
Adsorption dynamics of cobalt [Co(ii)] on rubber granules

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Abstract: The removal kinetics of Co(II) by waste tyre rubber granules was deliberated. Rubber granules (150–300 μm) were used as sorbent. At the 4 mg/l and 15 g/l concentrations of Co(II) and adsorbent respectively, 83.2% removal was found in 180 min. Reaction kinetic followed a second order equation that was applied for the analysis of rate constant. At 30°C, rate constant was calculated to be $1.25 \times 10^{-2} \text{ min}^{-1}$. Among different isotherm models, the Freundlich model was found to produce a better regression coefficient. Removal of Co(II) was found to be pH dependent.

Keywords: adsorption; cobalt [Co(II)]; rubber granule; reaction kinetic.

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1 Introduction

By the increased human activity and industrialisation, heavy metal pollution level has inevitably increased in water environment and it is a potential menace to the health and welfare of mankind. The treatment and disposal of heavy metal bearing wastes presents a unique challenge to the environmental engineer. Unlike many organic wastes, heavy metals cannot be degraded biologically into harmless products. Subsequently, because of their toxicity, environmental mobility and complex chemical forms, increasing attention is being directed towards studying their removal and recovery from metal bearing waste streams. Co(II) is one of the most hazardous elements to human health. Co(II) was chosen due to the level of environmental danger posed by its pollution of the natural ecosystem. It belongs to the group of rare metals and every change of the chemical balance in the natural environment causes not only distribution in the growth and development of flora and fauna, but also human health. Co(II) is also of considerable interest to allergology and allergency (Baralkiewicz and Siepak, 1999). Many physico-chemical processes are employed for the removal and recovery of heavy metals but the conventional methods are becoming non-effective and economically non-feasible to achieve the required stringent standards. Bio-sorption of heavy metals has been recognised as potential alternative to existing technologies for removal and recovery of heavy metals from industrial and natural water environment. Ye et al. (2001) reported that 39% removal of Co(II) is possible by wetland cells. In another study, Zheleznov and Lysotskii (2002) used fibrous carbon ferrocyanide for removal of Co(II) from aqueous solution. Reefy et al. (2003) used liquid emulsion membrane for removal of Co(II) successfully. In another study, iron and Co(II) were removed from aqueous solutions by ion exchange with Na-Y-Zeolite (Kim and Keane, 2002). Discharges from chemical manufacturing industries like electroplating industries increase the burden of cobalt on the ecosystem. Its high doses may cause paralysis, diarrhea, low blood pressure, lung irritation and bone defects. World Health Organization (WHO) has prescribed a maximum concentration of cobalt [Co(II)] in drinking water as 0.1 mg/l whereas the cobalt plating effluent water may contain upto 50 mg/l of cobalt. Thus, the effluent

water has to be treated for the removal of Co(II) comprises of chemical precipitation, exchange, sorption, osmosis and electrolysis, but adsorption is a single process that produces no sludge.

2 Materials and method

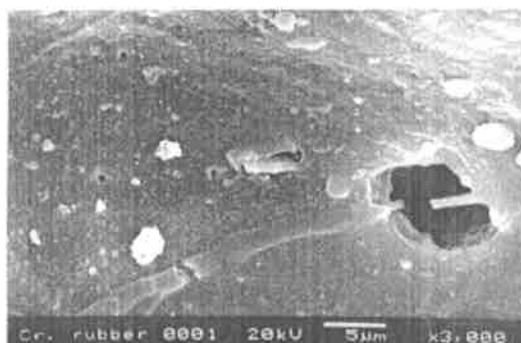
Co(II) was determined at 240.7 nm oxidising air acetylene flames by Atomic Absorption Spectrophotometer (Perkin Elmer, 50 B).

