CHAPTER IV

RESULT AND DISCUSSION

4.1 Characteristics of soils

Table 4.1 provides the major physical-chemical properties of the soils and sediment used in the sorption experiments. . The organic content and soil texture of each soil type were measured at the Argicultural chemistry division at department of agriculture and the BET surface area were measured at Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology of Ladkrabang. The organic carbon contents vary from 0 % for sand to as high as 2.96% for sediment. Three soils, Garden soil-1 and Garden soil- 3 and sediment were classified as having clay texture.

Table 4.1 soil properties

Soil	pH	Percent Organic carbon content	Percent Sand	Percent Silt	Percent Clay	Surface area (m^2/g)	Texture
Sand	8.1	0	95.3	2	2.7	58.76	Sand
Laterite soil	7	0.07	74	12.8	13.2	7.48	Sandy loam
Garden soil-1	7.8	0.56	18.6	34	47.4	49.09	Clay
Garden soil-2	8.3	1.06	42	23.6	34.4	37.90	Clay loam
Garden soil-3	7	1.36	17.8	28.8	53.4	62.58	Clay
Sediment	7.1	2.96	29.8	27.8	42.4	41.7	Clay

4.2 Selection of optimal soil/solution ratios and selection of equilibration time

The results to select the suitable optimal soil/solution ratios and the equilibrium time for sorption batch experiments are presented in Figures 4.1, 4.2 and 4.3 for sand, garden soil-1, and sediment. The suitable soil/solution ratio to be used for all types of soils except for sediment was selected based on the study using sand

and garden soil-1. In the case of sand (Figure 4.1) all three soil/solution ratios can be selected since all ratios gave final concentrations that were above the detection limit without using too high a MT concentration as the starting concentration. In the case of garden soil-1, sorption was high for the ratio 1:5 resulting in a sharp decline in the concentrations and with the final concentrations below the limit of detection. In order to use MT concentrations that were less than the solubility limit as the starting concentrations, the soil/solution ratio for garden soil-1 or soils with high organic carbon content should be 1:10.

In the case of sediment, even with a ratio of 1:20 very low concentration of MT remained in solution over the experimental period. To ensure detectable concentrations of MT were measured, a ratio of 1:30 was selected.

The equilibrium time was estimated from experiments for 3 types of soils (sand, garden soil-1, and sediment) as shown in Figure 4.1 – 4.3. During the first 6 hours of the experiment, sorption was rapid but the aqueous concentrations were fairly constant after 12 hours. The results suggested an equilibrium time of 12 hours would be sufficient for the batch sorption experiments.

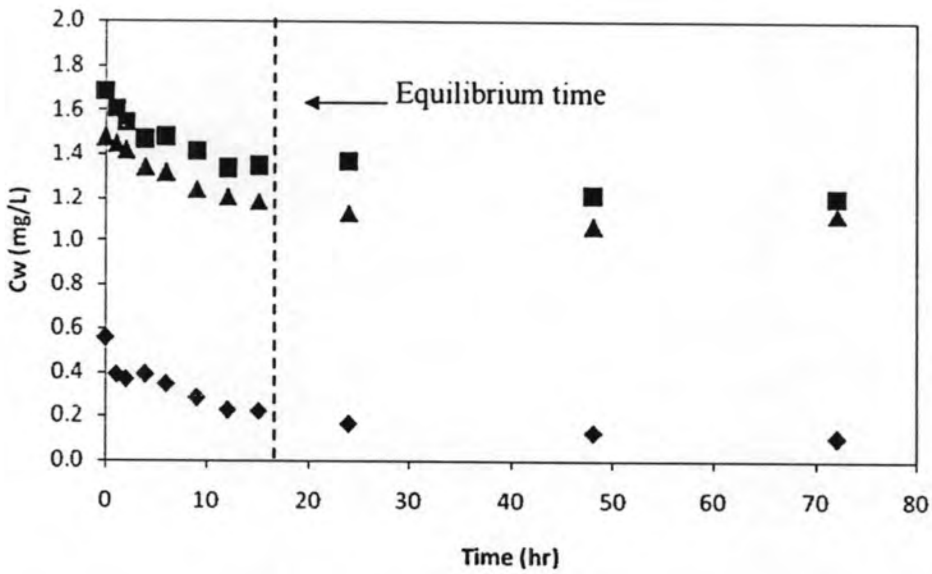

Figure 4.1 Kinetics of 17 alpha- methyltestosterone sorption onto sand for different soil/solution ratios of 1:1 (◆, 1:5 (▲, and 1:10 (■ test

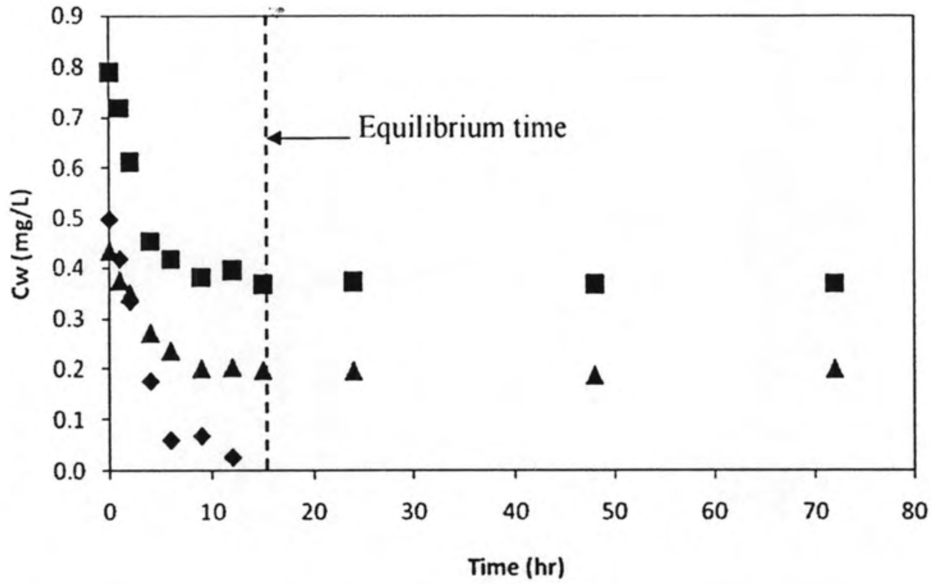

Figure 4.2 Kinetics of 17 alpha-methyltestosterone sorption onto garden soil-1 for different soil/solution ratios of 1:5 (◆), 1:10 (▲), and 1:20 (■) test

