CHAPTER 1

INTRODUCTION

1.1. Introduction

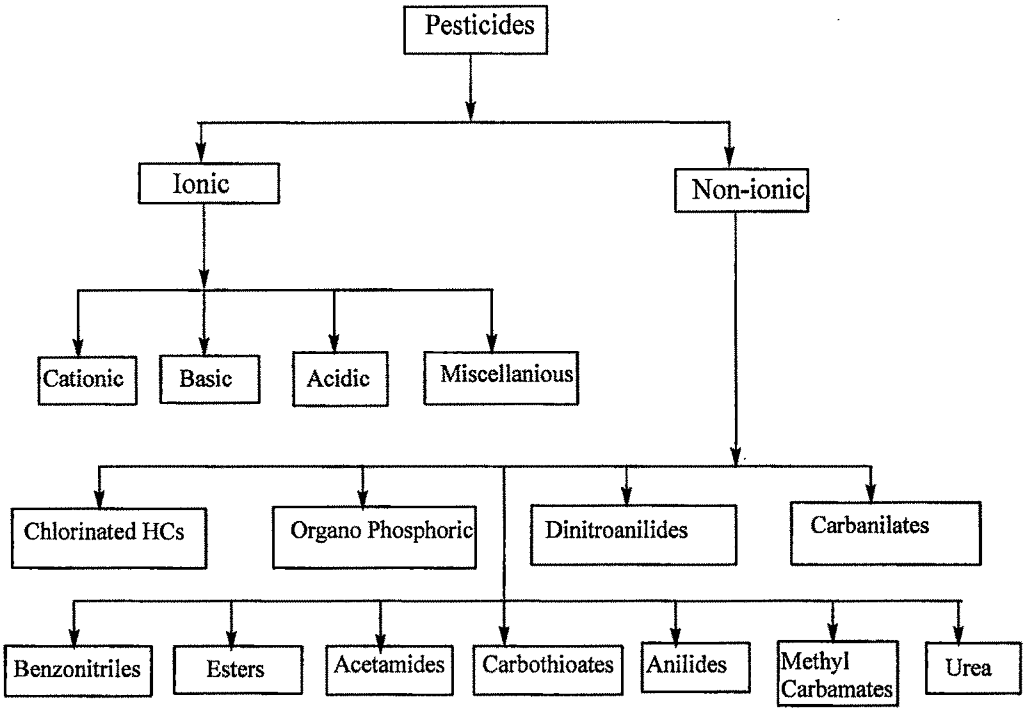
Water comprises over 70% of the Earth's surface and is undoubtedly the most precious natural resource that exists on our planet. Adequate supply of fresh and clean drinking water is a basic need for all human beings on the earth, yet it has been observed that millions of people worldwide are deprived of this. Water pollution is an important environmental concern in the world, and there are many sources such as industrial pollution, or agricultural runoff. However, industrial wastewater is the major point source of water contamination. Rapid industrialization has resulted in increased disposal of organic toxicants like dyes, pesticides, phenols and polycyclic aromatic hydrocarbons which persists indefinitely in the environment..

Dyes are extensively used, especially in the textile, leather, pulp and paper, and cosmetic industries. The textile industry is one of the industries that generate a high volume of waste water [1.1-1.3]. Many dyes are suspected to be carcinogenic, mutagenic, and toxic that might affect aquatic biota and also humans [1.4, 1.5] and usually the highest toxicity is found among the basic and diazo direct dyes [1.4, 1.6, and 1.7]. The waste effluents, discharged by such industries, become colored due to the residual dyes and when they are disposed to the natural water sources, they pollute water. Colored effluents are known to cause high oxygen demand, fluctuating pH, large solid load, and resistance to biological oxidation [1.4, 1.5, and 1.8]. Even a very small amount of dye in water is visible and it impedes light penetration and thus reduces photosynthesis in aquatic plants, affects their growth, and decreases gas solubility, interfering with the natural purification process [1.4].

Synthetic dyes are extensively used in the textile and printing industries [1.9-1.11]. Dyes are complex ionic, aromatic organic compounds with structures including aryl rings which have delocalized electron systems. The color of a dye is provided by the presence of a chromophore group. A chromophore is a radical configuration consisting of conjugated double bonds containing delocalized electrons. Other common chromophoric configurations include azo (-N=N-), carbonyl (=C=O); carbon (=C=C=); carbon-nitrogen (>C=NH or -CH=N-); nitroso (-NO or N-OH); nitro (-NO_2 or =NO-OH); and sulphur (C=S). The chromogen, which is the aromatic structure normally containing benzene, naphthalene or anthracene rings, is part of a chromogen-chromophore structure along with an auxochrome. The presence of ionizing groups known as auxochromes results in a much stronger alteration of the maximum absorption of the compound and provides a bonding affinity. Some common auxochrome groups include -NH_3, -COOH, -HSO_3, -OH. Dyes are classified as follows: anionic – direct, acid and reactive dyes; cationic – basic dyes; non-ionic – disperse dyes. The chromophores in anionic and non-ionic dyes are mostly azo groups or anthroquinone types. Azo dyes are the most important group of synthetic colorants [1.10, 1.11]. They are the largest class of dyes, and more than half of the annually produced amounts of dyes (estimated for 1994 worldwide as 1 million tones) are azo dyes [1.12].

The reductive cleavage of azo linkages is responsible for the formation of toxic amines in the effluent. Anthraquinone based dyes are more resistant to degradation due to their fused aromatic structures and thus remain coloured in the wastewater. Thus dye waste water from textile or dye stuff industry is one of the most difficult to treat because dyes have various synthetic origin and they contain complex aromatic molecular structures, which make them more stable and more difficult to be biodegraded [1.13, 1.14]. In fact textile wastewaters exhibit low BOD to COD ratios (<0.1) indicating non-biodegradable nature of dyes [1.15, 1.16]. Decolorization of dye effluents has therefore acquired increasing attention.

The widespread use and disposal of pesticides by farmers, institutions, and the general public lead to many possible sources of contamination by pesticides in the environment. Water pollution by pesticides during routine agricultural practices is a common and growing problem in major agricultural areas of the world. The various adverse health effects of pesticides include teratogenesis, oncogenesis (benign/malignant), mutagenesis and hemotoxic effects, neurotoxic effects, endocrine disruption and reproductive effects have been reported in literature [1.17,1.18]. In general, pesticide is defined as a diverse group or mixture of chemical substances, biological agents, antimicrobials, disinfectants or devices which are intentionally applied for selective administration and attenuation against any pests including insects, plant pathogens, weeds, mollusks, birds, mammals, fish, nematodes (roundworms) and microbes that compete for the production, processing, storage, transport, or marketing of food, agricultural commodes, destroy property, or widespread of diseases[1.19-1.21]. More precisely, pesticide is featured by its unique chemical structures developed to mimic and substitute for specific molecules to the targeted pests, which present a deleterious disruption to the desired biological reactions [1.22]. The classification of pesticides are based on its chemical structure or its targeted implications, where insecticide is corroborated to the protection of termites, ants, mosquitoes, and cockroaches while herbicides and rodenticides are linked to the weeds and rat infestations control (scheme 1.1).