2.1 Sorbent

The waste tyre rubber granules were provided by Rubber Technology Centre, IIT, Kharagpur, India, and sieved to size range 150–300 μm . Rubber granules were washed out by distilled water for removal of foreign materials keeping the mixture in plastic bottle at 150 rpm in a mechanical shaker for 6 h. After washing, it was dried for two days in sunlight. Then, it was oven dried at 50–60°C for 6 h to remove the moisture present in the pores. It was then cooled to room temperature, sieved to its original size, and stored in airtight bottles.

2.2 Characteristics of rubber granules sorbent

Tyres are generally composed of different types of rubber such as textile cords, fabric belts, and vulcanised rubber. Styrene Butadiene Rubber is the widely used polymer by the tyre industries. Carbon black, zinc oxide, natural rubber, sulphur etc. are also added. Carbon black is used to strengthen the rubber (Kim et al., 1997). Bulk specific gravity and porosity of rubber granules were measured using standard methods (APHA-AWWA-WPCF, 1989). The surface area was measured by nitrogen adsorption method (BET 624, Micromeritics, Germany). Scanning Electron Microscope studies of waste tyre rubber granules were carried out using SEM (LEO S-440, Germany) (Figure 1). It showed the presence of iron compounds, zinc, silica, etc. in the rubber granules samples. Zn content was measured by atomic absorption spectrophotometer (AAS 670, Shimazu, Japan). For this, Zn was brought to solution form by keeping 2 g rubber granules in 1 : 1 HNO_3 solution for 24 h and after filtration, the filtrate was diluted 25 times for the measurement of Zn. It was found to be 2.3%. The IR spectrum of rubber granules was carried out using IR spectrophotometer (Perkin-Elmer, UK). The peak at 3438 cm^{-1} in the IR spectrum indicated the presence of $-\text{COOH}$ or $-\text{OH}$ group. The peak at 2320 cm^{-1} indicated the presence of $\text{C}\equiv\text{N}$, $\text{C}\equiv\text{C}$ or $\text{C}=\text{C}$ or isocyanates group. The other bonding presence in tyre rubber granules were $>\text{C}=\text{O}$, $\text{C}-\text{H}$ and $\text{C}-\text{O}$ bonding. Thermo Gravimetric Analysis (TGA) was conducted for chemical analysis of waste tyre rubber granules using TGA (DT-40, Shimazu, Japan). It is used to find out the percentage of carbon black and polymer matrix in adsorbent. The physical and chemical characteristics of waste tyre rubber granules as determined by the above tests are described in Table 1.

Figure 1 SEM view of rubber granules used as adsorbent**Table 1** Physical and chemical characteristics of waste tyre rubber granules

<i>Parameters</i>	<i>Values</i>
Bulk specific gravity	0.284 g/cm ³
Porosity	12–14%
Surface area	0.45–0.78 g/m ²
Carbon black	48–52%*

Table 1 Physical and chemical characteristics of waste tyre rubber granules (continued)

<i>Parameters</i>	<i>Values</i>
Polymer matrix	30–33%*
Other materials	Silica, Zinc oxide, Iron etc**
Ash content	2–3%

As determined by *TGA test. **SEM test.

Source: Alam (2002)

2.3 Interruption test

The interruption test proposed by Zogorski et al. (1976) was performed to assess the rate limiting steps of sorption process. The reaction mixtures containing 200 ml of distilled water spiked with 4 mg/l of Co(II) in bottles and 15 g/l of sorbent was agitated in the mechanical shaker at a medium speed of 150 rpm at room temperature. After 10 min of reaction time, the 1st sample was withdrawn from the system and the sorbent was separated from the solution. After an interruption time of 15 min, the separated sorbent was reintroduced into the 1st solution and the agitation was continued. Again the 1st sample was withdrawn from the system, after a reaction time of 10 min and analysed for Co(II). Similarly, the 2nd, 3rd and 4th samples were taken out from the system after 10 min interval up to 80 min then after every 20 min interval.