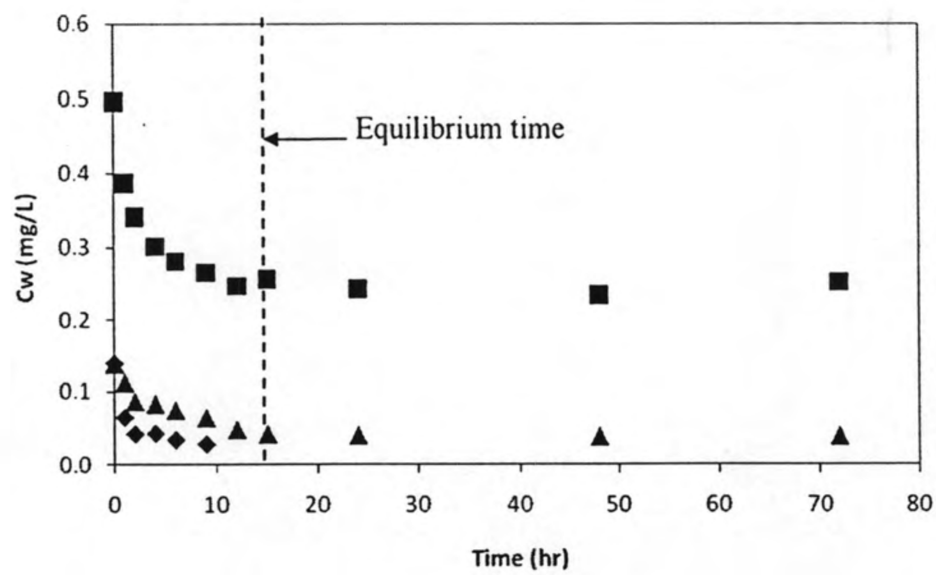

Figure 4.3 Kinetics of17 alpha-methyltestosterone sorption onto sediment at for different soil/solution ratios of 1:10 (◆), 1:20 (▲), and 1:30 (■ test

4.3 Effect of organic content on sorption under original condition

The results of batch sorption experiments of MT onto five different types of soil and a sediment are presented in Figures 4.4 to 4.9. Figure 4.10 combines all the isotherms onto one graph.

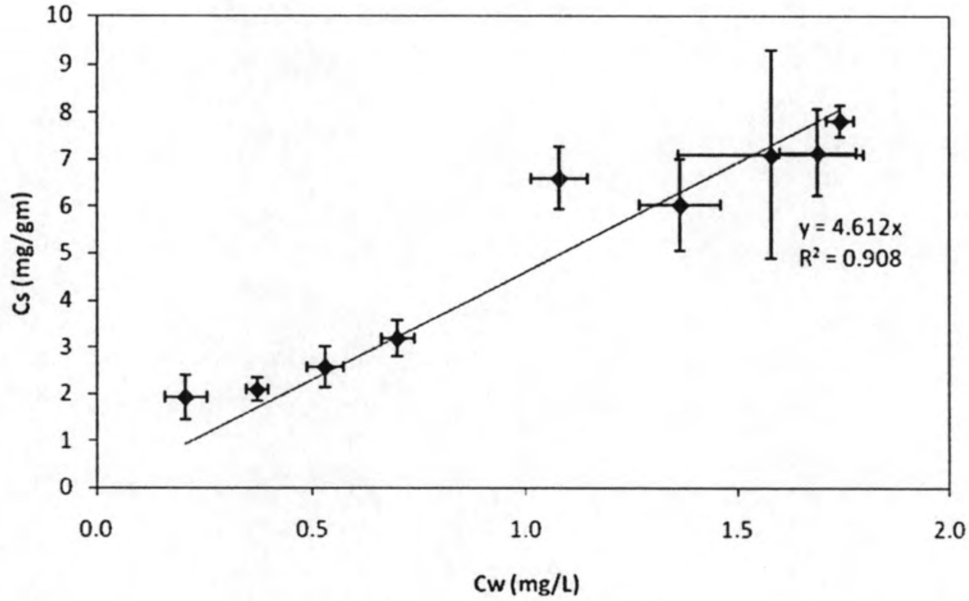

Figure 4.4 17 alpha-methyltestosterone sorption isotherm for Sand (pH = 7.2)