Scheme 1.1 Classifications of Pesticides

Recently, the infiltration of pesticide effluents into the waterways and aquifer systems, endorsed by the spray drift, soil leaching, tile drainage outflow, base-flow seepage, surface run-off, volatilization (diffuse-source inputs), sewer overflows, improper handling of tank mix leftovers, leaking of faulty equipments, incorrect storage of canisters, dripping from agricultural practices, accidental spillage and farmyard deposition (point source pathways) (from agriculture, horticulture, forestry, chemical industry and domestic activities) [1.23], constitutes an accumulative, persistent, threatening and detrimental deterioration towards the survival of aquatic compartments, flora, fauna and environmental matrix (water and soil) [1.24].

The real hazard setting aside aesthetic considerations is exacerbated when pesticide agents interfere with the transmission of light through water, retard photosynthetic activities, inhibit the growth of biota terrestrial ecosystems (carotenoid, aromatic and branched chain amino acid synthesis), affect the symbiotic process, damage the quality of the irrigation channels and impede the propagation of algae, thus upsetting biological processes within streams, resulting in food chain and ecological imbalance [1.25, 1.26]. Increasingly, acute exposure to pesticide substances was illustrated vulnerable to a wide spectrum of immunosuppressant neurobehavioral disorders and developmental toxicity presage as allergy, autoimmune disease, reproductive abnormalities, multiple myeloma, leukemia, malignant lymphoma, increased kid mortality, deformities, life-threatening bleeding and myocytes with burning sensation in the mouth and throat, nausea, vomiting, sweating, hyperventilation, pain, fasciculation, myotonia, weakness and myoglobinuria [1.27-1.29]. Nonetheless, sporadic and excessive susceptibility to the pesticides clastogenic action has been subjected to the alterations of cardiovascular system, musculoskeletal defects and thyroid function failure (acetanilide, ethylene bis dithio carbamates, nitroanilines, organophosphates and synthetic pyrethroids) ranging from predomination of neuromuscular complaints (lethargy, irritability, poor concentration, mood swings, depression, insomnia, muscleaches and pains), hyper-stimulation of parasympathetic autonomic nervous system, profuse diarrhea, salivation, urination, lacrimation, dyspnea, wheezing (muscarinic receptors), bradycardia, tremors, convulsions, respiratory paralysis (bronchial spasm and tonic convulsions), lung edema to even death [1.30-1.32].

Adsorption is one of the most effective processes of advanced wastewater treatment, which industries employ to reduce hazardous organic and inorganic wastes in the effluents. It is also used to remove toxic inorganic and organic compounds from the contaminated groundwater.

Methods of dye wastewater treatment have been reviewed by Pokhrel and Viraraghavan, 2004, Robinson et al., 2001, Slokar and Majcen Le Marechal, 1998, Delee et al., 1998 and Banat et al., 1996 and Cooper (1993) [1.33-1.38]. Fungal and bacterial decolorization methods have been reviewed by Aksu, 2005, Wesenberg et al., 2003, Pearce et al., 2003, McMullan et al., 2001 and Fu and Viraraghavan, 2001 and Stolz, 2001 [1.12, 1.39-1.43]. Hammed and Foo recently reviewed the pesticide waste treatment technologies (activated carbon and its advanced integrated technologies) [1.152]. There are several reported methods for the removal of pollutants from effluents (Table 1.1). The technologies can be divided into three categories: biological, chemical and physical [1.34]. All of them have advantages and drawbacks. Because of the high cost and disposal problems, many of these conventional methods for treating dye wastewater have not been widely applied at large scale in the textile and paper industries [1.44].

At the present time, there is no single process capable of adequate treatment, mainly due to the complex nature of the effluents [1.45, 1.46]. In practice, a combination of different processes is often used to achieve the desired water quality in the most economical way. A literature survey shows that research has been and continues to be conducted in the areas of combined adsorption-biological treatments in order to improve the biodegradation of dyestuffs and minimize the sludge production.

Table 1.1: Principal existing and emerging processes for pesticides and dyes removal

Processes	Technology	Advantages	Disadvantages
Conventional treatment processes	Coagulation Flocculation	• Simple, economically feasible	• High sludge production • Handling and disposal problems • Not useful for treatment of pesticides
	Biodegradation	• Economically attractive • Capable of treating wide range of pesticides and dyes which cannot be treated by membrane and chemical processes	• Slow process due to slow digestion rates necessary to create an optimal favorable environment, maintenance and nutrition requirements • Requires large area for implantation of treatment and biomass separation units • Hampered by the presence of bio refractory organics (humic acids and surfactants) • Limited suitability in treating less biodegradable pesticides and dyes due to the recalcitrant nature of its organic carbon •
	Adsorption on activated carbons	• The most effective adsorbent • Great capacity • Produces a high-quality treated effluent	• Ineffective against disperse and vat dyes • The regeneration is expensive and results in loss of the adsorbent • Non-destructive process •
Established recovery processes	Membrane separations	• Removes all dye and pesticide types • Produce a high-quality treated effluent • No phase change and no chemical conditioning required • Low energy consumption compared to advanced oxidation process	• High pressures • Expensive • Incapable of treating large volumes • Fouling takes place due to the presence of large spectrum of pollutants present in water resulting in short lifetime • The concentrate resulting after treatment has to be disposed off or treated

Processes	Technology	Advantages	Disadvantages
Established recovery processes	Ion-exchange	• No loss of sorbent on regeneration • Effective • Low power consumption and low operational cost	• Not effective for disperse dyes and nonionic pesticides • Improper for treatment of chlorinated pesticides • Requires different types of exchangers for different constituents • The presence of microorganisms can reduce the exchange capacity • Disposal of regeneration solution
	Oxidation	• Rapid and efficient process	• High energy cost • Chemicals required
Emerging removal processes	Advanced oxidation process	• No sludge production • little or no consumption of chemicals efficiency for recalcitrant dyes • Particularly useful for treating non-biodegradable pesticides and dyes • useful for treating multiple combinations of pesticides and dyes in a single step. • Process is accelerated by solar, UV or ultrasonic radiation	• Economically unfeasible, formation of by-products, technical constraints • Formation of chlorine or hypochlorite due to the potential of chlorine oxidation • Requires extra energy sources like solar, UV or ultrasonic radiation
	Selective bio adsorbents	• Economically attractive • Regeneration is not necessary • High selectivity	• Requires chemical modification • Non-destructive process
	Biomass	• Low operating cost • Good efficiency and selectivity • No toxic effect on microorganisms	• Slow process performance • Depends on some external factors (pH, salts)

1.2.2. Biological treatments

Biological treatment is often the most economical alternative when compared with other physical and chemical processes. Biodegradation methods such as fungal decolorization, microbial degradation, adsorption by (living or dead) microbial biomass and bioremediation systems are commonly applied to the treatment of industrial effluents because many microorganisms such as bacteria, yeasts, algae and fungi are able to accumulate and degrade different pollutants [1.37, 1.42, 1.43]. However, their application is often restricted because of technical constraints. Biological treatment requires a large land area and is constrained by sensitivity toward diurnal variation as well as toxicity of some chemicals, and less flexibility in design and operation [1.47]. Biological treatment is incapable of obtaining satisfactory color elimination with current conventional biodegradation processes [1.34]. Moreover, although many organic molecules are degraded, many others are recalcitrant due to their complex chemical structure and synthetic organic origin [1.48]. In particular, due to their xenobiotic nature, azo dyes are not totally degraded.

