PHOSPHORYLATED ORANGE ADSORBENT GEL FOR REMOVAL OF SELECTED HEAVY METALS

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ABSTRACT

Heavy metals pollution is the global problem which becomes a matter of great concern over last few decades. Automotive service and repair shops are one of the industrial which generate hazardous waste that harmful to public health and environment. This study is to determine the efficiency of bio-waste filter to remove the heavy metals and the efficiency between up-flow and gravity flow method in the treatment process. The phosphorylated orange adsorption gel (POAG) is chemically modified orange waste which consisted of orange peels and pulps. Besides cotton, glass beads, and glass filter, POAG is also part of the reactor for both up-flow and gravity flow method. The wastewater treatment is run for 7 hours time of interval. The wastewater samples are taken from the automotive service and repair shop at Gambang. The concentration of heavy metals and oil and grease of the samples are measured for each hour. From the data analysis, the average percentage removals of Copper using gravity flow and up-flow method are 94.12 % and 96.57 % respectively. The average percentage removals of Lead using gravity flow and up-flow method are 162.42 % and 188.51 % respectively. The average percentage removals of Nickel using gravity flow and up-flow method are 126.79 % and 139.29 % respectively. The average percentage removals of Zinc using gravity flow and up-flow method are 88.13 % and 88.44 % respectively. The average percentage removals of oil and grease using gravity flow and up-flow method are 99.02 % and 97.61 % respectively. Based on statistical analysis, both contact time and treatment methods are significant. By comparing the P-value of contact time and treatment methods, contact time is more significant than treatment methods because lower P-value of contact time. In conclusion, POAG has high ability to remove the heavy metals and oil and grease which contain in the samples. Up-flow method has the higher efficiency for removing heavy metals compare to gravity flow method. For removal of oil and grease, gravity flow method possesses higher efficiency compare to up-flow method.

ABSTRAK

Pencemaran logam berat merupakan suatu masalah global yang amat prihatin beberapa dekad yang lalu. Perkhidmatan automotif dan kedai-kedai pembaikan kenderaan adalah salah satu industri yang menjanakan sisa berbahaya yang boleh menjejaskan kesihatan awam dan alam sekitar. Kajian ini adalah untuk menentukan kecekapan bio-sisa penapis untuk menyingkirkan logam berat dan kecekapan di antara kaedah aliran ke atas dan aliran gravity dalam proses rawatan. POAG merupakan sisa oren yang terdiri daripada kulit oren dan pulpa oren. Sisa oren telah diubahsuai dengan menggunakan bahan kimia untuk menjadikannya sebagai POAG. Selain daripada kapas, manik kaca, dan kaca penapis, POAG adalah sebahagian daripada reaktor bagi kaedah aliran ke atas dan aliran graviti. Sampel air sisa diambil dari perkhidmatan automotif dan kedai pembaikan di Gambang. Rawatan air sisa telah dijalankan selama 7 jam. Daripada analisis data, purata peratusan penyingkiran Kuprum yang menggunakan kaedah aliran graviti dan kaedah aliran ke atas adalah 94.12% dan 96.57%. Purata peratusan Plumbum yang menggunakan kaedah aliran graviti dan kaedah aliran ke atas adalah 162.42% dan 188.51% masing-masing. Purata peratusan Nikel yang menggunakan kaedah aliran graviti dan kaedah aliran ke atas merupakan 126.79% dan 139.29% masing-masing. Purata peratusan Zink yang menggunakan kaedah aliran graviti dan kaedah aliran ke atas adalah 88.13% dan 88.44%. Purata peratusan minyak dan gris yang menggunakan kaedah aliran graviti dan kaedah aliran ke atas merupakan 99.02% dan 97.61%. Berdasarkan analisis statistik, kedua-dua masa sentuhan dan kaedah rawatan adalah penting. Dengan membandingkan P-nilai masa sentuhan dan kaedah rawatan, masa sentuhan adalah lebih penting daripada kaedah rawatan kerana P-nilai masa sentuhan lebih rendah. Kepekatan logam berat dan minyak dan gris telah diukur bagi sampel setiap jam. Kesimpulannya, POAG mempunyai keupayaan yang tinggi untuk menyingkirkan logam berat dan minyak dan gris yang mengandungi di dalam sampel. Selain itu, kaedah aliran ke atas mempunyai kecekapan yang lebih tinggi bagi penyingkiran logam berat berbanding dengan kaedah aliran graviti. Bagi penyingkiran minyak dan gris, kaedah aliran graviti memiliki kecekapan yang lebih tinggi berbanding dengan kaedah aliran ke atas.