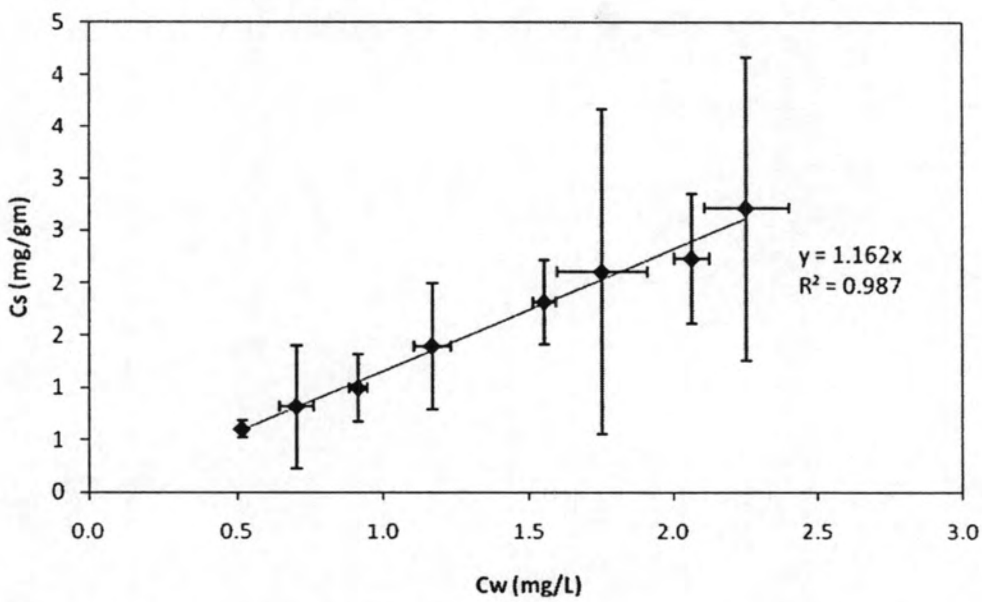

Figure 4.5 17 alpha-methyltestosterone sorption isotherm for Laterite soil (pH = 7.1)

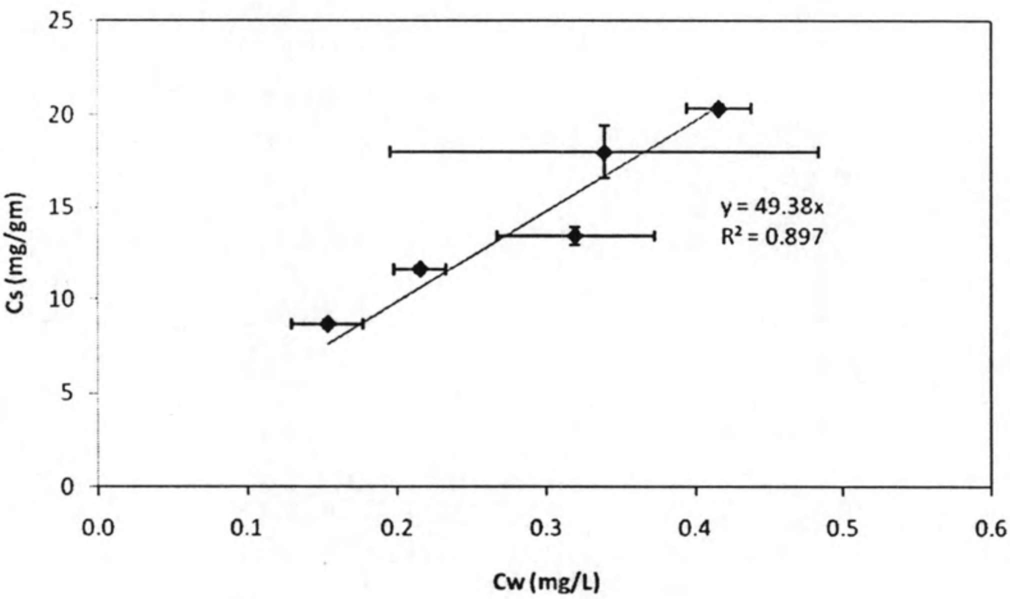

Figure 4.6 17 alpha-methyltestosterone sorption isotherm For Garden soil-1 (pH = 7.5)

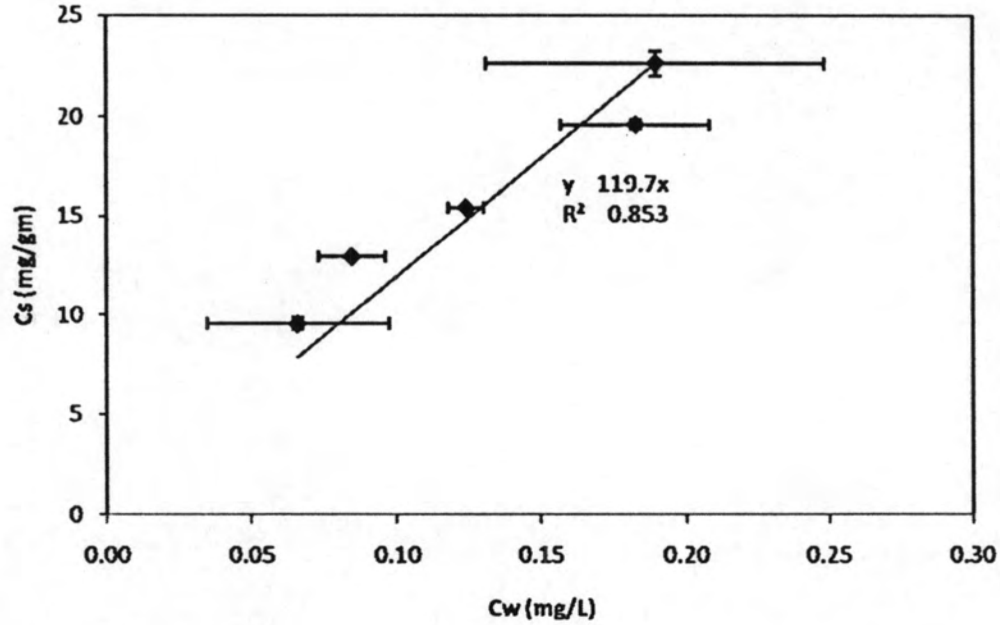

Figure 4.7 17 alpha-methyltestosterone sorption isotherm for Garden soil-2 (pH = 7.5)