1.2.3. Chemical methods

Chemical methods include coagulation or flocculation combined with flotation and filtration, precipitation–flocculation with $Fe(II)/Ca(OH)_2$, electro flotation, electro kinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), irradiation or electrochemical processes. These chemical techniques are often expensive, and although the dyes are removed, accumulation of concentrated sludge creates a disposal problem. There is also the possibility that a secondary pollution problem will arise because of excessive chemical use. Recently, other emerging techniques, known as advanced oxidation processes, which are based on the generation of very powerful oxidizing agents such as hydroxyl radicals, have been applied with success for pollutant degradation. Although these methods are efficient for the treatment of waters contaminated with pollutants, they are very costly and commercially unattractive. The high electrical energy demand and the consumption of chemical reagents are common problems.

1.2.4. Physical methods

Different physical methods are also widely used, such as membrane-filtration processes (nano filtration, reverse osmosis, electrodialysis) and adsorption techniques. The major disadvantage of the membrane processes is that they have a limited lifetime before membrane fouling occurs and the cost of periodic replacement must thus be included in any analysis of their economic viability. In accordance with the very abundant literature data, liquid-phase adsorption is one of the most popular methods for the removal of pollutants from wastewater since proper design of the adsorption process will produce a high-quality treated effluent. This process provides an attractive alternative for the treatment of contaminated waters, especially if the adsorbent is inexpensive and does not require an additional pre-treatment step before its application.

Adsorption is a well known equilibrium separation process and an effective method for water decontamination applications [1.49]. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances.

1.3. Use of commercial activated carbons

Adsorption techniques employing solid sorbents are widely used to remove certain classes of chemical pollutants from waters, especially those that are practically unaffected by conventional biological wastewater treatments. However, amongst all the adsorbent materials proposed, activated carbon is the most popular for the removal of pollutants from wastewater [1.50-1.52]. In particular, the effectiveness of adsorption on commercial activated carbons (CAC) for removal of a wide variety of dyes from wastewaters has made it an ideal alternative to other expensive treatment options [1.53]. Because of their great capacity to adsorb dyes and other organics, CAC are the most effective adsorbents. The capacity is mainly due to their structural characteristics and their porous texture which gives them a large surface area, and their chemical nature which can be easily modified by chemical treatment in order to increase their properties. However, activated carbon presents several disadvantages [1.50]. It is quite expensive (the higher the quality, the greater the cost), non-selective and ineffective against certain adsorbates like disperse and vat dyes. The regeneration of saturated carbon is also expensive, not straightforward, and results in loss of the adsorbent. The use of carbons based on relatively expensive starting materials is also unjustified for most pollution control applications [1.54]. This has led many workers to search for more economic adsorbents.

1.4. Non-conventional low-cost adsorbents

Due to the problems mentioned above, research interest into the production of alternative sorbents to replace the costly activated carbon has intensified in recent years. Cost is actually an important parameter for comparing the adsorbent materials. According to Bailey et al. (1999), an adsorbent can be considered low-cost if it requires little processing, is abundant in nature or is a by-product or waste material from another industry [1.55]. Certain waste products from industrial and agricultural operations, natural materials and bio sorbents represent potentially economical alternative sorbents. Many of them have been tested and proposed for dyes and pesticides removal. Table 1.2 shows a non-exhaustive list of various adsorbents used in the last 15 years for the removal of pesticides and dyes

Table 1.2: List of various adsorbents used for the removal of pesticides and dyes

Name of the Sorbent	Name of the Sorbate	Initial metal concentration/ pH/ temperature	Maximum adsorption capacity	Isotherm / kinetics	Reference	Author
Pu-erh tea powder	Methyl violet	25^0C, nano sized	294.12	Langmuir/ Pseudo 2^{nd} order	1.56	Ping Li
Grapefruit peel	Crystal violet	pH 6, 25mg/L, 1g/L, >60min	254.16 mg/g	Langmuir/ Pseudo 2^{nd} order	1.57	Asma Saeed
Pyrolyzed petrified sediment	Methylene Blue	pH 7, 30^0C, 8h	2.39 /mg	Langmuir and Freundlich Pseudo 1^{st} order	1.58	Ayse Z. Aroguz
Magnesium silicate	Methylene Blue	10g/L, 24h, pH8.5, 2500mg/L	144.9 mg/g	Langmuir/ Pseudo 2^{nd} order	1.59	Franco Ferrero
Ayous (Triplochiton schleroxylon) sawdust	Paraquat	200rpm, 6g/L, 30-55^0C,	36.83 mg/g	Langmuir/ Pseudo 2^{nd} order	1.60	Emmanuel Ngameni
Saw dust	Crystal violet	50-250 mg/L, 298 K, 2500rpm	341mg/g	Langmuir	1.61	Jayanta K. Basu
Rattan saw dust	Malachite green	30^0C	62.71 mg/g	Langmuir Pseudo 1^{st} order	1.62	B.H. Hameed
Australian Kaolins: Q38, K15Gr and Ceram	Congo red	150mg/L, 150 rpm, 24h,	5.44 mg/g, 6.81 mg/g, 7.27 mg/g	Langmuir Pseudo 2^{nd} order	1.63	Shaomin
Wood as an adsorbent						
Green waste biochar	Atrazine Simazine	Solid/ solution ratio: 1:1000 g/mL	1158 mg/Kg 1066 mg/Kg	Freundlich	1.64	Wei Zheng
Activated carbon derived from Borassus aethiopum flower biomass	Malachite Green	pH 6.0-8.0, 300K, 100μm,	48.48 mg/g	Langmuir/ Pseudo second order Film diffusion and intraparticle diffusion	1.65	A. Sivasamy
Cashew nut shell	Congo red	30 g/L; 90 min;	5.184 mg/g	Redlich Peterson/ Pseudo 2^{nd} order	1.66	P. Senthil Kumar