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LIST OF SYMBOLS

q_m	Maximum adsorption capacity
R	Percentage of Adsorption
b	Affinity constant related to the energy of adsorption
K_F	Freundlich constants related to the adsorption capacity
n	Adsorption intensity of the adsorbent

LIST OF ABBREVIATION

OW	Orange Waste
POW	Powdered Orange Waste
POAG	Phosphorylated Orange Adsorption Gel
Cu	Copper
Pb	Lead
Ni	Nickel
Zn	Zinc
Hg	Mercury
Cd	Cadmium
EQA	Environmental Quality Act
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
SS	Suspended Solid
DOE	Department of Environment
DMF	Dimethyl Formamide
HNO^3	Nitric Acid
PVC	Polyvinyl Chloride
AAS	Aomic Absorption Spectrometer
O/W	Oil-in-water
W/O	Water-in-oil

CHAPTER 1

INTRODUCTION

1.1 GENERAL

Water is the crucial resource in human life and it is necessary for survival, health and ecosystem. Wastewater consists of heavy metals and the point sources of the wastewater are industry, domestic residences, agriculture, and commercial properties. As Malaysia progressively becoming an industrial country, the water pollution problems will be arising gradually. During industrial activities, metal ions are produced in considerable amount and released behave a serious threat to the environment and are harmful to aquatic life and human health (Puspa Lal Homagai *et al.*, 2009).

There are numerous methods that can be applied to remove detrimental metal ions from industrial wastewater such as biosorption. Biosorption is becoming an alternative technique to the existing technologies for removing toxic pollutants from wastewaters. Recently biosorption have focused on the experiments by using waste materials from large scale of industrial operations or by-products such as orange waste, rice husks, sugarcane bagasse, etc (N. Ahalya *et al.*, 2003). It has the benefits to achieve high purity of treated wastewater by applying cheap absorbents (Alejandro Grimm *et al.*, 2006).

Orange waste is prepared as adsorption gel, which containing pectic acid by crosslinking with epichlorohydrin. It is low cost and found to be suitable for removing these impurities through phosphorylated pectin substances contained in these residues into pectic acid by calcium hydroxide followed by water washing and drying. The adsorption gels showed excellent adsorption behaviour for removing the impurity metal ions away from wastewater (Inoue K. *et al.*, 2003).

1.2 BACKGROUND OF STUDY

Biosorption is defined as the ability of materials of biological origin to bind the toxic metals and organic compounds to the surface of cellular wall or membrane in the equilibrium process. Biosorbent is the materials of biological origin that able to bind the toxic metals and organic compounds. In the past, physical adsorption was thought to be the dominating mechanism. However, recent studies showed that the mechanism is similar to ion-exchange process with the functional groups (amino, carboxyl, phosphate, sulfate, hydroxyl groups) exposed by the cellular wall, which is composed mainly of polysaccharides, proteins and lipids, and for this reason biosorbents can be considered as weak acidic cation-exchangers. The equilibrium of biosorption can be described with Langmuir Equation, since it is more suitable for description of chemisorptions process.

1.3 OBJECTIVE

The objectives of the research are:

1) To determine the efficiency of bio-filter to remove the selected heavy metals.
2) To compare the efficiency between up-flow and gravity flow method in the treatment process.

1.4 PROBLEM STATEMENT

Heavy metals pollution has become a matter of concern over last several decades as result of its toxicity and insusceptibility to the environment. One of the industrials that able to cause the heavy metal pollution is automotive service and repair shops. Automotive service and repair shops are the largest small quantity generators of hazardous waste. They create many different types of waste during their daily operations. These include used oil and fluids, dirty shop rags, used parts, asbestos from brake pads and waste from solvents used for cleaning parts. All of which are expensive to dispose of and sometimes hazardous. The most dangerous waste commonly created in auto repair shops is from the solvents used to clean parts. Many of the chemicals that make up the solvents are extremely dangerous to human and the environment.