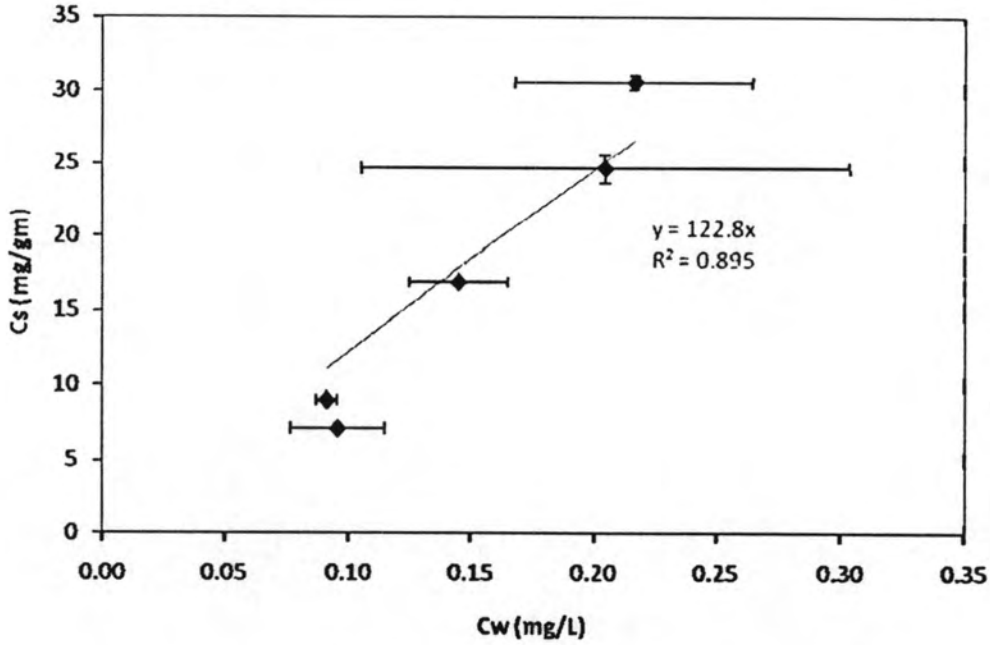

Figure 4.8 17 alpha-methyltestosterone sorption isotherm for Garden soil-3 (pH = 7.4)

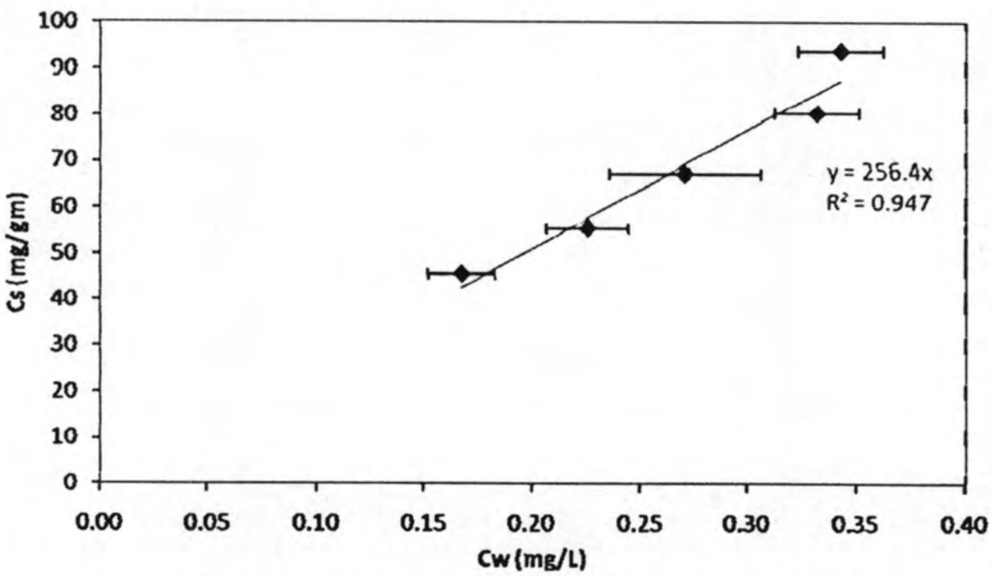

Figure 4.9 17 alpha-methyltestosterone sorption isotherm for Sediment (pH = 5.8)

All soil types demonstrated linear sorption isotherms (linear relationship between C_s and C_w). Sediment exhibited the highest K_d value followed by Garden soil-3, Garden soil-2, Garden soil-1, sand and laterite soil, respectively. Table 4.2 summarizes the sorption coefficients for both linear sorption model and Freundlich sorption model. K_d values ranged from 1.16 to as high as 168.80 L/kg. The K_d values were plotted against the percent organic contents as shown in Figure 4.11 and a straight line was obtained with an R^2 value of 0.984 indicating that K_d values were proportional to the percent organic contents. Work done by Li and Lee (1999), Mansell et al. (2004), and Casey et al. (2005) indicate that the sorption of estrogens and testosterone were proportional to the organic carbon content of the soils.

The K_{oc} values for the five media except for sand were computed as presented in Table 4.2. Values of K_{oc} ranged from 1,657 to 11,292. The range of K_{oc} values were similar to the range of K_{oc} values found by Lee et al. (2003) where the K_{oc} values of testosterone, 17 alpha-estradiol, and 17 Rethynyl estradiol for different soils indicate that hydrophobic partitioning was the dominant sorption mechanism..