Name of the Sorbent	Name of the Sorbate	Initial metal concentration/ pH/ temperature	Maximum adsorption capacity	Isotherm / kinetics	Reference	Author
Citrus sinensis biomass Free, Acid treated, Immobilised	Rreactiveyellow42 reactivered45	60, 120 min	36.36 mg/g 106.38 mg/g, 51.47 mg/g	Freundlich/ Pseudo 2^{nd} order	1.67	HaqNawazBhatti
Pinus sylvestris L.	Reactive Red 195	200 mg/L; 50^0C	7.38 mg/g	Pseudo 2^{nd} order, Elovich	1.68	Handan Ucun
Dimethyl terephthalate distillation residue	Safranine-T Brilliant Cresyl Blue Nile Blue Brilliant Green	500 mg/L;	17 mg/g 13 mg/g 22 mg/g 107 mg/g	Langmuir/ Pseudo 2^{nd} order	1.69	G. Guclu
Acid-activated beidellite	Simazine	0.5-5 ppm; 20^0C; 24h	≤ 5 ppm	-	1.70	Huaiyong Zhu
Organo-bentonite from Pacitan	Acid green 25	1000 mg/L; 60 min, 50^0C	3.72 mg/g	Langmuir/ Pseudo 2^{nd} order	1.71	Raymond Koswojo
Alginate encapsulated pillared clays	Pentachlorophenol, Safranine	24h; 200rpm; 22^0C; 50 µmol/L 285-4000 µmol/L	536 µmol/g 852 µmol/g	Freundlich Langmuir/ Pseudo 2^{nd} order	1.72	Jean-Philippe Basly
Calcined Lapindo volcanic mud	Methyl orange	13200rpm; 20 min	333.3 mg/g	Langmuir/ Pseudo 2^{nd} order	1.73	Aishah A. Jalil
Iron organo–inorgano pillared mont-morillonite clay	4-nitrophenol Basic yellow 28	pH 5, 7, 9; 200rpm; 24h; 80 µmol/L; 34.6 µmol/L	-	Freundlich/ Pseudo 1^{st} order	1.74	Jean-Philippe Basly
Zeolite	Methylene Blue Bisphenol A	20 mg/dm^3; 25^0C; pH7	-	Pseudo 2^{nd} order	1.75	Wen-Tien Tsai
Acid-activated zeolite-rich tuffs	Atrazine	1.25-125 mg/L; 10 days	-	-	1.76	Stefano Salvestrini
Clinoptilolite	Everzol Black, Everzol Red, Everzol Yellow	2h; 25mg/L;	2.9 mg/g 3.7 mg/g 7.6 mg/g	-	1.77	Mehmet S. Celik

Name of the Sorbent	Name of the Sorbate	Initial metal concentration/ pH/ temperature	Maximum adsorption capacity	Isotherm / kinetics	Reference	Author
Calcined hydrotalcite	2,4-D Clopyralid Picloram	pH 3, 6, 11;	813 µmol/g 2564 µmol/g 1176 µmol/g	Langmuir	1.78	M.A. Ulibarri
Fungi						
Phanerochaete chrysosporium	Direct Rede80 (DRe80) Mordant Bluee9 (MBe9)	10-200 mg/L	92% 94%	-	1.79	Kannan Pakshirajan
Scenedesmus obliquus Scenedesmus quadricauda	Dimethomorph Pyrimethanil Isoproturon	600 µg/L 600 µg/L 10 µg/L; 4 days	24 % 10 % 58 %	-	1.80	Philippe Eullaffroy
Free Laccase	Reactive blue 19 Dispersed blue Acid blue 74 Acid red 27 Reactive black 5	0.036 mM 0.072 mM 0.036 mM 0.036 mM 0.036 mM	90 % 87 % 68 % 80 % 18 %	-	1.81	J.A. Ramsay
Laccase immobilized on porous glass beads	Reactive blue 19 Dispersed blue Acid blue 74 Acid red 27 Reactive black 5	0.036 mM 0.072 mM 0.036 mM 0.036 mM 0.036 mM	77 % 78 % 74 % 40.6 % 12 %	-	1.81	J.A. Ramsay
Surfactant modified macro fungus	Reactive Red 2	100 mg/L; 25^{0}C	141.53 mg/g	Langmuir/ Pseudo 2nd order	1.82	Tamer Akar
Chlorella vulgaris	Supranol Red 3BW Lanaset Red 2GA Levafix Navy Blue EBNA		256.4 mg/g 345 mg/g 188.7 mg/g		1.83	Siew-Moi Phang
Aspergillus Niger	Direct Blue 199	400 mg/L 45 ^{0}C	29.96 mg/g	Langmuir, Freundlich/ Pseudo	1.84	Xiao-Jing Xionga

Name of the Sorbent	Name of the Sorbate	Initial metal concentration/ pH/ temperature	Maximum adsorption capacity	Isotherm / kinetics	Reference	Author
				2^{nd} order		
Baggase fly ash	Color from waste water DDD DDE Lindane Malathion Malachite green Congo red Orange-G Methyl violet Auramine-O Brilliant green Phenol 2-picoline	60 ^{0}C H_2O_2 pretreatment at 60^{0}C, 24h H_2O_2 pretreatment at 60^{0}C, 24h Hot water, 70^{0}C	29.07 mg/g 7.69 mg/g 6.67 mg/g 2.51 mg/g 2.08 mg/g 170.33 mg/g 11.89 mg/g 18.80 mg/g 26.25 mg/g 31.18 mg/g 116.28 mg/g 23.83 mg/g 59.88 mg/g	Langmuir, Freundlich, Redlich Peterson	1.85 1.86 1.86 1.87 1.87 1.88 1.89 1.90 1.90 1.91 1.92 1.93 1.94	Paitip Thiravetyan V.K. Gupta V.K. Gupta V.K. Gupta V.K. Gupta I.D. Mall I.D. Mall I.D. Mall I.D. Mall I.D. Mall I.D. Mall I.D. Mall I.D. Mall
Saw dust	Basic dye Crystal violet		341.00 mg/g		1.95	S.Chakraborty
Saw dust fly ash	Synthetic water based ink solution	30^{0}C	85.47 mg/g	Langmuir, Freundlich, Redlich Peterson	1.85	Paitip Thiravetyan
Activated carbon	Synthetic water based ink solution	30^{0}C	40.49 mg/g	Langmuir, Freundlich, Redlich Peterson	1.85	Paitip Thiravetyan
Granular activated carbon Filtersorb 300	2, 4-D Carbofuran	50-300 mg/L 30^{0}C, 120 rpm	181.82 mg/g 96.15 mg/g	Langmuir/ Pseudo 2^{nd} order Langmuir/ Pseudo 2^{nd} order	1.96	B.H. Hameed
Dimethyl terephthalate distillation residue	Safranine-T (ST), Brilliant Cresyl Blue (BCB),		107 mg/g 22 mg/g 17 mg/g	Langmuir/ Pseudo 2^{nd} order	1.97	G. Guclu

