CHAPTER 5

REMOVAL OF DRUGS FROM AQUEOUS SOLUTION USING CARBON BASED MATERIALS

Drugs have been shown to pass intact through conventional STPs, into water ways, lakes and aquifers and discharged pharmaceuticals may end up at landfill sites posing a threat to underlying ground water (Jones *et al.* 2003). Presently, all STPs are not designed to completely remove most pharmaceuticals and these compounds are consequently released into surface water (Zuccato *et al.* 2008; Carballa *et al.* 2004; Stackelberg *et al.* 2007), making it important to develop new methods to treat water containing such pollutants.

Whether or not trace pollutants can be eliminated in a WWTP essentially depends on the biological treatment stage. In Europe, biological wastewater treatment has been adapted step – by – step during the past 40 years in response to the tightening of discharge quality regulations.

Sorption: One of the most important elimination processes in WWTPs is sorption to suspended solids in the wastewater and subsequent removal by sedimentation as primary and secondary sludge. Sorption mainly occurs by absorption, involving hydrophobic interactions of the aliphatic and aromatic groups of a compound with the lipophilic cell membrane of the microorganisms and the fat fractions of the sludge, and by adsorption, where electrostatic interactions of positively charged groups (e.g., amino groups) with the negatively charged surfaces of the microorganisms are of importance. The quantity of a substance sorbed per liter of wastewater (C_{sorbed}) is expressed as a simplified linear equation:

$$C_{sorbed} = K_d \cdot SS \cdot C_{dissolved} \qquad (1)$$

where K_d is the sorption constant, defined as the partition of a compound between the sludge and the water phase; SS is the concentration of suspended solids in the raw wastewater; and $C_{dissolved}$ is the dissolved concentration of the substance. An example is the antibiotic ciprofloxacin, which was administered in the United States after anthrax attacks as a reserve antibiotic and is excreted as a metabolite of enrofloxacin.

Despite being an extremely polar compound, ciprofloxacin sorbs onto the suspended solids of the sewage sludge to a high degree (Golet *et al.* 2003). At

neutral pH, the sorption is likely to be based mainly on electrostatic interactions between the positively charged amino group and the negatively charged surfaces of the microorganisms. Microorganisms in the secondary sludge make up the greatest proportion of the suspended solids; therefore, a relatively high sorption constant of K_d 20 liters per gram of suspended solids (Lg_{SS}^{-1}) and a relatively high sorbed fraction was observed. However, primary sludge contains few microorganisms and has a large fat fraction, so the K_d of ciprofloxacin in the primary sludge is only - 2 L/g_{SS}. This means that ~20% of the ciprofloxacin is sorbed onto the primary sludge, whereas more than double this load partitions onto the secondary sludge.

Thus, when municipal sludge is applied to the land, substantial loading of ciprofloxacin may take place. On the other hand, the contraceptive 17 – ethinylestradiol exhibited similar K_d values (0.28 and 0.35 L g_{SS}^{-1}) for both primary and secondary sludge, which means that the removal via sorption is <10% (Ternes *et al.* 2004b). Musk fragrances like tonalide (AHTN) have much higher sorption portions. Because they lack functional moieties (such as –OH, –COOH, or $–NH_2$), these compounds are not charged at neutral pH; hence, the sorption is probably caused by nonspecific sorption interactions. Many acidic pharmaceuticals, such as the anti – inflammatory ibuprofen and acetylsalicylic acid and the lipid regulators clofibric acid and bezafibrate, are negatively charged at neutral pH, because their carboxylic moieties are deprotonated. For all these polar pharmaceuticals, sorption onto sludge was found to be negligible. Because of the high polarity, significant sorption by nonspecific interactions can be ruled out for many pharmaceuticals. Until now, specific interactions of pharmaceuticals have only been reported for fluorochinolones and tetracyclines; the latter tend to precipitate with Mg^{2+}, Ca^{2+}, or Fe^{3+}.

Biological degradation. In wastewater, PPCPs occur primarily at concentrations of $<10^{-4}$g L^{-1} (Ternes 1998; Ternes 2000; Haberer 2002b). At these levels, biological transformation or degradation of the trace pollutants occurs only if a primary substrate is available for the corresponding bacteria to grow on. Hence, co-metabolism probably occurs, in which case the bacteria break down or partially converts the trace pollutant and do not use it as a carbon source. In another likely

scenario, mixed-substrate growth takes place and the bacteria use the trace pollutant as a carbon and energy source and may mineralize it totally. A trace pollutant's affinity for the bacterial enzymes in the activated sludge influences the pollutant's transformation or decomposition. Two possible mechanisms could explain this trend. The bacterial population may become more diversified with increasing sludge age (i.e., longer residence time of microorganisms), possibly because slow growing bacteria eventually reach relevant numbers.

Alternatively, the microorganisms may diversify their metabolic activity in response to the lower sludge loading with bulk organics (i.e., lower substrate availability); in this case, an increased PPCP removal might be due only to the broadened enzyme spectrum and not necessarily to the microbial community. The anti-inflammatory diclofenac and the contraceptive 17 – ethinylestradiol are good examples. For both compounds, significant decomposition was observed only when the aerobic sludge age was at least eight days (Kreuzinger 2004; Tilton 2002; Buser *et al.* 1998b).

The redox conditions also affect bacteria's degradation ability. Degradation can occur under aerobic (molecular oxygen available), denitrifying (no molecular oxygen available, nitrate available), or anaerobic (neither molecular oxygen nor nitrate available) conditions. For example, the natural estrogens 17 estradiol and estrone degrade in the aerobic and anoxic tanks of the activated sludge system, whereas the synthetic contraceptive 17 – ethinylestradiol decomposes only under aerobic conditions (Lai 2000; Holbrook 2002; Matsui 2000; Johnson and Sumpter 2001; Andersen *et al.* 2003).

Because of the low concentrations of trace organic pollutants, the decomposition occurs primarily as a first – order reaction:

$$r_{decomposition} = k_{decomposition} \cdot SS \cdot C_{dissolved} \quad (2)$$

where $k_{decomposition}$ is the rate constant and $C_{dissolved}$ is the dissolved concentration of the pollutant. Hence, a cascade of denitrifying and aerated tanks operating at conditions similar to those of a plug – flow reactor is advantageous because it

results in lower discharge concentrations than is the case with a single, fully mixed reactor.

With respect to pharmaceuticals, the metabolites excreted by humans should be accounted for when the mass flux of a compound during wastewater treatment is described. For instance, aspirin and its metabolites can occur in raw wastewater at the $\mu g\ L^{-1}$ level with a removal rate generally >80%. Many pharmaceuticals are conjugated with glucuronic acid or sulfate to enhance their polarity prior to excretion. The conjugates of the natural hormones estrone and estradiol, for example, are generally present in the same concentration range as the free compounds in the raw wastewater (Adler *et al.* 2001).

However, the conjugates can be cleaved in WWTPs, which releases active pharmaceuticals (Ternes *et al.* 1999b). The anti – inflammatory ibuprofen, for instance, is directly conjugated or first hydroxylated and then conjugated. Approximately 15% of ibuprofen is excreted unchanged or as its glucuronide; the remaining percentage is allocated to further metabolites, such as hydroxyl – ibuprofen, carboxy – ibuprofen, and their respective conjugates.