2.4 Sorption isotherm studies

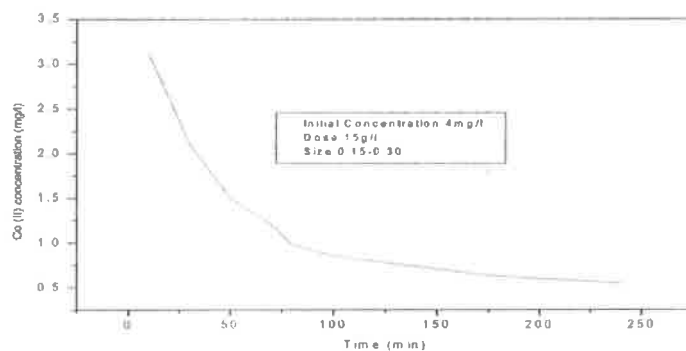
Sorption isotherm studies were conducted to understand the nature of the equilibrium distribution of Co(II) onto the sorbent. Equilibrium studies were conducted for specified size. In the studies, concentration range from 0.5 mg/l to 7.5 mg/l for Co(II) and different doses of adsorbent (5–23 g/l) were used. A reaction time or equilibrium time of 180 min for Co(II) was adopted in the isotherm experiments.

3 Result and discussion

3.1 Determination of kinetic profile

The kinetic profiles of sorption of Co(II) on to waste tyre rubber granules were generated at a concentration of 4 mg/l with optimal dose of 15 g/l. Initial concentration of Co(II) was found out in the contest of highest level of Co(II) found in the River Buriganga in Dhaka (Sohel, 1998). Waste tyre rubber granules were used as many authors found that rubber granules are an adsorbent for heavy metal removal, and moreover, dumping of waste tyre is creating threat to the environment of developing countries like India, Bangladesh (Griffith, 1975; Mahramanlioglu, 1997). The magnitude of Co(II) removal by waste tyre rubber granules at 4 mg/l initial concentration with adsorbent dose of 15 g/l is presented in Figure 2. The removal was 83.2% in 3 h at 4 mg/l for Co(II). For the 1st hour, the removal was faster and then it was slowed down.

Figure 2 Change in concentration with time for Co(II) sorption on rubber granules with initial concentration of 4 g/l



Source: Reza (2005)

The removal kinetics of Co(II) by the rubber granules for different concentrations is shown in Figure 1. It may be seen that more than 60% of the heavy metal were sorbed within 60 min of reaction time and this was due to the availability of the number of free sites within rubber granules and a high concentration gradient between the solution and the solid phase. The attainment of the equilibrium time for sorption of heavy metal or pesticides in Completely Mixed Batch Reactor (CMBR) was found in the range of few minutes to several hours by many researchers (Aly and Faust, 1965; Tsezos and Wang, 1991). After 180 min of reaction time, it was evident that the kinetics profiles gradually became horizontal, indicating the final equilibrium. The removal of Co(II) beyond

180 min of reaction time was very low and hence an equilibrium time of 180 min was standardised for the rest of the experiments. The curve is a non-smooth curve. The removal curves are non-smooth and continuous, indicating no formation of monolayer coverage of the adsorbate on the outer surface of the adsorbent. Different reaction kinetic equations were applied to experimental data shown in Table 2 and it was clear from Table 2 that reaction kinetic followed second-order reaction kinetic equation. Hyphal wall may be responsible for adsorption (Brunnert, 1979). For understanding of reaction kinetics, three fundamental reaction rate constant equations have been applied and it was clear from Table 2 that equation follows second order reaction kinetic equation.

Table 2 Regression coefficient of different order of reaction kinetics

Initial concentration of Co(II)	Order	Regression coefficient
4 mg/l	0th order	0.894
	1st order	0.976
	2nd order	0.9945