Name of the Sorbent	Name of the Sorbate	Initial metal concentration/ pH/ temperature	Maximum adsorption capacity	Isotherm / kinetics	Reference	Author
	Nile Blue (NB) Brilliant Green (BG)		13 mg/g			
Carbon from scrap tires	Rhodamine B	20-150 mg/L, 12 h, 45 ^{0}C	307.2 mg/g	Langmuir/ Pseudo 2nd order	1.98	Shuangxi Liu
Carbon from brewer's spent grain lignin	Phenolic compounds Color				1.99	Solange I. Mussatto
Grape fruit peel	Crystal violet	10-600 mg/L,	254 mg/g	Langmuir/ Pseudo 2nd order	1.57	Asma Saeed
Silk Almond waste			85.4 mg/g		1.100	F. Atmani
AC from male flowers of coconut tree			60.42 mg/g		1.101	S. Senthilkumaar
AC from rice husk			64.87 mg/g		1.102	K. Mohantay
Activated sludge			113		1.103	H.C. Chu
Pyrolysed petrified cement	Methylene blue			Langmuir, Freundlich/ Pseodu 1st order	1.104	Ayse Z. Aroguz
Clay						
Untreated clay	Acid red 88	pH 2.0, 15 min	1133.1mg/g	Langmuir/ Pseudo 2nd order	1.105	Sibel Tunali Akar
Humic acid-immobilized amine modified polyacrylamide/bentonite composite	Malachite Green (MG) Methylene Blue (MB) Crystal Violet (CV)	pH 6.0-8.0, 4h, 0.1g	656.5 μmol/g, 648.4 μmol/g, 510.4 μmol/g	Freundlich/ Pseudo 1st order	1.106	T.S. Anirudhan

Name of the Sorbent	Name of the Sorbate	Initial metal concentration/ pH/ temperature	Maximum adsorption capacity	Isotherm / kinetics	Reference	Author
Raw sepiolite Modified sepiolite	Crystal violet (CV)	pH 6.5	77mg/g 319mg/g	Langmuir/ Pseudo 2nd order	1.107	E. Eren
Regenerated bleaching earth	Basic violet 4, Basic violet 3, Basic red 9	5-20 ppm, pH 7.0, 400 rpm, 25^{0}C, 120 min, 0.25 g/L	50.76 mg/g, 69.93 mg/g, 344.83 mg/g	Langmuir, Freundlich/ Pseudo 2nd order	1.108	W.T. Tsai
Clinoptilolite	Amido Black 10B Safranine T	80 mg/L, pH 7.0, 2^{0}C	0.0112 mg/g, 0.05513 mg/g	Langmuir	1.109	Muqing Qiua
poly(epicholorohydrin dimethylamine) modified bentonite	Direct Fast Scarlet, Eosin Y, Reactive Violet K-3R	25±2 °C, pH 5	148.6 mg/g, 88.4 mg/g, 106.7 mg/g	Langmuir/ Pseudo 2nd order	1.110	Dazhong Shen
Bentonites	2,4-D Acetochlor	4 g/L, 100-1200 μmol/L, 25^{0}C, 4h	-	Freundlich	1.111	Jianfa Li
HDTMA bentonite	Acid Orange 10	50 ppm, 25^{0}C, 24h	-	Pseudo 2nd order	1.112	N. Jovic-Jovicic
Sepiolite	Diquat, Paraquat, Methyl green	5 g/kg, 0.01M, pH 6.7-7.4,	-	-	1.113	Giora Rytwo
Organo-clays	Fluridone	0.003 M, pH 2.74	100%	-	1.114	Dana Yaron-Marcovich
Calcined hydrotalcite, HT500, a Mg–Al mixed oxide	2,4-D, Clopyralid, Picloram	pH 3, 6, 11, 0.03 g/20 mL, 0.02 g/30 mL 0.03 g/20 mL	813 μmol/g 2564 μmol/g 1176 μmol/g	Langmuir	1.115	Pavlovica
Coal						
Activated carbon (T3K618): 1000m^2/g	Malachite green	100, 150, 200 mg/L; 25, 40, 50 ^{0}C	149, 200 mg/g	Langmuir/ Pseudo 2nd order	1.116	Y. Onal
Modified ultrafine coal	Methyl Orange	303^{0}C	18.52 mg/g	Langmuir,	1.117	Liu

Name of the Sorbent	Name of the Sorbate	Initial metal concentration/ pH/ temperature	Maximum adsorption capacity	Isotherm / kinetics	Reference	Author
powder				Freundlich/ Pseudo 1st order, Pseudo 2nd order		Zhuannian
Composite						
Chitosan–zinc oxide nanoparticle	Direct Blue 78 (DB78) Acid Black 26 (AB26)	25, 50, 75 and 100 mg/L; 0.5 g/L; pH2	34.48 mg/g, 52.63 mg/g	Temkin Langmuir/ Pseudo 2nd order	1.118	Mokhtar Arami
N,O-carboxymethyl-chitosan/montmorillonite nanocomposite	Congo red	200 mg/L, pH 7.5, 0.05 g, 30^{0}C, 480 min	74.24 mg/g	Langmuir/ Pseudo 2nd order	1.119	Aiqin Wang
Fly ash						
Alkaline treatment of biomass fly ash	Reactive Black 5	50–700 mg/L	107.53 mg/g	Langmuir/ Pseudo 2nd order	1.120	P. Pengthamkeerati
Fuel oil fly ash	Chlorophenol, Chloroaniline Methylene blue	140g/L; 1000 ppm; 24 h; 25^{0}C; 200 rpm	70 mg/g, 36 mg/g 47 mg/g,	Langmuir	1.121	Luciano Santoro
Fly ash	Reactive Red 23 Reactive Blue 171 Acid Black 1 Acid Blue193	60 min, 293 K, pH 7.5-8.5, pH 5-6,	2.102 mg/g, 1.860 mg/g, 10.331 mg/g, 10.937 mg/g,	Langmuir/ Pseudo 2nd order Langmuir/ Pseudo 2nd order Freundlich/ Pseudo 2nd order Freundlich/ Pseudo 2nd order	1.122	Deshuai Sun
Powdered activated carbon (PAC) Afsin-Elbistan fly ash (Turkey)	Reactive Black 5	5–100 mg/L; 200 rpm; 60min; RT (20^{0}C)	58.823 mg/g, 7.936 mg/g	Langmuir, Freundlich/ Pseudo2nd order	1.123	Filiz Nuran Acar

Name of the Sorbent	Name of the Sorbate	Initial metal concentration/ pH/ temperature	Maximum adsorption capacity	Isotherm / kinetics	Reference	Author
Deoiled mustard Charcoal	Indigocarmine	30^0C 40^0C	1.66 mol/g 0.560 mol/g	Langmuir, Freundlich	1.124	Vinod K. Gupta
LDH's						
Poorly crystalline Hydroxyapatite	Disperse Blue SBL	pH 4-10; 0.05-1.0 g/L; 50^0C	434.78 mg/g	Langmuir/ Exothermic	1.125	Barka Noureddine
Natural Mineral						
Organovermiculitebased adsorbent	Congo red	298 K; CEC-50%, 100%, 200%;	74.07 mg/g, 175.44 mg/g, 192.31 mg/g	Langmuir/ Pseudo 2nd order	1.126	Chaohai Wei
Algerian dolomite powders	Azo dye	20-200 mg/L; pH 5; 3.0 g/L; 25^0C, 4.8mg/L	29.5 mg/g	-	1.127	Fatima Boucif
Peat	Methylene blue	35-60^0C, 4.5 h	190-240 mg/g	Langmuir/ Endothermic/ Spontaneous	1.128	Andreia Neves Fernandes
Bentonite Sepiolite	Methylene Blue	600 ppm; 48 h; 25^0C	48.309 mg/g 59.53 mg/g	Langmuir	1.129	Ceyda Bilgic
Industrial byproducts						
Deoiled mustard Charcoal	Indigocarmine	30^0C; pH8.8; 40^0C; pH 2.3	1.66 mol/g 0.560 mol/g	Langmuir, Freundlich	1.124	Vinod K. Gupta
Abu-Tartour phosphate rock	Methylene blue	pH 5; 250 rpm; 30^0C	101.13 mg/g	Langmuir/ Elovich	1.130	Mohammad I. El-Khaiary
Activated carbons from tyre rubber waste	Acid blue-25 Acid yellow 117	-	0.45–0.71, 0.62–0.84, 0.23–0.42, (untreated) 0.29–0.40 mmol/g (acid-treated	Redlich-Peterson	1.131	Gordon McKay