Hence, the fate of metabolites is of major relevance for the mass balance. In the case of an ecotoxicological risk, such as when the receiving water is used for irrigation in agriculture or the WWTP outflow undergoes low dilution in surface water, ozonation of the biologically purified wastewater should be considered. If 5 – 10g m^{-3} of ozone are used, concentrations of many pharmaceuticals are reduced below detection limits (Ternes *et al.* 2004a). The effectiveness of the ozone treatment depends on the chemical properties of the compound and the back ground level of dissolved organic carbon in the waste water (Huber *et al.* 2003). Although ozonation costs only a few cents per cubic meter of wastewater, the energy expenditure is 0.1– 0.2 kilowatt – hours per cubic meter, which is significant in comparison with the total energy consumption of a WWTP. In addition, although initial results indicate significantly reduced toxicity, oxidation products formed during ozonation should be further investigated prior to large – scale application (Huber *et al.* 2004).

Adsorption by activated charcoal is frequently the most efficient and economical method for removing pollutants from water, particularly when these are present in low concentrations, whether it is a batch process or continuous flow treatment method. Literature reports several studies on use of activated charcoal for removal of a variety of pollutants from water (Garcia – Araya *et al.* 2003; Safarik *et al.* 1997). Charcoal, the forerunner of modern activated charcoal has been recognized as the oldest adsorbent known in wastewater treatment. Its ability to purify water dates back to 2000 B.C. Lowitz established the first used of charcoal for the removal of bad tastes and odours from water on an experimental basis in 1789 – 1790.

The credit of developing commercial activated carbon however goes to Raphael von Ostrejko whose inventions were patented in 1900 and 1901. Early applications of carbon in water treatment plant to remove chlorophenolics were reported by Balyis in U.S. and Sierp in Germany in 1929 (Bhatnagar and Minocha 2006). Activated charcoal is also recommended for removing poisonings caused by drugs in human body (Mohd *et al.* 2006; Eddleston *et al.* 2008).

The removal efficiency of activated charcoal for organic compounds may be increased by presence of metal ions or complexes on the surface of activated charcoal. Concept was to use the activated charcoal which has previously been used for removal of metals in effluents. Since disposal of such carbon is a problem (Bhatnagar and Minocha 2006). So before disposing, whether we can use the metal loaded carbon once more for removing pharmaceuticals or organic compounds. Aspirin and paracetamol were considered as target drugs for the present study of removal efficiency of commercially available activated charcoal (granular) and effect of metal complexes on it. Effect of oxygen on the efficiency of activated charcoal loaded with metal complex to remove these compounds was also studied.

It was expected that in presence of metal complexes and oxygen the non – polar part of organic pollutants would be oxidized and become more polar, increasing its affinity for carbon. Hence its removal should be more complete from water. This is because several transition metal ions and metal complexes are known to act as catalyst for oxidation of organic compounds in presence of oxygen (Jana *et al.* 2007; Silva *et al.* 2004; Silva *et al.* 2002).

EXPERIMENTS

Chemicals and Reagents

Copper chloride dihydrate ($CuCl_2.2H_2O$), manganese (II) chloride tetra hydrate ($MnCl_2.4H_2O$), copper sulphate pentahydrate ($CuSO_4.5H_2O$), nickel sulphate heptahydrate ($NiSO_4.7H_2O$), cobalt chloride hexahydrate ($CoCl_2.6H_2O$), nickel chloride hexahydrate ($NiCl_2.6H_2O$), acetylacetone, salicylaldehyde, ethylenediammine, alcohol, liquor ammonia, methanol (CH_3OH), chloroform ($CHCl_3$), acetonitrile (CH_3CN) A.R. grade obtained from Qualigens whereas, activated charcoal (granular) were obtained from National Chemicals.

Instrumentation

A UV/VIS spectrometer (Perkins Elmer Lambert 35) equipped with 1cm quartz cells (4ml each) was used for all absorbance measurements.

Treatment of activated charcoal

100g of charcoal (granular) was washed with conductivity water to remove fine carbon particles. After this, it was dried at temperature 110°C in hot air oven for 3hr. This was then used for further studies in small portions.

Synthesis of metal complexes

Copper Bisacetylacetonate: Bis(acetylacetonate) copper was prepared using procedures adapted from those described in the literature (Lipatova and Nizelskii 1968), by mixing redistilled acetylacetone with an aqueous suspension of copper hydroxide, freshly precipitated with ammonia. The precipitate obtained was filtered, washed with water and finally with alcohol and air dried at room temperature. *Anal. Calcd. ($C_{10}H_{14}O_4Cu$): C, 45.88; H, 5.35.Found C, 45.84; H, 5.37.*

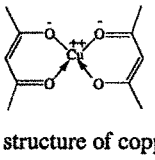

Figure 5.1. Chemical structure of copper bisacetylacetonate

Manganese Salen: The manganese (III) Schiff base complex was prepared using procedures adapted from those described in the literature (Silva *et al.* 2004), by refluxing equimolar quantities of an ethanolic solution of ligand and a methanolic solution of $MnCl_2.4H_2O$. *Anal. Calcd. ($C_{16}H_{14}N_2O_2MnCl$): C, 53.86; H, 3.92; N, 7.84. Found C, 53.2; H, 4.05; N, 7.81.*

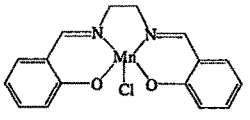

Figure 5.2. Chemical structure of manganese salen

Copper Salen: The copper Schiff base complex was prepared using procedure adapted from that described in the literature (Holm *et al.* 1966), by stirring equimolar quantities of an ethanolic solution of ligand and aqueous solution of $CuCl_2.2H_2O$. *Anal. Calcd. ($C_{16}H_{14}N_2O_2CuI$): C, 58.26; H, 4.24; N, 8.49. Found C, 58.28; H, 4.26; N, 8.50.*

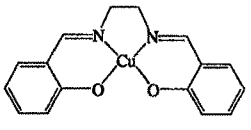

Figure 5.3. Chemical structure of copper salen

Preparation of stock drug solution

Drug Solution

Stock solutions and working standard solution of aspirin and paracetamol were prepared as mentioned in Chapter 2.

Metal Complex Solution

Stock solutions of 2000mg L^{-1} copper bisacetylacetonate and copper salen complex was prepared by dissolving 200mg respective metal complex in 100mL $CHCl_3$. Similarly Stock solution of 2000mg L^{-1} manganese salen complex was prepared in Acetonitrile. Working standard solutions were obtained by diluting standard solutions with respective solvents to obtain 100mL, 1000mg L^{-1} metal

complex solution. To obtain standard curve, solution of different concentration were prepared from stock solutions.

Metal Salt solution

0.2M Copper sulphate solution was prepared by dissolving 12.484g $CuSO_4.5H_2O$ in 250mL DDW. Similarly 0.2M Nickel sulphate, Cobalt chloride and Nickel Chloride solutions were prepared by dissolving 13.143g of $NiSO_4.7H_2O$, 11.896g of $CoCl_2.6H_2O$ and 11.884g of $NiCl_2.6H_2O$ in 250mL DDW respectively. Working standard solutions were obtained by diluting standard solutions with DDW to obtain 100mL, 0.1M metal salt solution. To obtain standard curve, solution of different concentration were prepared from stock solutions.