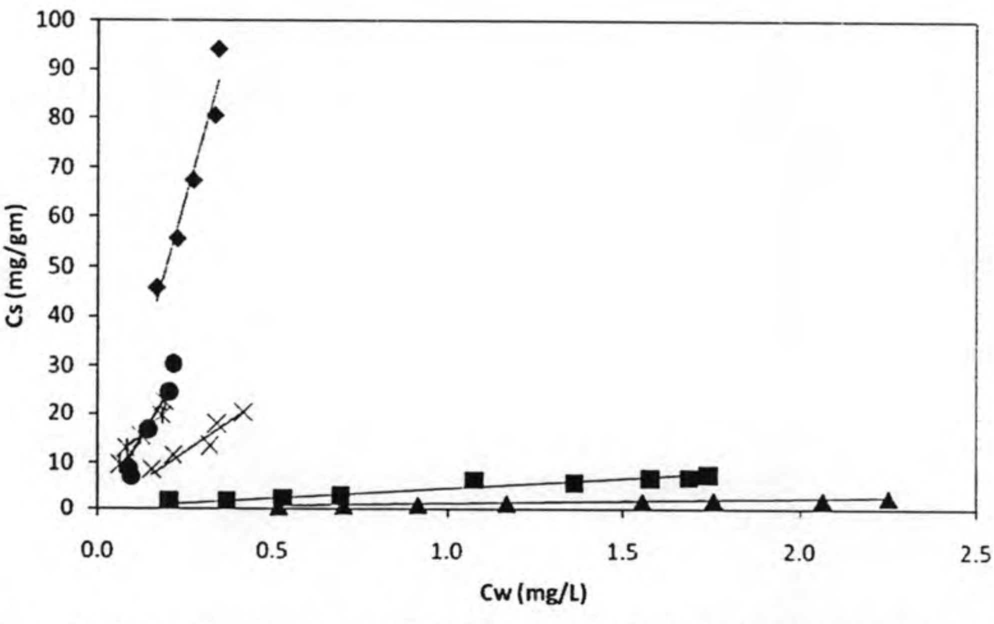

Figure 4.10 Sorption isotherms for 17 alpha-methyltestosterone: sand(■), laterite soil(▲), garden soil-1(×), garden soil-2(✻), garden soil-3(●), and sediment(◆)

Table 4.2 Isotherm coefficients for all types of soils

Soil	Percent organic content	Linear isotherm			Freundlich isotherm		
		K_d (L/kg)	R^2	Koc (L/kg)	K_f	n	R^2
Sand	<DL	4.61±1.66	0.91	-	4.93 ±0.18	0.73	0.93
Laterite soil	0.07	1.16±0.05	0.99	1,657	1.15±45.81	1.01	1.00
Garden soil-1	0.56	49.38±5.63	0.90	8,817	40.46±0.03	0.83	0.93
Garden soil-2	1.06	119.70±18.70	0.86	11,292	70.96±0.06	0.72	0.97
Garden soil-3	1.36	122.80±24.81	0.90	9,029	291.08±0.07	1.51	0.96
Sediment	2.96	256.40±15.63	0.95	8,662	238.79±0.00	0.95	0.96

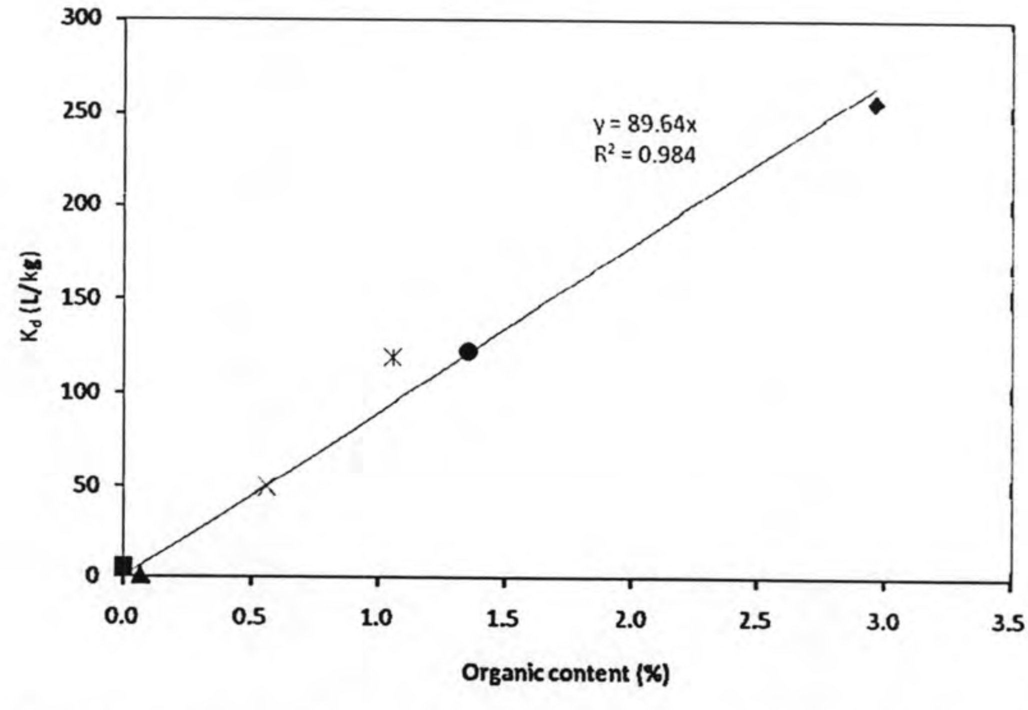

Figure 4.11 Linear sorption coefficient (K_d) versus organic content (%) for: sand (■), laterite soil(▲), garden soil-1(×), garden soil-2(⁎), garden soil-3(●), and sediment(◆)

Figure 4.12 and Figure 4.13 show the plots between K_d values and the percent sand and percent clay contents. The results showed that the sorption coefficients were not correlated with the percent sand and percent clay in the soils and sediment tested.

In the case of sand and laterite soil, both soils have low percent organic content and it is possible that surface area may have affected the sorption of MT. The surface area of sand and laterite soil were 58.76 and 7.48 m^2/gm, respectively. As shown by the K_d values of sand and laterite soil, the higher the surface area the higher was the K_d value. Casey et al. (*2003*) reported a high correlation between 17â-estradiol sorption and soil surface.