Name of the Sorbent	Name of the Sorbate	Initial metal concentration/ pH/ temperature	Maximum adsorption capacity	Isotherm / kinetics	Reference	Author
Modified basic oxygen furnace slag (BOF slag)	Reactive Blue 19 Reactive Black 5 Reactive Red 120	pH 2; 500mg/L	60 mg/g 76 mg/g 55 mg/g	Langmuir, Redlich Peterson/ Pseudo 1st order	1.132	Yongjie Xue
Powdered waste sludge	Remazol red RR Chrisofonia direct yellow 12 Sumifix Blue Turquoise blue G	4 g/L; 6h	87 mg/g 77 mg/g 22 mg/g 78 mg/g	Langmuir/ Second order	1.133	Fikret Kargi
Shale oil ash	Drim yellow-K4G Drim blue-KBL Drim red K4BL	400 rpm; 25^{0}C; 50-380 ppm	-	Langmuir	1.134	Z. Al-Qodah
De-Oiled Soya Bottom Ash	Methyl orange	pH 3.0; 0.05g; 36 mesh 0.1g; 100 mesh	13.46×10^{-4} 13.35×10^{-4}	Langmuir, Freundlich/ Intraparticle diffusion	1.135	Alok Mittal
Pulp fibers	Toluidine blue	-	-	Diffusion	1.136	Theo G.M. van de Ven
Activated carbon agro waste						
Carbon- from Brazilian-pine fruit shell	Reactive orange 16	20.0mL soln. (20.00e1500.0 M), for 0.25-8 h , 298-323 k, 2.0-10.0 pH and adsorbent 20-200 mg	34 mgg^{-1}, 456 mgg^{-1}	Sips/ Fractionary-order	1.137	Eder C. Lima
Activated carbon-epicarp of Ricinus communis	Malachite green	Initial conc. (25 – 200 mg L^{-1}, at (27±2 ^{0}C). pH (2-10), 0.2-1.0 g /50 ml of adsorbent	99.04% removal At pH=7.0 and 50 min	Langmuir, Freundlich, Dubinin–Radushkevich (D–R) and Tempkin/ Pseudo 2nd order	1.138	T. Santhi
Carbon- Arundo donax root	Malachite green	100 ml soln. Conc. (10–100 mg/L), pH (3–10),	8.69 mg/g	Langmuir/ pseudo 2nd order	1.139	Jian Zhang

Name of the Sorbent	Name of the Sorbate	Initial metal concentration/ pH/ temperature	Maximum adsorption capacity	Isotherm / kinetics	Reference	Author
		carbon dose (0.15–1.0 g/100 mL), at 293, 303, 313 K for 180 mnt				
Activated carbon- Euphorbia rigida (H_2SO_4 activation)	Methylene blue	50 mL of a 200 mgL^{-1} Soln., 0.1 g of AC, pH 3-10, at (20, 30 40^{0}C),	114.45 mg g^{-1} at 40 °C.	Langmuir isotherm/ pseudo 2nd order	1.140	Ozgul Gercel
Apricot stone activated carbon	Basic dye	Dye conc. (50–300mg/L), pH (4–10), AC(2–8 g/L) 25–50^{0}C temp	221.23 mg/g at 50 °C	Langmuir, Freundlich	1.141	E. Demirbas
Activated carbon- date stones	2,4-D pesticide	Inial conc. (50-400 mgl^{-1}), pH 2-11, 0.2 g of AC, 130 rpm, 30^{0}C, 9 hrs 30 min	238.10 mg/g	Langmuir/ pseudo1st order	1.142	B.H. Hameed
Activated Carbon from Jatropha Husk	Anions, Heavy Metals, Organics and Dyes	50 mL of 10 mgL^{-1} soln., with 50–1000 mg loading, pH 2-11, 150 rpm, at 30^{0}C. 3h	Listed in table		1.143	C. Namasivayam
Activated carbon	Fluroxypyr	288-308 K, 0.05 g /500mL of herbicide solutionsat of (5 to 90 mg/L conc.)		Freundlich	1.144	Moreno-Castilla
Granular activated carbon (GAC)	Lindane	At 25 ^{0}C, 10 mg/L conc. of soln., at 400 rpm		Dubinin–Radushkevich	1.145	J.L. Sotelo
activated carbon	Avermectins	303.15 K, 100 mL of solution of conc. (2, 4, 6 g/l) with 500 mg of carbon.		Pseudo 2nd order Langmuir	1.146	GU Wei
Activated carbon-cloth	Bentazon Propanil	25^{0}C for 48h, 18mg, 4.5X10^{-5}M,		Freundlich	1.147	Erol Ayranci

Name of the Sorbent	Name of the Sorbate	Initial metal concentration/ pH/ temperature	Maximum adsorption capacity	Isotherm / kinetics	Reference	Author
Clinoptilolite	Dyes	4 mg/L of initial dye conc., 80 mg/L of solid conc., pH 7.0 and 2 ^{0}C for 360 min	0.05513 mg/g and 0.0112 mg/g for Safranine T and Amido Black 10B respectively	Langmuir	1.148	Muqing Qiua
Activated carbon	Anionic dyes Cationic dyes	Temp (30–65 ^{0}C), initial conc. of dye (300–500 ppm) and pH (3.0–9.0)	708.8 mg/g MB dye at pH 7 and 65 °C and 568.5 mg/g MB dye at pH 3 and 65 °C	Langmuir/ Pseudo 2nd order	1.149	Araceli Rodríguez,
Activated carbon	Pesticide waste	20μg/L,	334 mg/g		1.150	B.H. Hameed
Agro Waste						
EDTAD-modified sugarcane bagasse-adsorbent	Methylene Blue	50 mg L^{-1}, at 25^{0}C, at pH from (2-8).	85% efficiency for subsequent	Langmuir/ Pseudo 2nd order	1.151	Yun Xing
Granular activated carbon (GAC) from black stone cherries	Methylene blue and phenol	0.100 g of GAC mixed with MB (1000 ppm) in 250 flasks stirred at 150rpm for 72 h.	321.75 mg of Methyleneblue /g GAC and 133.33 mg of phenol/g GAC	Langmuir	1.152	René Reyes Mazzoco
Modified sugarcane bagasse- low-cost biosorbent	Dye	100 ml of dye soln., (50–250 mg/L), at pH (2-12), 400 mg of adsorbents; at (26±1 ^{0}C), at 160 rpm for	0.940 for SBC	Langmuir, Freundlich/ Pseudo 2nd order	1.153	S.A. Saad