Loading of metal complexes (MAC)

The copper bisacetylacetonate complex was dissolved in $CHCl_3$ (500mg L^{-1}). 5g of Activated charcoal (AC) was put into the copper bisacetylacetonate $CHCl_3$ solution for 3 hours at room temperature with occasional stirring. The resulting material (MAC_1) was filtered off, washed, dried and stored in bottle.

Similarly manganese salen was laoded on activated charcoal by dissolving in ACN to get manganese salen laoded activated charcoal (MAC_2) and copper salen by dissolving in $CHCl_3$ to get copper salen laoded activated charcoal (MAC_3) respectively.

The amount of the metal complex remaining in the filtrate was determined by recording absorbance of the solution at the λ_{max} of the respective metal solution and computing the concentration from corresponding calibration curve of respective metal solution. The amount of metal complex adsorbed on charcoal was computed using absorbance value for solution before passing it through charcoal.

Leach out test for Metal Complex loaded Activated Charcoal

1.0g of activated charcoal loaded with a particular metal complex was treated with 10.0mL respective solvent with occasional shaking for 30 minute. It was then

filtered and absorbance was recorded in the filtrate using UV – Visible spectrophotometer at respective wavelength of metal complex solution.

Loading of metal ions (MC)

5.0g of activated charcoal was put into 50mL of 0.1M $CuSO_4$ solution for 3hr. at room temperature with occasional stirring. The resultant material (MC_1) was filtered off, washed, dried and stored in bottles.

Similarly $NiSO_4$ was loaded on activated charcoal to get $NiSO_4$ loaded activated charcoal (MC_2), $CoCl_2$ was loaded on activated charcoal to get $CoCl_2$ loaded activated charcoal (MC_3) and $NiCl_2$ was loaded on activated charcoal to get $NiCl_2$ loaded activated charcoal (MC_4)

The amount of the metal salt remaining in the filtrate was determined by recording absorbance of the solution at the λ_{max} of the respective metal solution and computing the concentration from corresponding calibration curve of respective metal solution. The amount of metal salt adsorbed on charcoal was computed using absorbance value for solution before passing it through charcoal.

Leach out test for Metal ion loaded Activated Charcoal

1.0g of activated charcoal loaded with a particular metal salt was treated with 10.0mL conductivity water with occasional shaking for 30 minute. It was then filtered and absorbance was recorded in the filtrate using UV – Visible spectrophotometer at respective wavelength of metal complex solution.

Drug Removal Procedures

The following two sets of experiments were applied to the three aqueous solutions of aspirin, paracetamol and mixture of aspirin and paracetamol.

Set 1: 10mL (50mg L^{-1}) aspirin solution was added into two different stoppered tubes containing AC and MAC respectively for 30 minutes with constant stirring. Then the

resultant solution was filtered and absorbance was measured through UV – Visible Spectrometer.

Set 2: 10mL (50mg L^{-1}) aspirin solution was added into two different stopper tubes containing AC and MAC respectively for 30 min with constant supply of oxygen. Then the resultant solution was filtered and absorbance was measured through UV – Visible Spectrometer.

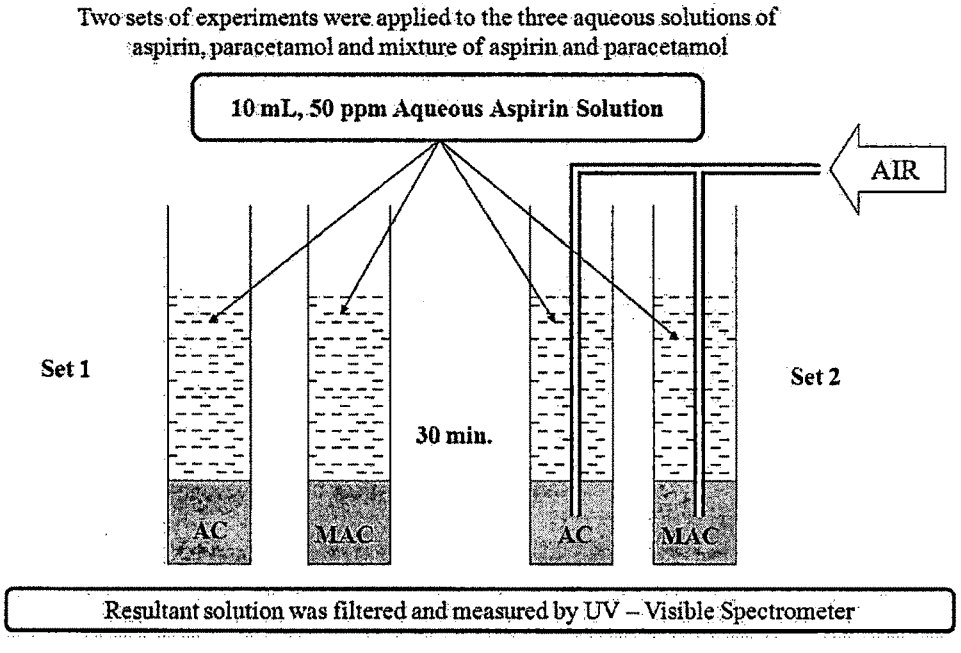

Figure 5.4. Experimental set up for drug removal procedure

The same above mentioned set of experiments were applied individually to all charcoal samples loaded with three metal complexes and metal solutions respectively. The experimental set up used is shown in figure 5.4.

RESULTS AND DISCUSSION

The removal efficiency of AC may be increased by presence of some metal complexes on the surface of AC. In this study the effect of air (oxygen) on three different metal complexes for removal of aspirin and paracetamol from water is reported. For the study two different drugs aspirin and paracetamol are considered. These are the most reported drugs as water pollutant.

The amount of metal complex and metal salts loaded on activated charcoal is given in Table5.1.

Table 5.1. Percentage loading of metal complexes and metal ions on activated charcoal

Adsorbent	Concentration of metal complex (mg L^{-1})					Percentage Loaded
	Before	After	Adsorbed	Leached out	Loaded	
MAC_1	1000	110	890	N.D.	890	89.0
MAC_2	1000	95	905	N.D.	905	90.5
MAC_3	1000	150	850	N.D.	850	85.0
Adsorbent	Concentration of metal ions (M)					Percentage Loaded
	Before	After	Adsorbed	Leached out	Loaded	
MC_1	0.1	0.094	0.006	N.D.	0.006	6.0
MC_2	0.1	0.096	0.004	N.D.	0.004	4.0
MC_3	0.1	0.089	0.011	N.D.	0.011	11.0
MC_4	0.1	0.087	0.013	N.D.	0.013	13.0

N.D. = Not detected. Percentage loaded = (Adsorbed concentration / Initial concentration) x 100.

The MACs were prepared and the drug solutions containing a known concentration of aspirin and paracetamol were treated. The amount of unabsorbed drug in filtrate was measured by UV – Visible spectrometer and the adsorption percent was calculated.