1.5 SCOPE OF STUDY

The bio-filter consisted of a series of filter elements which consist of cotton, glass beads, orange waste gel, and glass filter to improve the quality of discharge water from automotive workshop (industrial wastewater) at Gambang area. The experiment is carried out in this project will be divided into two stages. Firstly, the adsorbent gel made by orange waste is prepared. The experiment is carried out through up-flow and gravity flow at second stage. Same flow rate which is 9.50 ml/min is applied on the samples that filter through up-flow and gravity flow approaches. The sample is tested before and after the filtration to determine the heavy metals (Copper, Lead, Nickel, Zinc) and oil and grease contain in the wastewater.

1.6 SIGNIFICANCE OF STUDY

The study is beneficial to human being in identifying appropriate method on wastewater treatment. On the other hand, the wastewater problems can be reduced and the seriousness of the wastewater may be lightened. Furthermore, the biomass waste (orange waste) is almost at no cost and it is suitable for wastewater treatment because of its environmental friendly nature. Thus, it is not a waste that causes part of the pollution.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

In this chapter is discussed about the biosorption, orange waste, heavy metals, standards as guidance and the previous study of the biosorption. The biosorption is discussed about the definition, process, and the history of biosorption. Orange waste part is focused on the problem disposal of the orange waste, the application of orange waste, characteristic of orange waste and the function of orange waste. For the heavy metals, the heavy metals are discussed including copper, lead, nickel and zinc. Each of the heavy metals are included the characteristic, sources of contamination, and effects to human health. The standard applied on this study was Environmental Quality (Industrial Effluent) Regulations 2009 which is the sources from Department of Environment (DOE). There are two type of biosorption equation can be applied on biosorption study which is Langmuir Equation and Freundlich Equation. The previous study will include the biosorption capacity, q_m of each related case study.

2.2 BIOSORPTION

Biosorption is an ability of the biological origin materials to bind toxic metals to the surface of membrane or cellular wall during the equilibrium process (Chojnacka, 2009). Biosorption is a process which able to remove the heavy metals by using inexpensive dead biomass. It is particularly feasible to use for removal of these contaminants from industrial effluents (David Kratochvil and Bohumil Volesky, 1990).

The adsorbents have been classified into five different categories based on their state of availability: (1) waste materials from agricultural and industry, (2) fruit waste, (3) plant waste, (4) natural inorganic materials, and (5) bioadsorbents (Pankaj Sharma *et al.*, 2011). In recent years, agricultural by-products have been widely studied for metal removal from water which including peat, wood, pine bark, banana pith, soy bean, and cottonseed hulls, peanut, shells, hazelnut shell, rice husk, sawdust, wool, orange peel, compost, humic substances, and leaves. This aspect indirectly plays an important role in improving a zero-wastes economic policy especially in the case of the re-use of biomasses coming from food, pharmaceuticals, and wastewater treatments (G.H. Pino *et al.*, 2006).

The biosorbent can then be packed in sorption columns which are the most effective device for the continuous removal of heavy metals. The cycles of experiment of biosorption column consist of loading, regeneration, and rinsing. The experiment begins by loading the sorbent material whereby wastewater sample is passed through the packed-bed and the heavy metals are adsorbed from the liquid by the biosorbent. When the metal sorption capacity of the biosorbent is exhausted the column is taken out and its bed can be regenerated with solutions of acids and/or hydroxides. The regeneration produces small volumes of heavy metal concentrates suitable for conventional metal recovery processes. Rinsing and/or backwashing of the bed with water are the last step of the experiment to remove the remains of the regenerants and suspended solids which are captured in the column. In order to make the biosorption process truly continuous, pairs of columns are installed in parallel so that during the regeneration and rinsing of one of the columns the other is being loaded with heavy metals (David Kratochvil and Bohumil Volesky, 1990).

The advantages of biosorption are good performance in metal removal if compare to ion exchangers and it is cost-effectiveness since making use of raw materials for fermentation and the agricultural process (G.H. Pino *et al.*, 2006). Table 2.1 is shown the summary of the biosorption process which is the current trends in research and Figure 2.1 is shown the process of the biosorption of metal ions by the biosorbent.