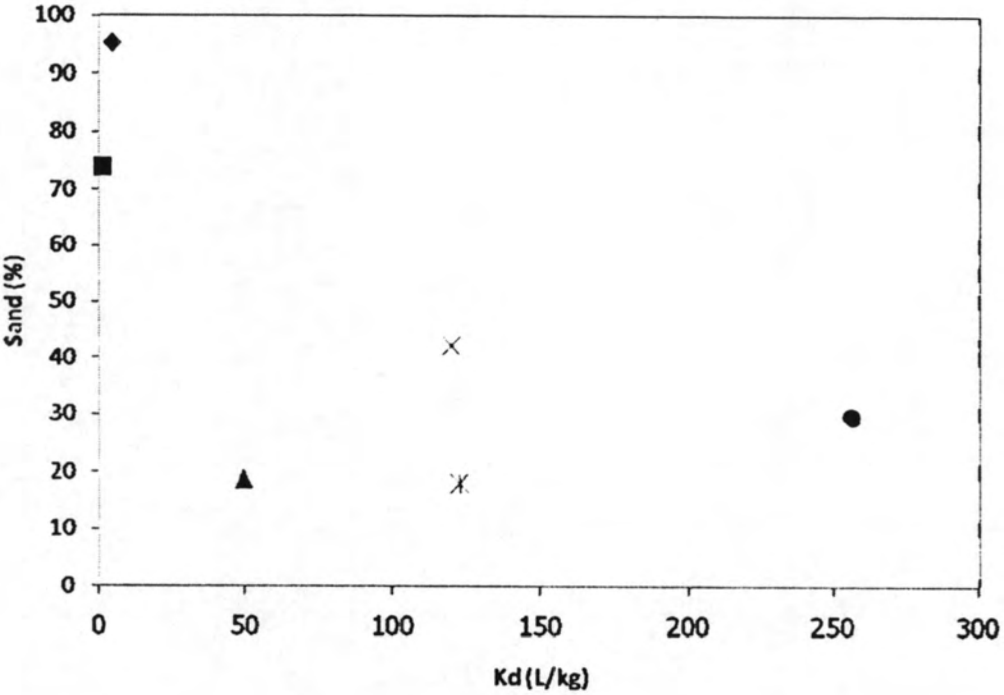

Figure 4.12 Percent sand content (%) vs linear sorption coefficient (K_d) of 17 alpha-methyltestosterone for soils: sand (■), laterite soil (▲), garden soil-1(×), garden soil-2 (✱), garden soil-3 (●), and sediment (◆)

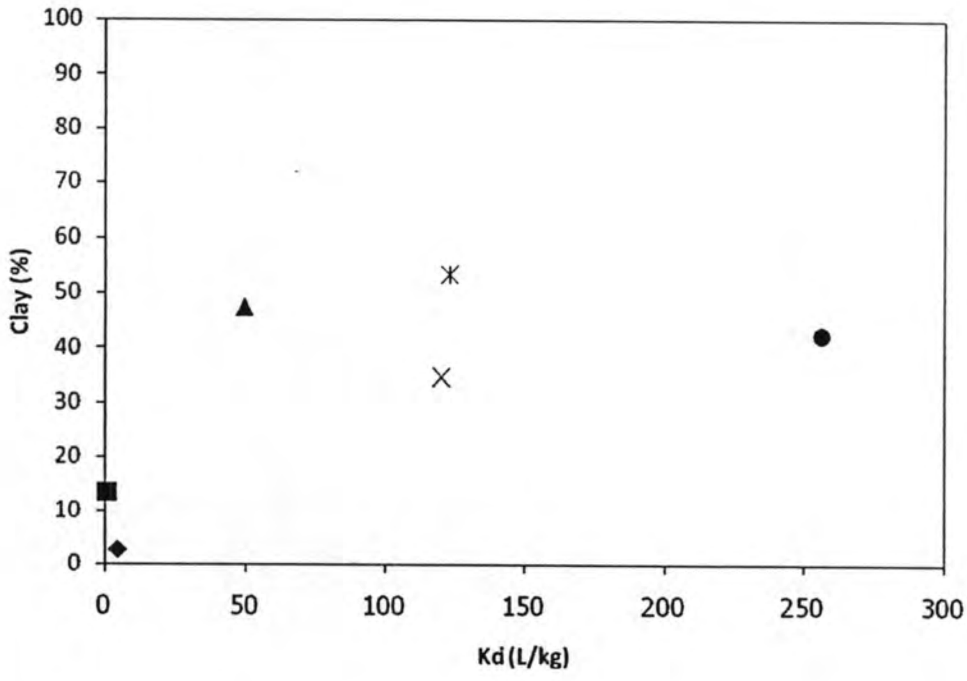

Figure 4.13 Percent clay content (%) vs Linear sorption coefficient (K_d) of 17 alpha-methyltestosterone for soils: sand (■), laterite soil (▲), garden soil-1 (×), garden soil-2 (✱), garden soil-3 (●), and sediment (◆)

4.4 Effect of pH on sorption

The effect of pH on sorption was conducted using three types of soils: sand, garden soil-1, and sediment. The test was performed with three pH values: the original pH of soil, 0.5 units above the original pH of soil, and 0.5 units below the original pH of soil. As the pHs of sand, garden soil-1, and sediment were 7.1, 7.3, and 5.9, the pH used for sand was 6.6, 7.1, and 7.6 and whereas that the pH used for garden soil-1 were 6.8, 7.2, and 7.8 and for the sediments the pH used were 5.4, 6.9, and 6.4. The results of the effect of pH are shown in Figure 4.14 to Figure 4.16 and in Table 4.3.

In the case of sand and garden soil-1, no correlation between K_d values and pH was observed. On the other hand, an increase in pH appeared to decrease the sorption coefficients of sediments. Since MT is a slightly polar organic compound and has higher solubility in alkaline solution than acid solution, it is probable that at low pH, MT is transfered from the liquid phase to the solid phase, which leads to higher adsorption. As reported by Guangming et al. (2006), sorption of Bisphenol A was found to increase for a decrease in pH.

