1–3, Pages 100-105.(2011).

[9]Jianhua Guo, Yongzhen Peng, Huijun Huang, Shuying Wang, Shijian Ge, Jingrong Zhang, Zhongwei Wang " Short- and long-term effects of temperature on partial nitrification in a sequencing batch reactor treating domestic wastewater", *Journal of Hazardous Materials*, Volume 179, Issues 1–3, Pages 471-479.(2010).

[10]Sevil Veli, Tuba Ozturk, Anatoly Dimoglo "Treatment of municipal solid wastes leachate by means of chemical and electrocoagulation", *Separation and Purification Technology* Volume 61, Issue 1, Pages 82-88.(2008).

[11]A.A. Ahmad, B.H. Hameed "Reduction of COD and color of dyeing effluent from a cotton textile mill by adsorption onto bamboo-based activated carbon", *Journal of Hazardous Materials*, Volume 172, Issues 2–3, Pages 1538-1543.(2009).

[12]Krishna, R.S. and M.K.N. Yenkee. "Preparation of carbon from pyrolysis of coconut husk and evaluation of its adsorption characteristics", *Indian Journal Environmental Protection*, 17(1) , pp. 35-41. (2001).

[13]Prasad,S and G. Singh., " Application of activated carbon for treatment of wastewater with special emphasis on coke oven effluents", *Indian Journal Environmental Protection*, 14(9), pages 695-699.(1994)

[14]Treybal R.E., "Mass Transfer Operations" *McGraw Hill* 3rd Edition,pages 565-645(1992).

[15]Sushmita Mishra, J. Bhattacharya, "Potential of Leaf Litter for Phenol Adsorption-a Batch Study", *Indian Journal of Chemical Technology*, Vol-13,pages 298-301.(2006).

[16]K. Suneel Kumar, Kaustubha Mohanty, B. C., Meikap, "Treatment of phenolic wastewater in a multistage bubble column adsorber using activated carbon prepared from Tamarindus indica wood", *Journal Environmental Protection* Science,4,pages1-7.(2010).

[17]Barbooti, M., Ageena, N., Toma, M.,"Removal of Chromium from Electroplating Wastewater by Simple Chemical Treatment and Ion Exchange", *Eng. And Tech.*,26,pages 200-2012(2008).

[18] Christofordis, A., Valsamidu, E.,"Removal of Nickel, Copper, Zinc and Chromium from Synthetic and Industrial Effluent by Electrocoagulation", International Journal of *Environmental Sciencies*,1,pagse 697-69(2010).

[19] Stasinakis, Anthenasios, S., Thomaidis, Mamias, Daniel, Ppanicolau, Evangelia, Taskon, "Effect of Chromium Addition on Activated Sludge Process",*Water Research*,37, pages 2140(2003).

[20] Stasinakis, Anthenasios, S., Thomaidis, Mamias, Daniel, karivali, Mariana and Lekkas,"Chromium species Behavior in Activated Sludge Process",*Chemosphere*,52,pages 1059(2003).

[21] Rengaraj, S., Yeon, K., Moon,S., 2001,"Removal of Chromium from Wastewater by Ion Exchage Resins", *Journal of Hazardous Material*, 87, pages 273-287(2001).

[22]Kalidhasan, S., Sricharan, S., Ganesh, m., Rejesh, N.,"Liquid Liquid Extraction of Chromium wih Tricaprylmethylammonium Chloride Using Isoamyl Alcohol as the Diluent and Its Application to Industrial Effluents", Journal of Chemical Engineering Data, 55, pages 5627-5633(2010).

[23]Kumar,A., Kalidhasan, S., Vidyarajesh, Rejesh, N, " Application of Cellulose Clay Biosorbent towards the Effective Adsorption and Removal of Chromium from Industrial Wastewater", *Ind. Engg. Chem. Res*., 52, pages 58-69(2012).

[24]Red, S., Mirbagheri, S., Mohammadi, T.," Using Reverse Osmosis Membrane for Chromium Removal from Aqueous Solution", *World Academy of Science, Engineering and Technology*, 57. Pages 347-350(2009).

[25] Nian-Xi Van, Song-An Huang & Ya-Jun Shi "Removal of Acetic Acid from Wastewater with Liquid Surfactant Membranes: An External Boundary Layer and Membrane Diffusion Controlled Model", *Separation Science and Technology*, Volume 22, Issue 2-3, pages 801-818,(1987).

[26] S.C.Nawle, S.V.Patil, "Experimental studies on acetic acid removal from waste water using fly ash" *Nuicone 11*, Institute Of Technology, Nirma University, Ahmedabad,pages 481-482, (2011).