Table 2.1: Summary of Biosorption Process

Process	**Metabolically-Passive, reversible, single stage**
Mechanism	Adsorption
Equilibrium concentration of metal ions	Intermediate
Biomass applied	Not alive
Nutrients	Not required
Rate	High
Effect of Toxicity	No danger
Cellular growth	Not occur

Source: Chojnacka (2009)

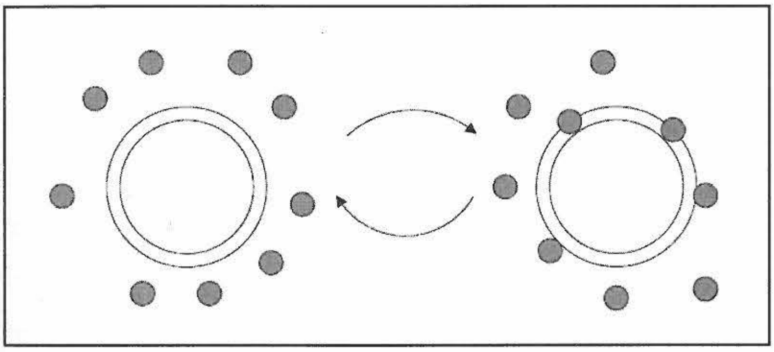

Figure 2.1: Biosorption of Metal Ions

Source: Chojnacka (2009)

2.2.1 History of Biosorption

During 18th and 19th centuries, the ability of the living microorganism to take up metals from aqueous solution was investigated but the living and non-living microorganism use as adsorbents for removing or recovering the materials from aqueous solution is begins at last 3 decades. Ames Crosta Mills & Company Ltd was registered the first patent of the biological apparatus which is used for biological treatment of wastewater. The first quantitative study on the metal biosorption was done by L.Hecke, who reported on the copper uptake by fungal spores of T.tritici and

U.crameri in 1902. F.Pichler and A. Wobler was reported the similar studies on uptake of Ag, Cu, Ce, and Hg by using corn smut in 1922.

Activated sludge efficiently removed even radioactive metals like plutonium-239 from contaminated domestic wastewater was reported by Ruchloft in 1949. B. Volesky and M. Tsezos were awarded the first patent on the use of biosorption technology for removing uranium or thorium ions from aqueous suspension/solution in 1982. The practical use of biosorption technology for monitoring trace heavy metals in the environment was reported by Goodman and Roberts (1971) and Neufeld and Hermann studied the kinetics of biosorption by activated sludge and reported uptakes of Cd, Hg, and Zn rapidly in the first few min, followed by a slow uptake over the next 3 h in 1975.

Friedmann and Dugan (1968) used a pure culture of Zoogloea for a metal-binding study. Gould and Genetelli (1984) examined the competition between metal ions for binding sites of anaerobic sludge, and reported a binding affinity order of: Cu > Cd > Zn > Ni. Y. Chiu and his coworkers (1976) analyzed biosorption of uranium on mycelia of Penicillium C-1, while M. Tsezos and B. Volesky (1981) focused on biosorptive removal of uranium and thorium by dead fungal biomass of Rhizopus arrhizus. Steen and Karickhoff (1981) reported uptake of hydrophobic organic pollutants by mixed microbial populations (Donghee Park *et al.*, 2010).

2.3 ORANGE WASTE

Orange waste (OW) is waste materials which are a low cost adsorbent instead of activated carbon, environmentally friendly nature and require little processing. (Pankaj Sharma *et al.*, 2011). As a low cost, orange waste is an attractive and inexpensive option for the biosorption removal of dissolved metals. It has been employed for metal ions removal from simulated wastewater. Some orange waste is used as a precursor material for the preparation of an adsorbent by common chemical modifications such as alkaline, acid, ethanol and acetone treatment (Ningchuan Feng *et al.*, 2011).

2.3.1 Disposal Problem of Orange Waste

Orange waste consists of peel, pulp, and seeds of the fruit. The orange baggase is a waste of orange juice industries which is constitutes about 49% of the orange fruit. Brazil is the major orange producer in the world. There are several million tons of orange baggase are generated per year. Therefore, the alternative way to solve the disposal problem caused by the large quantity of the orange baggase is re-utilization the orange baggase. Thus, it is profitably to orange juice and environmental friendly to the earth (Lewinsky, 2007).

2.3.2 Application of Orange Waste

The application of orange waste can be extended to heavy metals industrial wastewaters treatment, particularly when the reverse process i.e. desorption which able for solving the storage problem of huge amounts of charged solid supports (Khalfaoui Amel *et al.*).