3.2 Determination of rate constant

First-order kinetic equation is

$$\ln [1-U(t)] = -kt \quad (1)$$

where k is overall rate constant and $U(t) = X/X_e$ is called fractional attainment. According to Snoeyink and Jenkins (1980), a linear plot between $\ln[1-U(t)]$ and t indicates the reaction to be first-order reversible. In this case, points up to equilibrium time were considered for regression analysis. Moreover, as the calculations with initial points created the biased error due to the initial drop (Venkobachar, 1990), two initial points were omitted for calculation of regression analysis. Second-order kinetic equation has been applied for analysis of rate constant for sorption of cobalt on waste tyre rubber granules. The second-order equation gave a better fit than the first-order equation. Gonzalez-Pradas et al. (1997) have given the following second-order equation

$$-dC/dt = k_1C(X_M - X) - k_2X \quad (2)$$

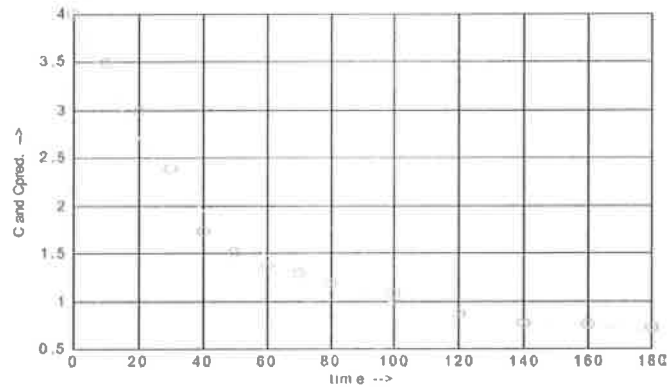
where k_1 and k_2 are specific rate constants; X_M is number of moles of adsorbate retained by 1 g of adsorbent when the monolayer is complete; X is $(C_0 - C)/2m$; C_0 is initial concentration; C is concentration at any time t and m is mass of adsorbent.

The solution of the equation (2) is:

$$\begin{aligned} & \ln(2k_1C + 2mk_1X_M - k_1C_0 + k_2 + [(2mk_1X_M - k_1C_0 + k_2)^2 \\ & + 4k_1k_2C_0]^{0.5}) / (2k_1C + 2mk_1X_M - k_1C_0 + k_2 - [(2mk_1X_M - k_1C_0 + k_2)^2 \\ & + 4k_1k_2C_0]^{0.5}) = \ln((2k_1C_0 + 2mk_1X_M - k_1C_0 + k_2 + [(2mk_1X_M - k_1C_0 + k_2)^2 \\ & + 4k_1k_2C_0]^{0.5}) / (2k_1C_0 + 2mk_1X_M - k_1C_0 + k_2 - [(2mk_1X_M - k_1C_0 + k_2)^2 \\ & + 4k_1k_2C_0]^{0.5})) / \{[(2mk_1X_M - k_1C_0 + k_2)^2 + 4k_1k_2C_0]^{0.5} / 2m\} t. \end{aligned} \quad (3)$$

The kinetic sorption rates were found out by computer program in MATLAB by using least square concept for experimental data (Figure 3). The rate constant, k_1 , calculated from the program was found to be $1.25 \times 10^{-2} \text{ min}^{-1}$.

Figure 3 Fitting of experimental data with second-order kinetic equation model (equation (3)) for Co(II) (see online version for colours)



4 Isotherm study

Experimental isotherms are useful for describing sorption capacity to evaluate the efficiency of an adsorbent. Many models have been developed for the prediction of adsorption capacity. They are Langmuir, BET, Freundlich, modified Langmuir and Lopez–Gonzalez model (L-G model) (Alam, 2002). Among all the above models, Langmuir, BET, L-G and Freundlich models are very widely used. Langmuir model assumes that the sorption energy is constant and independent of surface coverage. In this study, experimental data have been plotted in different types of isotherm equations and found that it was fitted with Freundlich model (Figure 4). It was clear from Table 3 that Freundlich model produced better regression coefficient.

$$\text{Langmuir model } q_e = (b \times C_e \times Q_{\max}) / (1 + b \times C_e)$$

BET model developed by Brunauer, Enmelt and Teller (1938)