Table 4.3 The linear isotherm in the different pH

Soil	Percent organic content	initial pH	final pH	Linear isotherm		Freundlich isotherm		
				K_d (L/gm)	R^2	K_f	n	R^2
Sand	0	6.6	7.4	2.39±0.59	0.74	1.70±27.47	1.33	0.70
		7.1	7.5	2.42±0.15	0.96	2.67±23.63	0.89	0.98
		7.6	7.5	2.16±0.68	0.71	1.53±27.11	2.27	0.97
Garden soil-1	0.56	6.8	7.0	9.12±0.91	0.92	8.18	1.22	0.96
		7.3	7.4	10.62±0.91	0.93	10.84	0.92	0.94
		7.8	7.5	9.62±1.39	0.90	10.62	0.76	0.91
Sediment	2.96	5.4	5.6	433.10±79.52	0.61	81.10±0.01	0.62	0.95
		5.9	5.9	303.60±145.89	0.33	160.69±0.01	0.48	0.97
		6.4	6.1	299.00±70.77	0.86	63.39±0.01	0.65	0.92

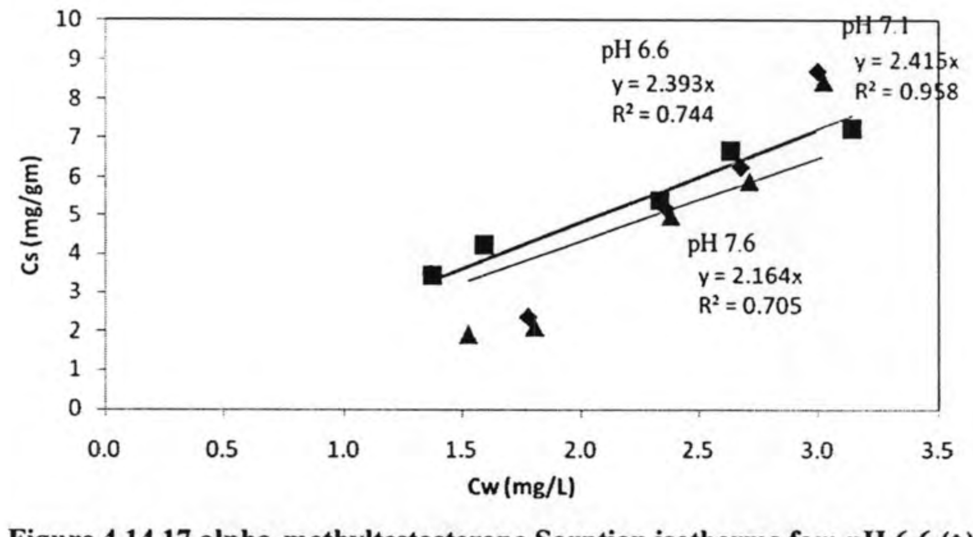

Figure 4.14 17 alpha-methyltestosterone Sorption isotherms for: pH 6.6 (◆), pH 7.1 (■), and pH 7.6 (▲)

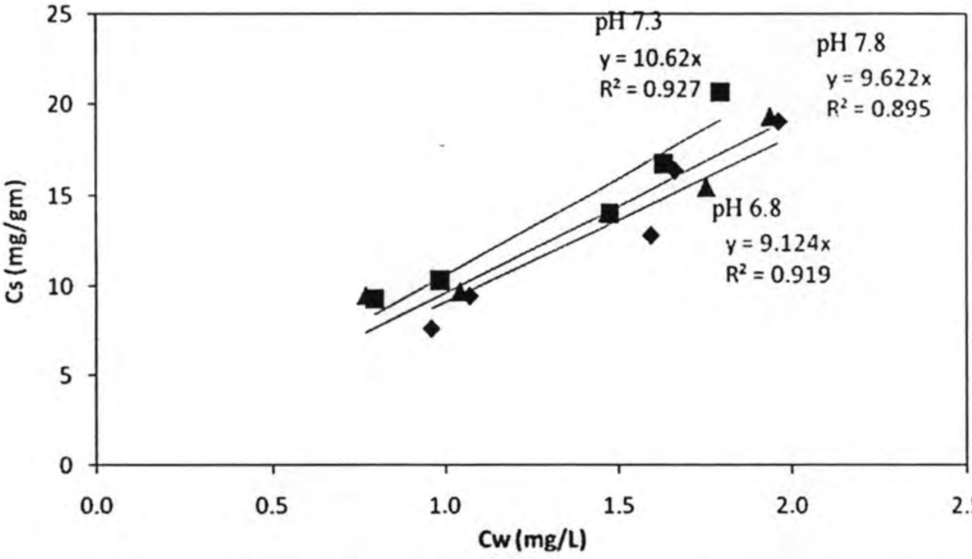

Figure 4.15 17 alpha-methyltestosterone sorption isotherms for garden soil-1: pH 6.8(♦), pH 7.3(■), and pH 7.8(▲)

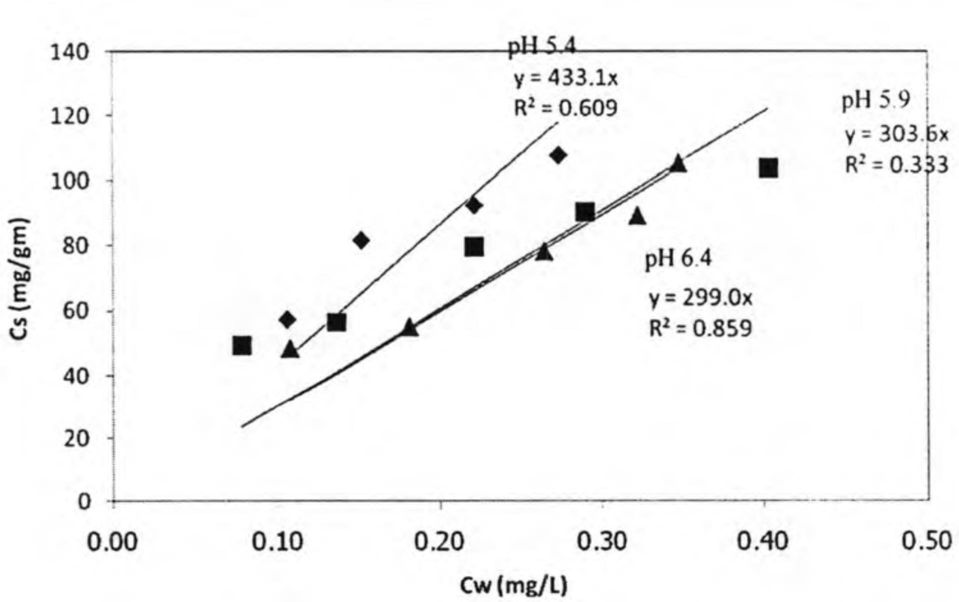

Figure 4.16 17 alpha-methyltestosterone sorption isotherms for sediment: pH 5.4(♦), pH 5.9(■), and pH 6.4(▲)