The amount of the individual drugs present in mixture was determined by solving the equations obtained adding Beer – Lambert's law (A = abc), for two components mixture as mentioned in chapter 2. Amount of aspirin and paracetamol in water was determined by the calibration curves given in Figure 2.4 and Figure 2.15 in chapter 2.

AC removes 14.29% aspirin and 47% paracetamol from water when the individual aqueous drug solutions were treated with it, and in presence of oxygen the percentage of removal increases for both drugs. Results shown in Table 5.2. Sr. No. 1 and 2.

Table 5.2. Percentage removal of drugs by activated charcoal

Sr. No.	Drug in aqueous solution		Percentage of drug removed from aqueous solution by AC	
			without O_2	with O_2
1.	Individual	Aspirin	14.29	20.93
2.		Pracetamol	47.00	94.00
3.	Mixture	Aspirin	18.72	58.23
4.		Pracetamol	30.84	97.89

When the mixture of aqueous drug solution was treated with AC, the percentage removal of individual drug increases compared with the individual treatment with AC except paracetamol whose adsorption decreases in absence of oxygen as shown in Table 5.2. Sr. No. 4.

MAC_1 removes 27% aspirin and 39.25% paracetamol from water when the individual aqueous drug solutions were treated with it, and in presence of oxygen the percentage of removal increases for both drugs. Results shown in Table 5.3. Sr. No. 1 and 2.

Table 5.3. Percentage removal of drugs by MAC_1

Sr. No.	Drug in aqueous solution		Percentage of drug removed from aqueous solution by MAC_1	
			without O_2	with O_2
1.	Individual	Aspirin	27.00	70.00
2.		Pracetamol	39.25	90.19
3.	Mixture	Aspirin	17.49	78.50
4.		Pracetamol	19.57	78.54

When the mixture of aqueous drug solution was treated with MAC_1, the percentage removal of individual drug increases in presence of oxygen compared with the treatment in absence of oxygen. The percentage removal of aspirin by MAC_1 with oxygen increases in present of paracetamol. Results shown in Table 5.3. Sr. No. 3 and 4.

MAC_2 removes 12.96% aspirin and 41.98% paracetamol from water when the individual aqueous drug solutions were treated with it, and in presence of oxygen the percentage of removal increases for both drugs. Results shown in Table 5.4. Sr. No. 1 and 2.

Table 5.4. Percentage removal of drugs by MAC_2

Sr. No.	Drug in aqueous solution		Percentage of drug removed from aqueous solution by MAC_2	
			without O_2	with O_2
1.	Individual	Aspirin	12.96	20.37
2.		Pracetamol	41.98	92.59
3.	Mixture	Aspirin	27.23	66.39
4.		Pracetamol	42.31	99.74

When the mixture of aqueous drug solution was treated with MAC_2 in presence of oxygen, the removal percentage of drugs form aqueous solution increases. Results shown in Table 5.4. Sr. No. 3 and 4.

Similar trends were observed with MAC_3. In presence of oxygen, drug removal efficiency of MAC_3 increases. Results shown in Table 5.5.

Table 5.5. Percentage removal of drugs by MAC_3

Sr. No.	Drug in aqueous solution		Percentage of drug removed from aqueous solution by MAC_3	
			without O_2	with O_2
1.	Individual	Aspirin	25.58	34.88
2.		Pracetamol	50.00	89.65
3.	Mixture	Aspirin	19.22	62.95
4.		Pracetamol	52.64	99.97

In case of individual drug solutions, MAC_1 removes maximum amount of aspirin from water when compared with other three adsorbents in absence of oxygen. In presence of oxygen the trend remains same but removal efficiency of MAC_1 for aspirin increases to 38% compared to that with absence of oxygen. Whereas MAC_3 separates maximum amount of paracetamol from water when compared with other three adsorbent in absence of oxygen. In presence of oxygen the removal efficiency of MAC_1, MAC_2 and MAC_3 increases with maximum. Comparison of results is shown in Table 5.6.

Table 5.6. Percentage removal of drugs individually by MAC_s

Sr. No.	Adsorbent	Aspirin		Paracetamol	
		without O_2	with O_2	without O_2	with O_2
1.	AC	14.29	20.93	47.00	94.00
2.	MAC1	27.00	70.00	39.25	90.19
3.	MAC2	12.96	20.37	41.98	92.59
4.	MAC3	25.58	34.88	50	89.65

In case of treatment of drugs in presence of each other, MAC_2 separates maximum amount of aspirin from water when compared with other three adsorbent in absence of oxygen, whereas in presence of oxygen MAC_1 separates maximum amount of aspirin. When paracetamol is considered, MAC_3 adsorbs maximum in absence of oxygen and almost 100% in presence of oxygen. Comparison of results is shown in Table 5.7.

Table 5.7. Percentage removal of drugs in presence of each other by MAC_s

Sr. No.	Adsorbent	Aspirin		Paracetamol	
		without O_2	with O_2	without O_2	with O_2
1.	AC	18.72	58.23	30.84	97.89
2.	MAC1	17.49	78.50	19.57	78.54
3.	MAC2	27.23	66.39	42.31	99.74
4.	MAC3	19.22	62.95	52.64	99.97

MC_1 removes 62.5% aspirin and 48.84% paracetamol from water when the individual aqueous drug solutions were treated with it, and in presence of oxygen the percentage of removal remains same for both drugs. Results shown in Table 5.8. Sr. No. 1 and 2.

Table 5.8. Percentage removal of drugs by MC_1

Sr. No.	Drug in aqueous solution		Percentage of drug removed from aqueous solution by MC_1	
			without O_2	with O_2
1.	Individual	Aspirin	62.5	62.5
2.		Pracetamol	48.84	48.84
3.	Mixture	Aspirin	54.51	54.47
4.		Pracetamol	55.27	55.48

When the mixture of aqueous drug solution was treated with MC_1, the percentage removal of aspirin drug decreases compared with its individual treatment with MC_1 and the percentage of removal of paracetamol increases compared with its individual treatment with MC_1 as shown in Table 5.8. Sr. No. 3 and 4. Presence of oxygen does not change the drug removal efficiency of MC_1 as shown in Table 5.8.

MC_2 removes 50% aspirin and 55.82% paracetamol from water when the individual aqueous drug solutions were treated with it, and in presence of oxygen the percentage of removal remains same for both drugs. Results shown in Table 5.9. Sr. No. 1 and 2.

Table 5.9. Percentage removal of drugs by MC_2

Sr. No.	Drug in aqueous solution		Percentage of drug removed from aqueous solution by MC2	
			without O_2	with O_2
1.	Individual	Aspirin	50.00	50.00
2.		Pracetamol	55.82	54.65
3.	Mixture	Aspirin	62.71	62.74
4.		Pracetamol	62.02	62.00

When the mixture of aqueous drug solution was treated with MC_2, the percentage removal of individual drug increases compared with the individual treatment with MC_2 and in presence of oxygen the percentage of removal remains same for both drugs. Results shown in Table 5.9.

MC_3 removes 60.42% aspirin and 48.84% paracetamol from water when the individual aqueous drug solutions were treated with it, and in presence of oxygen the percentage of removal remains same for both drugs. Results shown in Table 5.10. Sr. No. 1 and 2.