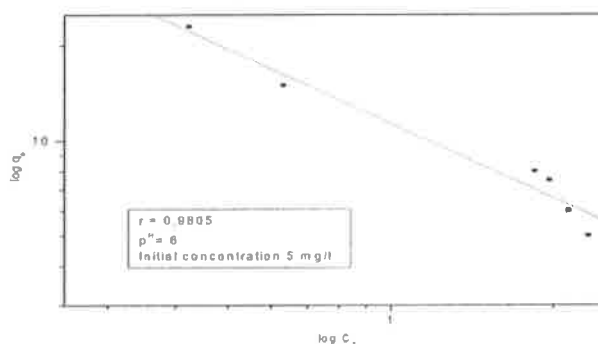
$$C_e / \{(C_s - C_e) \times q_e\} = 1 / (b \times Q_{\max}) + \{(B - 1) / (b \times Q_{\max})\} \times (C_e / C_s)$$

$$\text{Freundlich isotherm, } Q_e = k_f \times C^{1/n}$$

Lopez–Gonzalez (L-G) model

$$C_e / (q_e \times C_s) [1 + k_1 (C_e / C_s)] = 1 / (B \times Q_{\max}) + (1 / Q_{\max}) \times (C_e / C_s)$$

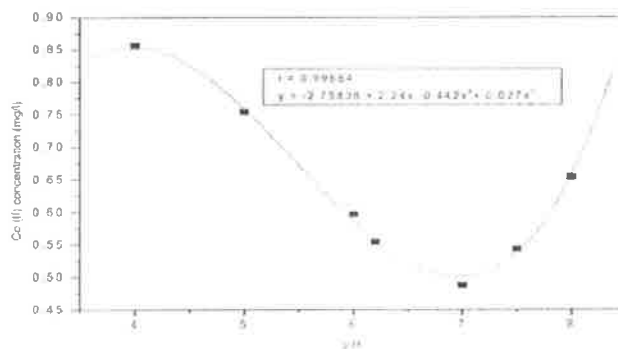
where C_e is equilibrium concentration (mg/l), C_s is saturated concentration; q_e is the amount of pollutant absorbed at equilibrium, Q_{\max} is the maximum amount of pollutant absorbed; b, B, k_f are the constants.

Figure 4 Fitting of experimental data of sorption of Co(II) on waste tyre rubber granules (see online version for colours)**Table 3** Correlation coefficients for rubber granules for different adsorption equilibrium models

Type of heavy metal	Langmuir model	BET model	Freundlich model	L-G model	Selected model
Co (II)	0.90	0.962	0.9805	0.954 (K1 = 0.1)	Freundlich model

4.1 Effect of pH

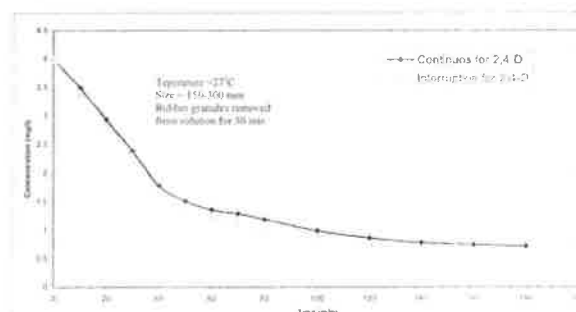
Figure 5 shows the effect of pH on the removal of Co(II) from aqueous solution. At a pH of 2, only 5% of the total Co(II) is adsorbed. At a pH of 6, approximately 59% of the Co(II) is removed. The extent of Co(II) removal between a pH of 6 and 8 increased marginally 4.6%. Decreasing trend in adsorption observed above pH 8. Adsorption of metal ions from solutions by solid phase can occur with the formation of surface complex between the adsorbed ligands and the metal. However, the sites responsible for the adsorption process are not exclusively due to the adsorbed ligands. The variation of sorption of Co(II) as a function of pH can be explained in terms of pH_{zpc} that was found to be 5.9 (Sudhakar, 1998). Significant adsorption was observed above pH_{zpc} at which sorbent surface is negative and sorbate species (Co^{2+} , and $Co(OH)^{2+}$) are positively charged. At lower pH (below pH_{zpc}), the adsorbent surface is protonated; as a result unfavourable condition for adsorption of cations prevails.