2.3.3 Characteristic of Orange Waste

Orange waste consists of both peel and pulp. They are highly susceptible to hydrolysis by mixtures of cellulolytic and pectinolytic enzymes which able to change the feedstock to value added products through biological conversion. The peel consists of 16.9% soluble sugars, 9.21 % cellulose, 10.5 % hemicellulose and 42.5 % pectin as the most crucial components and the pulp is rich in carbohydrate (Biniyam Yalemtesta *et al.*, 2010). Pectin is a carboxylated polysaccharide in which pectic acid is partly esterfied by a methyl group. It can be easily converted into pectic acid by saponification with alkalis and can be loaded with metal to make adsorption gel (B.K. Biswas *et al.*, 2007). The OW contains cellulose, hemicellulose, pectins, water soluble sugars, limonene, and other low molecular weight compounds. The cellulosic and hemicellulosic contents of OW was phosphorylated for the conversion of alcoholic hydroxyl groups into phosphate groups that has high affinity for the binding of metal ions according to the following reaction which is as shown in Figure 2.2 (Kedar Nath Ghimire *et al.*, 2008).

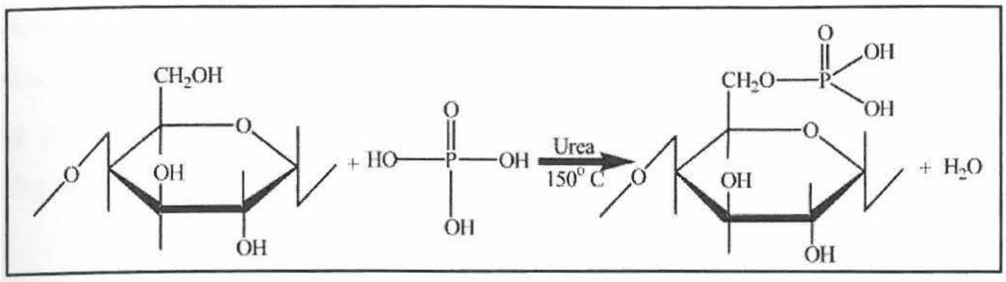

Figure 2.2: Chemical Reaction between Alcholic Hydroxyl Group and Phosphate Group

Source: Kedar Nath Ghimire *et al.* (2008)

2.3.4 Use of Orange Waste

Biowaste was evaluated as a new biosorbent for removal of toxic heavy metals, Hg (II), Pb (II), Cd (II), Cu (II), Zn (II), and Ni (II). The efficiency of phosphated fruit residues was higher than fruit residue especially at low pH values. The order of removal of heavy metal by phosphate fruit residues was Cu (II) > Pb (II) > Ni (II) > Zn (II) > Hg (II) = Cd (II) (Senthikumar S *et al.*, 2000). Table 2.2 is shown the adsorption capacities of orange peel by using Freundlich equation.

Table 2.2: Adsorption Capacities (q_m) of orange peel

Metals Ions	q_m, mg/g	Equilibrium Kinetic Model
Copper	3.65	Freundlich
Nickel	6.01	Freundlich
Zinc	5.25	Freundlich
Lead	-	Freundlich

Source: Thomas Anish Johnson *et al.* (2008)

2.4 PREVIOUS STUDY OF ORANGE WASTE

In the case study of "Adosrption Separation of Metal Ions onto Phosphorylated Orange Waste", the biosorbent is a highly selective and efficient biosorbent has been prepared from the orange waste where the orange waste is phosphorylated. It found to exhibit brilliant behaviour for some kinds of the metal ions through the experiment by using packed column. The maximum adsorptions capacities are recorded in term of mol/kg dry gel were 0.97 for Cu and 1.15 for Pb (Kedar Nath Ghimire *et al*, 2008).

The case study, "Biosorption of heavy metals from aqueous solutions by chemically modified orange peel" is completed by applying Langmuir and Freundlich isotherm models to describe the biosorption of the metal ions onto the copolymerization-modified orange peel (OPAA). According to Langmuir equation, the maximum uptakes capacities for Pb and Ni are 476.1 and 162.6 mg/g, respectively (Ningchuan Feng *et al.*, 2011).