Table 5.10. Percentage removal of drugs by MC_3

Sr. No.	Drug in aqueous solution		Percentage of drug removed from aqueous solution by MC_3	
			without O_2	with O_2
1.	Individual	Aspirin	60.42	60.42
2.		Pracetamol	48.84	48.84
3.	Mixture	Aspirin	42.41	42.40
4.		Pracetamol	54.30	54.31

When the mixture of aqueous drug solution was treated with MC_3, the percentage removal of aspirin drug decreases compared with its individual treatment with MC_3 and the percentage of removal of paracetamol increases compared with its individual treatment with MC_3 as shown in Table 5.10. Sr. No. 3 and 4. Presence of oxygen does not change the drug removal efficiency of MC_3 as shown in Table 5.10.

MC_4 removes 87.5% aspirin and 58.14% paracetamol from water when the individual aqueous drug solutions were treated with it and in presence of oxygen the percentage of removal for aspirin decreases where as for paracetamol it increases. Results shown in Table 5.11. Sr. No. 1 and 2.

Table 5.11. Percentage removal of drugs by MC_4

Sr. No.	Drug in aqueous solution		Percentage of drug removed from aqueous solution by MC_4	
			without O_2	with O_2
1.	Individual	Aspirin	87.5	77.03
2.		Pracetamol	58.14	60.46
3.	Mixture	Aspirin	32.25	32.27
4.		Pracetamol	43.20	43.16

When the mixture of aqueous drug solution was treated with MC_4, the percentage removal of aspirin and paracetamol decreases compared with its individual

treatment with MC_3 as shown in Table 5.11. Sr. No. 3 and 4. Presence of oxygen does not change the drug removal efficiency of MC_4 as shown in Table 5.11.

In case of individual drug solutions, MC_4 separates maximum amount of aspirin from water when compared with other four adsorbents in absence of oxygen. In presence of oxygen the trend remains same but removal efficiency of MC_4 for Aspirin decreases to 77.03% compared to that with absence of oxygen i.e. 87.5%. Similarly MC_4 separates maximum amount of paracetamol from water when compared with other four adsorbent in absence of oxygen. Presence of oxygen does not affect the drug removal efficiency of all adsorbents except AC and MC_4. Comparison of results is shown in Table 5.12.

Table 5.12. Percentage removal of drugs individually by MC_s

Sr. No.	Adsorbent	Aspirin		Paracetamol	
		without O_2	with O_2	without O_2	with O_2
1.	AC	14.29	20.93	47	94
2.	MC_1	62.5	62.5	48.84	48.84
3.	MC_2	50.0	50.0	55.82	54.65
4.	MC_3	60.42	60.42	48.84	48.84
5.	MC_4	87.5	77.03	58.14	60.46

In case of treatment of drugs in presence of each other, MC_2 separates maximum amount of aspirin and paracetamol from water when compared with other four adsorbent in absence of oxygen. Presence of oxygen does not affect the drug removal efficiency of all four adsorbents except AC. Comparison of results is shown in Table 5.13.

Table 5.13. Percentage removal of drugs in presence of each other by MC_s

Sr. No.	Adsorbent	Aspirin		Paracetamol	
		without O_2	with O_2	without O_2	with O_2
1.	AC	18.72	58.23	30.84	97.89
2.	MC_1	54.51	54.47	55.27	55.48
3.	MC_2	62.71	62.74	62.02	62.0
4.	MC_3	42.41	42.40	54.30	54.31
5.	MC_4	32.25	32.27	43.20	43.16

The relation of percentage removal of drugs by activated charcoal loaded with copper complex and copper ion was also studied. The relation shows, the removal efficiency of activated charcoal loaded by copper complex increases in presence of

oxygen whereas no change is observed in case of activated charcoal loaded by copper ion in presence of oxygen. The relation between percentage removal of activated charcoal loaded with copper ion and copper complex is shown in Table 5.14.

Table 5.14. Percentage removal of drugs by copper complexes and copper ion

Adsorbent	Drug solution		Without O_2	With O_2
Activated Charcoal	Individual	Aspirin	14.29	20.93
		Paracetamol	47.00	94.00
	Mixture	Aspirin	18.72	58.23
		Paracetamol	30.84	97.89
89.0% Copper Biacetylacetonnate Loaded Activated Charcoal	Individual	Aspirin	27.00	70.00
		Paracetamol	39.25	90.19
	Mixture	Aspirin	17.49	78.50
		Paracetamol	19.57	78.54
85.0% Copper Salen Loaded Activated Charcoal	Individual	Aspirin	25.58	34.88
		Paracetamol	50.00	89.65
	Mixture	Aspirin	19.22	62.95
		Paracetamol	52.64	99.97
6.0% Copper Sulphate Loaded Activated Charcoal	Individual	Aspirin	62.50	60.42
		Paracetamol	48.84	48.84
	Mixture	Aspirin	54.51	55.27
		Paracetamol	54.47	55.48

Similarly percentage removal of drugs by activated charcoal loaded with nickel ion was studied. Removal efficiency of activated charcoal increases in presence of nickel but in presence of oxygen no improvement was observed. The relation between percentage removal of activated charcoal loaded with nickel ion is shown in Table 5.15.

Table 5.15. Percentage removal of drugs by nickel ions

Adsorbent	Drug solution		Without O_2	With O_2
Activated Charcoal	Individual	Aspirin	14.29	20.93
		Paracetamol	47.00	94.00
	Mixture	Aspirin	18.72	58.23
		Paracetamol	30.84	97.89
4.0% Nickel Sulphate Loaded Activated Charcoal	Individual	Aspirin	50.00	50.00
		Paracetamol	55.82	54.65
	Mixture	Aspirin	62.17	62.74
		Paracetamol	62.02	62.00
13.0% Nickel Chloride Loaded Activated Charcoal	Individual	Aspirin	87.50	77.03
		Paracetamol	58.14	60.46
	Mixture	Aspirin	32.25	32.27
		Paracetamol	43.20	43.16

The result also shows, in case of metal ions, nickel removes maximum amount of drugs from water although much difference is not seen in presence of oxygen. Whereas in case of metal complexes more than 98% of drugs are removed from water particularly paracetamol when treated in presence of oxygen. The percentage removal of drugs by metal loaded activated charcoal increase in presence of oxygen.

Surface studies (BET) were done to study the surface properties of activated charcoal and metal loaded activated charcoal. Surface studies shows that surface area of metal loaded activated charcoal decreases after removing drugs from water. This shows the adsorption of drugs on metal loaded activated charcoal.

Analytical performance characteristics

Linearity was established with a series of working standard solutions prepared by diluting the stock solution with respective solvents individually to the final concentrations for each metal complex. Calibration curves were obtained by measuring the UV absorbance of the standard solutions of Metal complex in a range of 200 – 1000mg L^{-1} and Metal salt solution in a range of 0.002 – 0.1M at their respective wavelengths. Absorbance of each concentration was measured in triplicate and the mean value of peak area was taken for the calibration curve.

Copper Bisacetylacetonate

Maximum absorbance was measured at 547nm for copper bisacetylacetonate in chloroform. Linearity experiment in the range of 200 – 1000mg L^{-1} was carried out. The absorbance values with respective concentrations are tabulated in Table 5.16.