Figure 5 Effect of pH on adsorption of Co(II) on rubber granules (see online version for colours)

5 Interruption test

Several factors of the adsorbents, adsorbate and solution phase are of importance in determining the rate-limiting step. The factors include the particle size of the adsorbent, concentration of adsorbate, degree of mixing, affinity of adsorbate for adsorbent and diffusion coefficients of the adsorbate in bulk solution and within the porous adsorbent. The rate of adsorption of butachlor at initial concentration of 4 mg/l appeared to be limited by both intra-particle transport and external diffusion to the rubber granule surface. This observation is based on getting the slight increase in the removal, found in the interruption test (Alam, 2002). Zogorski et al. (1976) also had found similar results in case of dichlorophenol-activated carbon system. Figure 6 shows the effect of single point interruption test. The single point interruption test results indicated that as there was no sharp up and rise before and after the interruption, the external transport or intra-particle diffusion to the rubber-granules surface is not the rate-limiting step in the adsorption process. It is evident from the experimental data that the external diffusion is of equal importance with intra-particle diffusion in determining the overall rate of the transfer of the adsorbate to the adsorption sites in this case.

Figure 6 Kinetic profiles of Co(II) sorption onto rubber granules –interruption and un-interruption tests (see online version for colours)



5 Conclusions

Industrial effluent containing heavy metals like Co(II) is a threat to aquatic ecosystem as well as to humans. Many dyeing, fabric and chemical manufacturing industries of developing countries like Bangladesh are discharging their liquid waste into the nearby receiving water bodies without proper treatment. On the other hand, every year waste tyre rubber has created dumping problem in developed countries as well as in Bangladesh. Use of tyre has increased by about 2.3 times in the last five years (CRRI, 1998). So, tyre-dumping problem is being worsened and is also creating threat to the environment. In this paper, an attempt has been undertaken to find out the suitability of waste tyre rubber granules for the treatment of cobalt removal.

It was clear from kinetic study that at 4 mg/l initial concentration with adsorbent dose of 15 g/l, the removal was 83.2% in 3 h. For the 1st hour, the removal was faster and then it was slowed down. The kinetic sorption rate was determined by using least square concept for experimental data. The rate constant, k_1 , calculated from the program was

found to be $1.25 \times 10^{-2} \text{ min}^{-1}$. It was clear from isotherm study that experimental data was fitted well with Freundlich model. It means that Freundlich model produced better regression coefficient. In this study, effect of pH was tested. Significant adsorption was observed above pH_{zpc} (zero potential charge) at which sorbent surface is negative and sorbate species (Co^{2+} , and $\text{Co}(\text{OH})^{2+}$) are positively charged. At lower pH, the adsorbent surface is protonated; as a result, unfavourable condition for adsorption of cations prevails. It is evident from single point interruption test that the external diffusion is of equal importance with intra-particle diffusion in determining the overall rate of the transfer of the adsorbate to the adsorption sites in this case, as there was no sharp up and rise before and after the interruption.