Name of the Sorbent	Name of the Sorbate	Initial metal concentration/ pH/ temperature	Maximum adsorption capacity	Isotherm / kinetics	Reference	Author
		180 min				
Novel biosorbent (Canola hull)	Cationic dye	initial dye conc. 50 mg/L, Canola hull: 0.4 g/L for BB41, 2 g/L for BR46 and 1 g/L for BV16, pH 8, T 20^{0}C, and agitating speed of 200 rpm).	67.6 mg/g is achieved for BB41	Pseudo 2nd order	1.154	Mokhtar Arami
Coconut husks	Cyanosine	Dye concentration 4x10^{-5} M; temperature 30^{0}C; amount of AC 0.26 g/L	At pH 3.6	Pseudo 1st order	1.155	Vinod K. Gupta
Luffa cylindrica	Model basic dye	0.05 g of adsorbent in 20mL of Soln. of conc. (20–100mgL−1) for 5 h at 200rpm	29.4 mg/g at 308 K	Langmuir/ Pseudo 2nd order	1.156	Yoldas, Seki
Impregnated activated carbons- Typha orientalis	Neutral Red	200 mg/L dye conc. with 0.100 g/100 mL carbon and 22^{0}C for 4.5 h	monolayer capacities were as 217.39 mg/g and 285.71 mg/g at 298 K and 318 K, respectively.	Langmuir/ Pseudo 2nd order	1.157	Jian Zhang
Peanut husk	Neutral Red	10 mL of soln.,60 mg/L conc., 0.02 g adsorbent, at pH 2-7, for 4 h, 95 rpm,	37.5 mg/g at 295 K.	Toth, Langmuir/ Pseudo 1st order, Pseudo 2nd order	1.158	HAN Runping1,2
Luffa cylindrica fibers	Dye	50mL of soln.		Langmuir	1.159	Fu-Shen Zhang

Name of the Sorbent	Name of the Sorbate	Initial metal concentration/ pH/ temperature	Maximum adsorption capacity	Isotherm / kinetics	Reference	Author
Agricultural waste: dried Seagrape (Caulerpa lentillifera)	Basic dyes	Initial conc. (100–1,800 mg/L)adsorbent dose 0.5 g; initial pH 7.0; 130 r/min; temperature 25^{0}C.	113.64 mg/g	Langmuir, Freundlich	1.160	Prasert Pavasant
Low-cost adsorbents	Methylene blue			Langmuir	1.161	Mohd. Rafatullaha,
Activated carbon-Hevea brasiliensis	Basic dye	250 mL soln., initial concentration (50–500 mg/L) at 30 ^{0}C, 125 rpm, for 8 h, 0.1 g of carbon loading	227.27 mg/g at 30 ^{0}C	Freundlich/ Pseudo 2nd order	1.162	B.H. Hameed,
Phoenix tree leaf powder	Methylene blue	2.0 g, 293 K, 30 mgl^{-1} and 50 mgl^{-1}, pH 4-10	149 mg/g	Freundlich	1.163	Runping Hana,
Wheat shells	Direct blue 71	50–250 mg L^{-1}, at 293, 303 and 313 K, 0.5g, 50 mL soln., 150 rpm	46.30 mg g^{-1} at 313 K	Langmuir/ Pseudo 2nd order	1.164	Yasemin Bulut
Carica papaya seeds	Methylene blue dye	Inial conc. (10–400mg L^{-1}),pH 7.04-7.5, 0.5 g of DPS adsorbent, 180 rpm, 298K, 2 h	1250 mgg^{-1}	Langmuir, Freudlich/ Pseudo 2nd order	1.165	Emmanuel I. Unuabonah
Natural bio- polymers	Surfactant, organic acids and dyes	0.1 g of adsorbent, 100 mL of soln., 130 rpm, 30 ^{0}C, The initial concentrations of LAS, tannic acid, humic acid, RR222, AO51, and MB were in the range	1546 g/kg for Tannic acid	Langmuir, Freudlich/ Pseudo 1st order	1.166	Ruey-Shin Juang

Name of the Sorbent	Name of the Sorbate	Initial metal concentration/ pH/ temperature	Maximum adsorption capacity	Isotherm / kinetics	Reference	Author
		100–1000, 100–1000, 20–200, 150–1500, 60–600, and 50–500 g/m3, respectively.				
$ZnCl_2$ activated coir pith carbon	Anions, heavy metals, organics and dyes	20–400 mg of AC, with 50 ml of soln. of 20 mg/L conc., at pH 2.0 - 11.0, 200 rpm, 35^0C			1.167	C. Namasivayam,
Biomass						
Laccase	Remazol Brilliant Blue R	133 mg/L, initial conc.	44% was obtained in 42 h	-	1.168	Johann F. Osma
A. filiculoides	Basic Orange	100 mg/L, dose of adsorbent 5 g/L, pH 7.0, temp 303K,	833 mg/g at 303 K.	Langmuir	1.169	Zu-liang Chen
Biosorbents	Dye	-	-	-	1.170	T.Viraraghavan
Staphylococcus Epidermidis	Triphenylmethane dyes	pH = 7.5 and at 25^0C, Conc. 750 ppm.	-	-	1.171	Lamia Ayed
Fungal biomass	Acid dyes	Initial conc. (50 – 500) mg/L, 0.03 and 0.10 g loading of adsorbent, at 35^0C, and 110 rpm	Max. adsorotion capacity is between 300 and 600mgdye/gDM.	Langmuir, Freundlich/ Pseudo 1st order, Pseudo 2nd order	1.172	A. Marzocchella
Chemically treated Citrus	Reactive azo dyes	0.50 g of biosorbent to (50 mg/L) conc. and 60		Freundlich/ Pseudo 2nd order	1.173	A. Mahwish

Name of the Sorbent	**Name of the Sorbate**	**Initial metal concentration/ pH/ temperature**	**Maximum adsorption capacity**	**Isotherm / kinetics**	**Reference**	**Author**
sinensis waste biomass		min, pH (1–6)				
Coal						
Activated carbon	Malachite green	initial concentration (100, 150 and 200 mg/L) and temperature (25, 40 and 50^{0}C) 40 min time.0.1 g of AC with 50 mL of dye soln at 400 rpm.	200 mg/g	Langmiur isotherm/ Pseudo second-order kinetics	1.174	Y. Onal
Ultrafine Coal Powder	Methyl Orange	50 ml of MO soln with known initial conc. (100 mg/L) at 303, 313, and 323 K for 3 h with 0.5 g of coal powder.		first-order and pseudo second-order kinetic	1.175	LIU Zhuannian