Table 5.16. Linearity experiment for copper biacetylacetonate in chloroform: Concentration Vs absorbance

Observation No.	Concentration (mg L^{-1})	Absorbance
1.	200	0.1774
2.	400	0.3492
3.	600	0.5205
4.	800	0.7054
5.	1000	0.8693

The calibration data was subjected to regression analysis. The result of the regression analysis is given in Table 5.17. The plot of absorbance Vs concentration for copper biacetylacetonate in $CHCl_3$ was shown in Figure 5.5.

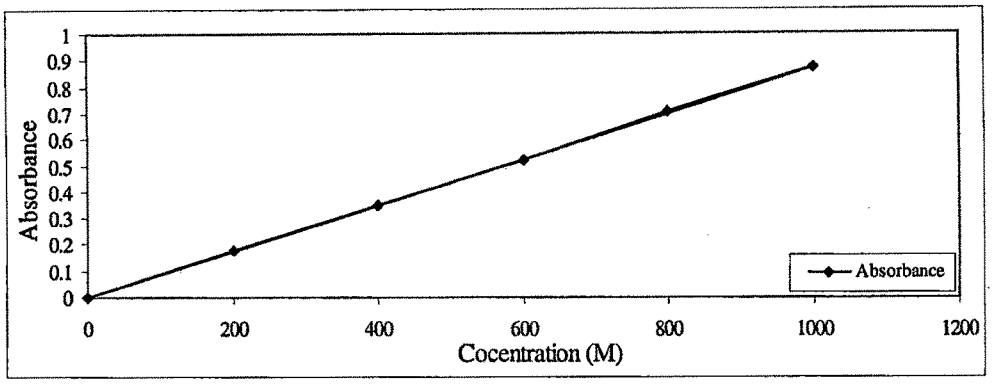

Figure 5.5. Linear working range of copper bisacetylacetonate in chloroform

Table 5.17. Results of regression analysis: Copper bisacetylacetonate in chloroform

Parameters	Copper Bisacetylacetonate in $CHCl_3$
Regression Equation (y)	
Correlation Coefficient (r^2)	0.9997
Slope, a	0.0009
Intercept,	0.0022
No. of observations	5

The calibration graph is described by the following equation: $y = 0.0009x + 0.0022$ ($r^2 = 0.9997$).

Manganese salen

Maximum absorbance was measured at 480nm for manganese salen in acetonitrile. Linearity experiment in the range of 200 – 1000mg L^{-1} was carried out. The absorbance values with respective concentrations are tabulated in Table 5.18.

Table 5.18. Linearity experiment for manganese salen in acetonitrile: Concentration Vs absorbance

Observation No.	Concentration (mg L^{-1})	Absorbance
1.	200	0.4766
2.	400	0.9366
3.	600	1.3835
4.	800	1.8566
5.	1000	2.3166

The calibration data was subjected to regression analysis. The result of the regression analysis is given in Table 5.19. The plot of absorbance Vs concentration for manganese salen in CH_3CN was shown in Figure 5.6.

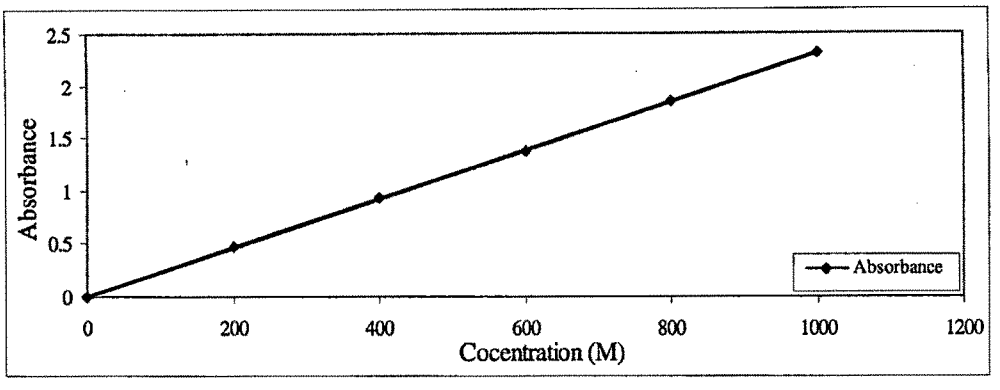

Figure 5.6. Linear working range of manganese salen in acetonitrile

Table 5.19. Results of regression analysis : Manganese salen in acetonitrile

Parameters	Manganese Salen in Acetonitrile
Regression Equation (y)	
Correlation Coefficient (r^2)	0.9999
Slope, a	0.0023
Intercept,	0.0066
No. of observations	5

The calibration graph is described by the following equation: $y = 0.0023x + 0.0066$ ($r^2 = 0.9999$).

Copper Salen

Maximum absorbance was measured at 565nm for copper salen in chloroform. Linearity experiment in the range of 200 – 1000mg L^{-1} was carried out. The absorbance values with respective concentrations are tabulated in Table 5.20

Table 5.20. Linearity experiment for copper salen in chloroform: Concentration Vs absorbance

Observation No.	Concentration (mg L^{-1})	Absorbance
1.	200	0.0354
2.	400	0.0757
3.	600	0.1114
4.	800	0.1462
5.	1000	0.1853

The calibration data was subjected to regression analysis. The result of the regression analysis is given in Table 5.21. The plot of absorbance Vs concentration for copper salen in $CHCl_3$ is shown in Figure 5.7.

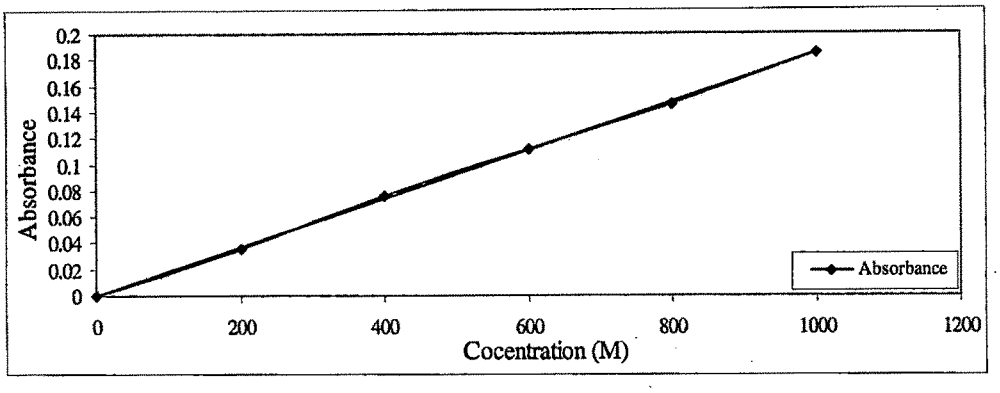

Figure 5.7. Linear working range of copper salen in chloroform

Table 5.21. Results of regression analysis: Copper salen in chloroform

Parameters	Copper Salen in $CHCl_3$
Regression Equation (y)	
Correlation Coefficient (r^2)	0.9996
Slope, a	0.0002
Intercept,	0.0002
No. of observations	5

The calibration graph is described by the following equation: $y = 0.0002x + 0.0002$ ($r^2 = 0.9996$).