"Effective removal of heavy metals from aqueous solutions by ornage peel xanthate" is a case study where the orange peel is prepared as orange peel xanthate and subjected to various parameters including equilibrium pH, initial metal ion concentration and adsorption time on the adsorption process. The maximum adsorption capacities of Cu, Pb, Zn and Ni are 77.60, 218.34, 49.85 and 15.45 mg/g, respectively. All the adsorption able to achieve equilibrium within 20 min and the kinetics was well fitted to the psesudo-second order equation (Liang Sha *et al.*, 2009).

The results from the experiment of each case study are included in the Table 2.3 below. It is as a summary from the case studies which related to orange waste.

Table 2.3: Previous Studies

Biosorbents	Biosorption Capacity, q_{max} (mol/kg)				References
	Cu	Pb	Ni	Zn	
Phosphorylated Orange Waste	0.97	1.15	-	-	(Kedar Nath Ghimire, Jun-ichi Inoue, Kaysutoshi Inoue, Hidetaka Kawakita, and Keisuke Ohto, 2008)
Orange Peel	-	4.19	1.43	-	(Ningchuan Feng, Xueyi Guo, Sha Liang, Yanshu Zhu, Jianping Liu, 2011)
Xanthates Orange Peel	0.68	1.92	0.14	0.44	(Liang Sha, Guo Xue-yi, Feng Ning-Chuan, Tian Qing-Hua, 2009)

2.5 INDUSTRIAL WASTEWATER

Industrial wastewaters (including agro-industrial wastewaters) are effluents that result from human activities including raw-material processing and manufacturing. Water pollution occurs when potential pollutants in the streams reach at a certain amounts.

2.5.1 Characteristic of Industrial Wastewater

Industrial wastewaters have very varied compositions depending on the type of industry and materials processed. Some of these wastewaters can be organically very strong, easily biodegradable, largely inorganic or potentially inhibitory (Jern, 2006). The main parameteras for the characterisation of industrial wastewater are Biochemical

Oxygen Demand (BOD), Chemical Oxygen demand (COD), suspended solid (SS), oil and grease, phenils, pH, and metals (Sperling, 2007).

2.5.2 Standard

Environment Division is an enforcement agency. It is known as Department of Environment (DOE) in 1983 was institutionalised in 1975. Environmental management in Malaysia become more focussed with the gazzettement of the Environmental Quality Act (EQA) on 14 March 1974. The Department's main role is to prevent, control and abate pollution through the enforcement of the EQA, 1974 and its 34 subsidiary legislation made there under. Table 2.4 shown the accepted conditions for discharge of industrial effluent or mixed effluent of standards A & B. To determine the acceptable standard of the samples to be tested, it is necessary refer to the Environmental Quality (Industrial Effluent) Regulations 2009.

Table 2.4: Acceptable Conditions for Discharge of Industrial Effluent or Mixed Effluent of Standards A & B

Parameter	Unit	Standard	
		A	B
Temperature	°C	40	40
pH Value	-	6.0 – 9.0	6.0 – 9.0
BOD_5 at 20°C	mg/L	20	40
Suspended Solids	mg/L	50	100
Mercury	mg/L	0.005	0.05
Cadmium	mg/L	0.01	0.02
Chromium, Hexavalent	mg/L	0.05	0.05
Chromium, Trivalent	mg/L	0.20	1.0
Arsenic	mg/L	0.05	0.10
Cyanide	mg/L	0.05	0.10
Lead	mg/L	0.10	0.50
Copper	mg/L	0.20	1.0
Manganese	mg/L	0.20	1.0
Nickel	mg/L	0.20	1.0
Tin	mg/L	0.20	1.0
Zinc	mg/L	2.0	2.0
Boron	mg/L	1.0	4.0
Iron (Fe)	mg/L	1.0	5.0
Silver	mg/L	0.1	1.0
Aluminium	mg/L	10	15
Selenium	mg/L	0.02	0.5
Barium	mg/L	1.0	2.0
Fluoride	mg/L	2.0	5.0
Formaldehyde	mg/L	1.0	2.0
Phenol	mg/L	0.001	1.0
Free Chlorine	mg/L	1.0	2.0
Sulphide	mg/L	0.50	0.50
Oil and Grease	mg/L	1.0	10
Ammoniacal Nitrogen	mg/L	10	20
Colour	ADMI*	100	200

ADMI – American Dye Manufactures Institute

Source: Environmental Quality (Industrial Effluent) Regulations 2009