In recent years, advanced oxidation processes (AOPs) have also been intensively investigated as a technique for treatment of pesticide containing environmental samples. AOPs are potentially useful for treating pesticide wastes because a powerful oxidant, hydroxyl radical ($OH^{\cdot}$), is generated in the processes. The $OH^{\cdot}$ could be produced by reacting hydrogen peroxide, H_2O_2, with either Fe (II) (i.e., Fenton's process, FP), [1.176, 1.177] Fe (III), [1.178] or iron oxide. The AOPs were practically applied in some textile and dye industries on dye removal. [1.179]. Radiation process is one of the most powerful AOPs, where irradiation with a beam of accelerated electrons or gamma radiation is employed for decomposition of various pollutants. Numerous publications are devoted to the degradation of organic compounds by ionizing radiation [1.180], but only few of them investigated the degradation by-products during the radiation process. Because of the possibility of transient formation of more toxic pollutants during irradiation, the detection of degradation by-products are important in assessment of the effectiveness of applied treatment processes. The radiolytic degradation of pollutants has been employed in recent years for treatment of natural waters and wastes of different origins and it was also used for drinking water treatment [1.181]. For degradation of several pesticides, gamma-irradiation has been evaluated by several investigators. Ionizing radiation has been used for degradation of different triazine herbicides [atrazine[1.182-1.187], ametryn and simazine [1.188], chlorinated pesticides [aldrin and chlorothalonil [1.189], DDT and lindane [1.190] and kelthane acaricide [1.191], organophosphorus pesticide diazinon [1.192,1.185] carbamate insecticide lannate and pyrethroid insecticide fenvalerate ([1.193], and also 2,4-dichlorophenoxyacetic acid (2,4

D) [1.194-1.198]. Accordingly, limited data is available on the radiolytic degradation of organophosphate and organochlorine pollutants in aqueous solutions.

In addition to the need for removal of pesticides there is an increasing demand for developing methods for the determination of pesticides in food and environment due to their toxicity. There is therefore, a need for highly sensitive analytical methods effective for monitoring pesticides especially in water employed for human consumption to keep these levels in check. For analysis of pesticides in food and environmental water samples, sample preparation is required in order to isolate the analytes from the complex matrices, remove interfering compounds and achieve a sufficient sensitivity.

Because of the wide applicability and high toxicity of monocrotophos, numerous instrumental methods have been described for the detection/determination of monocrotophos, such as, infrared spectrophotometry [1.199], mass spectrometry [1.200], liquid chromatography, reversed-phase column liquid chromatography[1.201], high performance liquid chromatography[1.202,1.203], gas chromatography[204,205],vivo test system[1.206],etc. A few spectrophotometric methods using sulphanilamide or sulphanilic acid [1.207] iron (III) complex & aromatic amine [1.208] and Sodium iodide-bromide have also been reported. Different chromatographic methods for the determination of chlorpyrifos residues and its main metabolites in food and environmental samples have also been developed [1.209-1.211]. These methods are either expensive, complicated and time consuming or some clean-up and pre-concentration steps are required before analysis, to have sufficient sensitivity.

Thermally stimulated luminescence (thermo-luminescence) is known to be a very sensitive technique and has been used to identify trace compounds. Thermo-luminescence is the emission of light from a substance when it is heated. It is the thermally stimulated emission of light following the previous absorption of energy from radiation. Thermo-luminescence is a common tool to study the structure of solids, and it has been utilized following irradiation of samples at room temperature and below room temperature for the purpose of dosimetry, age determination, geology or solid-state defect structure analysis [1.212]. More recently, it has been investigated as future dating technique for icy bodies in the solar system [1.213]. Low-temperature thermo-luminescence was also utilized to study properties of liquids through turning them into stable solids with the use of very low temperatures [1.214]. Utilizing thermo-luminescence, an anomalous effect was observed with ultra-high dilutions of lithium chloride (10-30 g/cm3), prepared in successive steps alternating vigorous mechanical stirring and 1:100 dilution with deuterium oxide. Although theoretically, such dilutions consist of pure deuterium oxide (D_2O), thermo-luminescence was reported to differ from that of pure D_2O without previously dissolved and diluted lithium chloride [1.215]. Such data resulted in discussions about the memory capacity of ultra-high dilution regarding original salts dissolved initially [1.216]. Low-temperature thermo-luminescence has been used in attempt to understand the particular structure of ultra high dilutions. Experimental results showed that, in the course of re-warming, the thermo-luminescent glow is substantially different between dilutions of different substances. It is suggested that the dispersed gas phase might play a role in this process [1.217]. However there are no reports where thermo-luminescence has been used for the study of ultra high dilutions of pesticides.

1.5. Aim and Objectives

Thus taking into account the high costs involved in the preparation and regeneration process, the feasibility of alternate adsorbents has been studied recently by scientists. These include industrial as well as agricultural byproducts. Some of the industrial waste products are slurry from fertilizer plants and slag from blast furnaces. A variety of agricultural waste biomass has been used for adsorption processes, namely rice straw, coconut husk, rice husk, bagasse, and tree bark. The use of novel alternative sorbent materials continues to attract attention because of economic considerations, availability, and adsorption efficiency. In a country like India where agriculture is the primary occupation, agricultural waste biomass such as corncobs, coconut shells, mango seeds, etc are abundantly available and the use of pesticides is wide spread. Therefore, it would be worthwhile to develop a cost effective low-cost adsorbent from the waste biomass palm shells available in plenty in Asian countries including coastal India, which would in turn assist in environmental decontamination processes for the removal of dyes and pesticides. Also there is a need for the determinations of low concentration of pesticides which are prove to enter the human food chain from environmental water samples.

The present investigation is planned to explore a number of possibilities.

- ➢ *Production of agro based adsorbents based on palm shell:*

Adsorbent will be produced using palm shell as a starting material. The palm shell will be modified by carbonizing with acid

- ➢ *Adsorbent Characterization:*

The new adsorbents will be characterized using various techniques, for example, BET surface area, pore size distribution, pore volume, surface functionality and surface group density using SEM, FTIR and XRD.

- *Adsorption performance will be tested using the following adsorbates:*
  - Dyes- Cationic Dyes (Methylene Blue and Rhodamine 6G), Anionic Dyes (Acid Orange II, Acid Violet 7 and Disulphine Blue) and Reactive Dyes (Reactive Blue 21 and Reactive Red 141)
  - Pesticides-Organochlorine (Chloropyrifos) and Organophosphorous (Monocrotophos)
- *Study of the thermodynamics and kinetics involved in the uptake of pesticides and dyes under study:*
  - To collect quantitative data for the sorption reaction as a function of the most important parameters (pH, ionic strength, metal ion concentration)
  - To identify sorbed species involved, and to understand sorption mechanism
  - To develop appropriate thermodynamic models for the sorption reactions based on the experimentally obtained Adsorption data will be characterized using the Freundlich adsorption and noncompetitive Langmuir adsorption model in terms of maximum binding capacities (q_{max}).
  - Kinetic models will be used to model experimental batch adsorption rate studies for the design of adsorption system
- *Study the possibility of degradation of pesticide using low dose irradiation*
- *Develop sensitive method for the detection of low concentrations of pesticides using thermoluminescence.*

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