Copper Sulphate

Maximum absorbance was measured at 800nm for copper sulphate in DDW. Linearity experiment in the range of 0.002 – 0.1M was carried out. The absorbance values with respective concentrations are tabulated in Table 5.22.

Table 5.22 Linearity experiment for copper sulphate in water: Concentration Vs absorbance

Observation No.	Concentration (M)	Absorbance
1.	0.002	0.0253
2.	0.004	0.0522
3.	0.006	0.0794
4.	0.008	0.1044
5.	0.01	0.1276
6.	0.02	0.2612
7.	0.04	0.5066
8.	0.06	0.7433
9.	0.08	0.9862
10.	0.1	1.2083

The calibration data was subjected to regression analysis. The result of the regression analysis is given in Table 5.23. Figure 5.8. shows the plot of absorbance Vs concentration for copper sulphate in DDW.

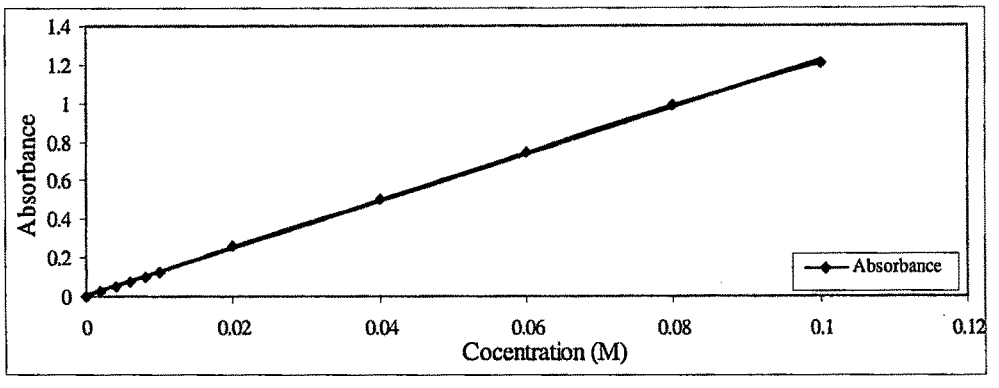

Figure 5.8. Linear working range of copper sulphate in water

Table 5.23 Results of regression analysis: Copper sulphate in water

Parameters	Copper Sulphate in water
Regression Equation (y)	
Correlation Coefficient (r^2)	0.9996
Slope, a	12.161
Intercept,	0.0073
No. of observations	10

The calibration graph is described by the following equation: $y = 12.161x + 0.0073$ ($r^2 = 0.9996$).

Nickel Sulphate

Maximum absorbance was measured at 393nm for nickel sulphate in water. Linearity experiment in the range of 0.002 – 0.1M was carried out. The absorbance values with respective concentrations are tabulated in Table 5.24.

Table 5.24 Linearity experiment for nickel sulphate in water: Concentration Vs absorbance

Observation No.	Concentration (M)	Absorbance
1.	0.002	0.008
2.	0.004	0.017
3.	0.006	0.0246
4.	0.008	0.0335
5.	0.01	0.0425
6.	0.02	0.0852
7.	0.04	0.1768
8.	0.06	0.2664
9.	0.08	0.356
10.	0.1	0.447

The calibration data was subjected to regression analysis. The result of the regression analysis is given in Table 5.25. The plot of absorbance Vs concentration for nickel sulphate in DDW is shown in Figure5.9.

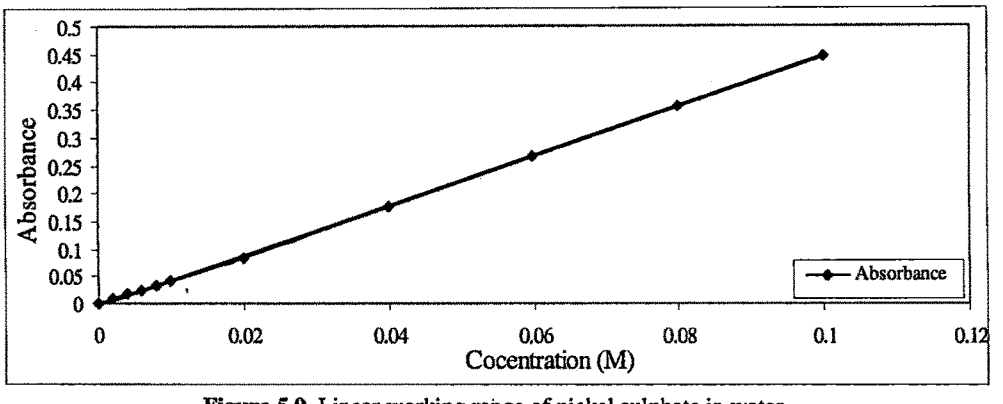

Figure 5.9. Linear working range of nickel sulphate in water

Table 5.25 Results of regression analysis: Nickel sulphate in water

Parameters	Nickel Sulphate in water
Regression Equation (y)	
Correlation Coefficient (r^2)	0.9999
Slope, a	4.4763
Intercept,	- 0.002
No. of observations	10

The calibration graph is described by the following equation: $y = 4.4763x - 0.002$ ($r^2 = 0.9999$).

Cobalt Chloride

Maximum absorbance was measured at 510nm for cobalt chloride in DDW. Linearity experiment in the range of 0.002 – 0.1M was carried out. The absorbance values with respective concentrations are tabulated in Table 5.26.

Table 5.26 Linearity experiment for cobalt chloride in water: Concentration Vs absorbance

Observation No.	Concentration (M)	Absorbance
1.	0.002	0.004
2.	0.004	0.0128
3.	0.006	0.0217
4.	0.008	0.0306
5.	0.01	0.0386
6.	0.02	0.0856
7.	0.04	0.1724
8.	0.06	0.2642
9.	0.08	0.3486
10.	0.1	0.4376

The calibration data was subjected to regression analysis. The result of the regression analysis is given in Table 5.27. The plot of absorbance Vs concentration for cobalt chloride in DDW was shown in Figure 5.10.

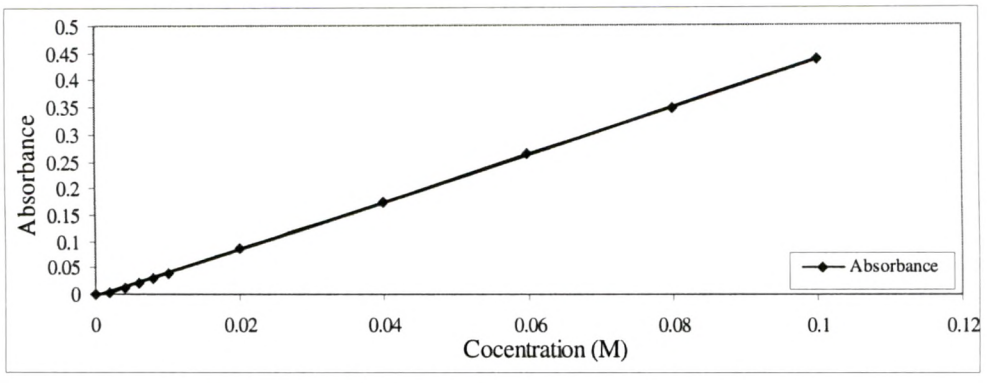

Figure 5.10. Linear working range of cobalt chloride in water

Table 5.27 Results of regression analysis: Cobalt chloride in water

Parameters	Cobalt Chloride in water
Regression Equation (y)	
Correlation Coefficient (r^2)	0.9999
Slope, a	4.419
Intercept,	- 0.0039
No. of observations	10

The calibration graph is described by the following equation: $y = 4.419x - 0.0039$ ($r^2 = 0.9999$).