References

- Alam, J.B. (2002) *Removal of Herbicides from Water Environment and Its Management*, PhD Thesis, Civil Engineering Department, Indian Institute of Technology, Kharagpur, India.
- APHA-AWWA-WPCF (1989) *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, New York.
- Aly, O.M. and Faust, S.D. (1965) 'Removal of 2, 4 - dchlorophenixy acetic acid derivatives from natural waters', *Journal of American Water Works Association*, Vol. 13, No. 2, pp.221–230.
- Brunnert, J.H. (1979) *Aspects of Structure and Growth of Hyphal Wall: In Fungal Walls and Hyphal Growth*, Cambridge University Press, UK, pp.1–25.
- Baralkiewicz, D. and Siepak, J. (1999) 'Chromium, nickel and cobalt in environmental samples and existing legal norms', *Polish J. of Environmental Studies*, Vol. 8, No. 4, pp.201–208.
- CRRRI (1998) *Laboratory Investigation of TBM-Super Modifiers for Hot Mixing Paving Applications*, Central Road Research Institute, New Delhi, India.
- Gonzalez-Pradas, E., Villafranca-Sanchez, M., Gallego-Campo, A., Urena-Amate, D. and Fernandez-Perez, M. (1997) 'Removal of Atrazine from aqueous solution by natural and activated bentonite', *J. Environ. Qual.*, Vol. 26, pp.1288–1291.
- Griffith, G.P. (1975) *Removal of Ionic Mercury from Wastewater using Modified Scrap Rubber-Removal of Soluble Mercury from Wastewater Complexing Techniques*, Bulletin 74, Virginia, Virginia Water Resources Research Center, USA.
- Kim, J.Y., Park, J.K. and Edil, T.B. (1997) 'Sorption of organic compounds in the aqueous phase onto tire rubber', *J. Environmental Engineering, ASCE*, Vol. 123, No. 9, pp.827–834.
- Kim, J.S. and Keane, M.A. (2002) 'The removal of iron and cobalt from aqueous solutions by ion exchange with Na-Y Zeolite batch, semi batch and continuous operation', *J. Chemical Technology and Biotechnology*, Vol. 77, No. 6, pp.633–640.
- Mahramanlioglu, M., Kizilcikili, I. and Bicer, I.O. (1997) *Adsorption of Organic Pollutants on the Activated Carbon Produced from Used Tires*, MSc Thesis, Department of Chemistry, Istanbul University, Turkey.
- Reza, I. (2005) *Management of Industrial Waste by Rubber Granules*, BSc Engineering Thesis, Civil and Environmental Engineering Department, Shahjalal University of Science and Technology, Sylhet-3114, Bangladesh.
- Reefy, S.A., Selim, Y.T., Hassan, M.A. and Aly, H.F. (2003) 'Assessment of liquid emulsion membrane for clean up of aqueous waste effluents from hazardous elements', *WM'03 conference, Arizona, USA*, February, pp.23–27.
- Sohel, A. (1998) *Pollution Status of Different Rivers in and Around Dhaka*, MSc Engineering Thesis, Bangladesh University of Engineering and Technology, Dhaka, Bangladesh.
- Sudhakar, Y. (1998) *Selection of Different Adsorbents for Pollutant Removal from Water Environment*, MSc Engineering Thesis, Indian Institute of technology, Kharagpur, India.

- Snoeyink, V.L. and Jenkins, D. (1980) *Water Chemistry*, John Wiley and Sons Inc., New York.
- Tsezos, M. and Wang, X. (1991) 'Study on the kinetics of hazardous pollutants adsorption and desorption by biomass: mechanistic considerations', *J. Chem. Tech. Biotech*, Vol. 34, No. 2, pp.34–38.
- Venkobachar, C. (1990) 'Metal removal by waste biomass to upgrade wastewater treatment plants', *Wat Sci. Tech.*, Vol. 22, Nos. 7–8, pp.319–320.
- Ye, Z.H., Lin, W.Z.Q., Lytle, C.M., Qian, J.H. and Terry, N. (2001) 'Removal and distribution of Co(II), Fe, Mn and Ni within a Pennsylvania constructed wetland treating coal combustion by product leachate', *J. Environmental Quality*, Vol. 30, No. 8, pp.1464–1473.
- Zogorski, J.S., Faust, S.D. and Haas, O.H. (1976) 'The kinetics of adsorption of phenol by granular activated carbon', *J. Colloid and Interface Sci.*, Vol. 55, No. 2, pp.329–341.
- Zheleznov, V.V. and Lysotskii, V.L. (2002) 'Application of fibrous carbon ferrocyanide sorbents for removing cesium and cobalt from large volumes of sea water', *Atomic Energy*, Vol. 92, No. 6, pp.493–500.