Nickel Chloride

Maximum absorbance was measured at 394nm for nickel chloride in DDW. Linearity experiment in the range of 0.002 – 0.1M was carried out three times. The absorbance values with respective concentrations are tabulated in Table 5.28.

Table 5.28 Linearity experiment for cobalt chloride in water: Concentration Vs absorbance

Observation No.	Concentration (M)	Absorbance
1.	0.002	0.0092
2.	0.004	0.0201
3.	0.006	0.0301
4.	0.008	0.0352
5.	0.01	0.0454
6.	0.02	0.0854
7.	0.04	0.1756
8.	0.06	0.2581
9.	0.08	0.3441
10.	0.1	0.4352

The calibration data was subjected to regression analysis. The result of the regression analysis is given in Table 5.29. The plot of absorbance Vs concentration for nickel chloride in DDW was shown in Figure 5.11.

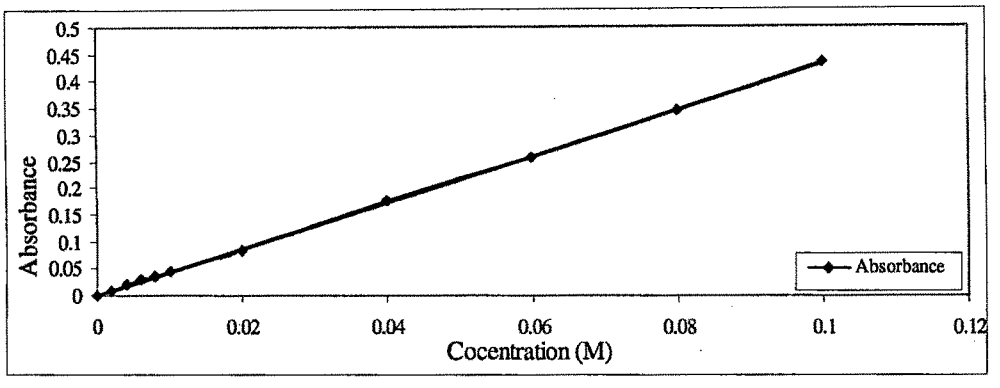

Figure 5.11. Linear working range of nickel chloride in water

Table 5.29 Results of regression analysis: Nickel chloride in water

Parameters	Nickel Chloride in water
Regression Equation (y)	
Correlation Coefficient (r^2)	0.999
Slope, a	4.312
Intercept,	0.001
No. of observations	10

The calibration graph is described by the following equation: $y = 4.312x + 0.001$ ($r^2 = 0.999$).

Acceptability of linearity data is judged by examining the coefficient of determination and the y – intercept as follows.

a. The plot of concentration Vs absorbance (mean of three observations) for the linear working range is depicted in Table 5.16 for copper bisacetylacetonate in chloroform, in Table 5.18 for manganese salen and in Table 5.20 for copper salen in chloroform. The plot shows that a linear relationship exists between concentration and absorbance in the range of concentration 200 – 1000mg L^{-1} obeying Beer's – Lambert's law for determination of all three metal complexes in their respective solution. The plot of concentration Vs absorbance (mean of three observations) for the linear working range is depicted in Table 5.22 for copper sulphate, in Table 5.24 for

nickel sulphate, in Table 5.26 for cobalt chloride and in Table 5.28 for nickel chloride. The plot shows that a linear relationship exists between concentration and absorbance in the range of concentration 0.002 – 0.1M obeying Beer's – Lambert's law for determination of all three metal salts in DDW.

b. The coefficient of determination i.e. 0.9997 for copper bisacetylacetonate in chloroform, 0.9999 for manganese salen in acetonitrile, 0.9996 for copper salen in chloroform, 0.9996 for copper sulphate in DDW and 0.9999 for nickel sulphate in DDW, 0.9999 for cobalt chloride in DDW and 0.999 nickel chloride in DDW means that almost 99.9% of variation in y i.e. the change in the response of the analyte can be explained by the change in x i.e. concentration of the analyte in the respective solutions. The correlation coefficient is a measure of goodness of the fit of the calculated line to the sample data.

c. The slope of the regression line is 0.0009 for copper bisacetylacetonate in chloroform, 0.0023 for manganese salen in acetonitrile, 0.0022 for copper salen in chlorofrom,12.161 for copper sulphate in DDW and 4.4771 for nickel sulphate in DDW, 4.419 for cobalt chloride in DDW and 4.312 nickel chloride in DDW this indicates that one unit increase in the concentration of copper bisacetylacetonate in chloroform, manganese salen in acetonitrile, copper salen in chloroform, copper sulphate, nickel sulphate, cobalt chloride and nickel chloride in DDW will result in an increase in the absorbance value by 0.0022, 0.0009, 0.0023, 12.161, 4.4771, 4.419 and 4.312 units respectively.

CONCLUSION

Almost in all cases of metal complex loaded activated charcoal, the adsorption of drugs increases in presence of oxygen with respect to their corresponding adsorbent. In case of MAC_1 a distinct difference on the adsorption behavior of aspirin and paracetamol is observed: aspirin and paracetamol in presence of each other adsorbed less compared to individual treatment in absence of oxygen, but in presence of oxygen adsorption of aspirin increases and paracetamol decreases in presence of each other. Similarly in case of MAC3 amount of aspirin adsorbs in less amount when treated with paracetamol in absence of oxygen compared to its individual treatment

but in presence of oxygen adsorption efficiency of MAC_3 increases both for aspirin and paracetamol in presence of each other as compared to individual treatment. At this juncture we are unable to provide suitable explanation for the observed trend.

All most in all cases of metal salts loaded activated charcoal, the adsorption of drugs increases in absence of oxygen with respect to activated charcoal which is not loaded with metal salts. The effect of oxygen was not observed on the absorption of adsorbents except AC. MC_2 removes maximum about of drugs in absence of oxygen and presence of oxygen increases removal efficiency of MC_2. In case of MC_1 and MC_3 a distinct difference on the adsorption behavior of aspirin and paracetamol is observed: When treated individual aspirin adsorbed more compared to paracetamol and where as paracetamol adsorbed more compared to aspirin when treated in presence of each other. In case of MC_4, the percentage removal of both aspirin and paracetamol in presence of each other decreases compared to its individual treatment.

From the removal study it can be concluded that metal complex and metal ion loaded activated charcoal can remove drugs present in water. Its removal efficiency increases in presence of oxygen. Metal loaded charcoal can be used for removal of drugs present in water as tertiary treatment in water treatment plants. However, no specific trend could be observed in terms of use of metal salt or metal complex.