4.5 Effect of salinity on sorption

The effect of different salinity on the sorption of MT for three type of soils sand, garden soil-1 and sediment are presented in Figures 4.17 – 4.19. The three soils were tested based on their surface area and percent organic content. The salinity conditions tested were: original salinity of soils (with 0.1 M $CaCl_2$), 5 g/L, 10 g/L, and 20 g/L. For sand and garden soil-1, the salinity did not have an effect on the sorption of MT as seen by the lack of correlation between K_d values and salinity. However, for the sediment, increasing salinity appeared to result in higher K_d values (Table 4.4). This is probably caused by a decrease in MT aqueous solubility due to the presence of salts, resulting in the compound having a preference for the sediment particles over the aqueous phase. This is usually referred to as "salting out" effect (Bowman et al., 2002). In similar work by Bowman et al. (2002) on the effect of different concentrations of salinity on sorption of hormones, they found that the sorption of hormones increased when the ionic strengths of the solution were increased by adding salts to the solution. Brunk et al. (1997) studied the effect of salts on the sorption of phenanthrene onto extracellular polymer and kaolinite and they found that increasing the salinity the overall sorption coefficient increased by 55% as compared to freshwater values. From their results, they attribute the effect to the salting out effect where the solubility of chemical was decreased by increasing of the ionic strength.

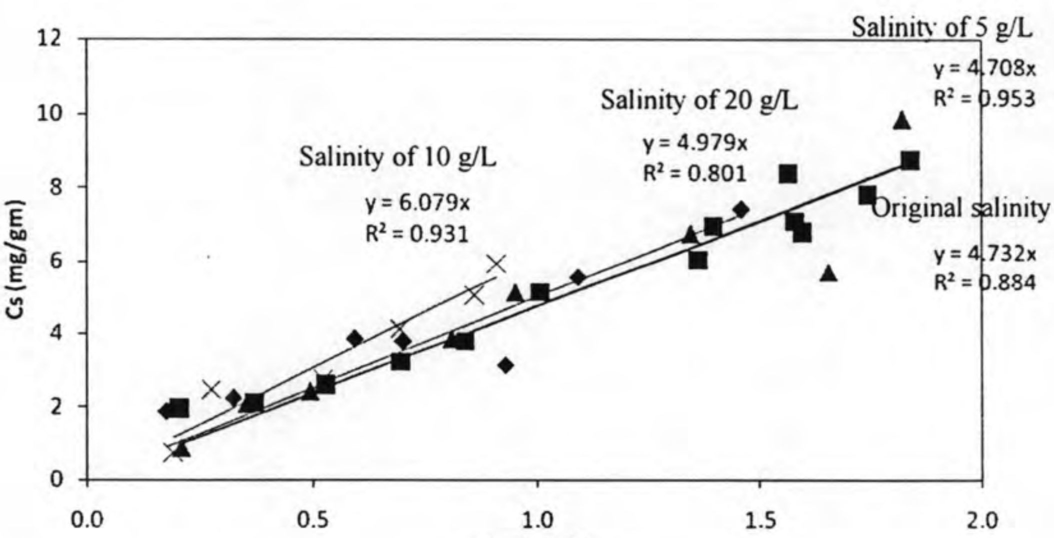

Figure 4.17 17 alpha-methyltestosterone sorption isotherms for sand: original salinity (lower than 0.5 g/L) (■), salinity of 5 g/L (▲), salinity of 10 g/L (×), salinity of 20 g/L (◆)

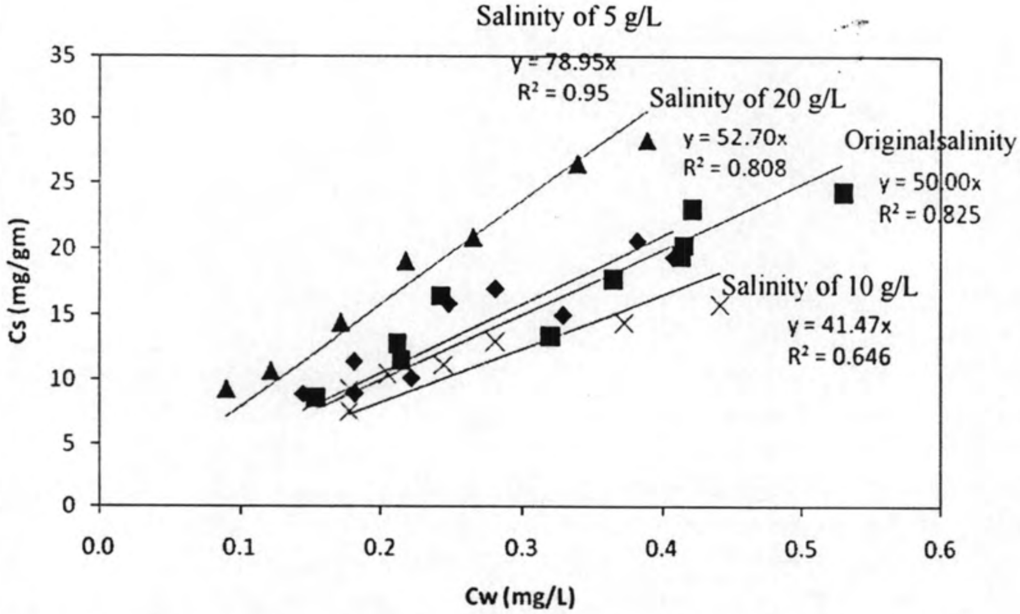

Figure 4.18 17 alpha-methyltestosterone sorption isotherms for garden soil-1: original salinity (lower than 0.5 g/L) (■), salinity of 5 g/L (▲), salinity of 10 g/L (×), salinity of 20 g/L (◆)

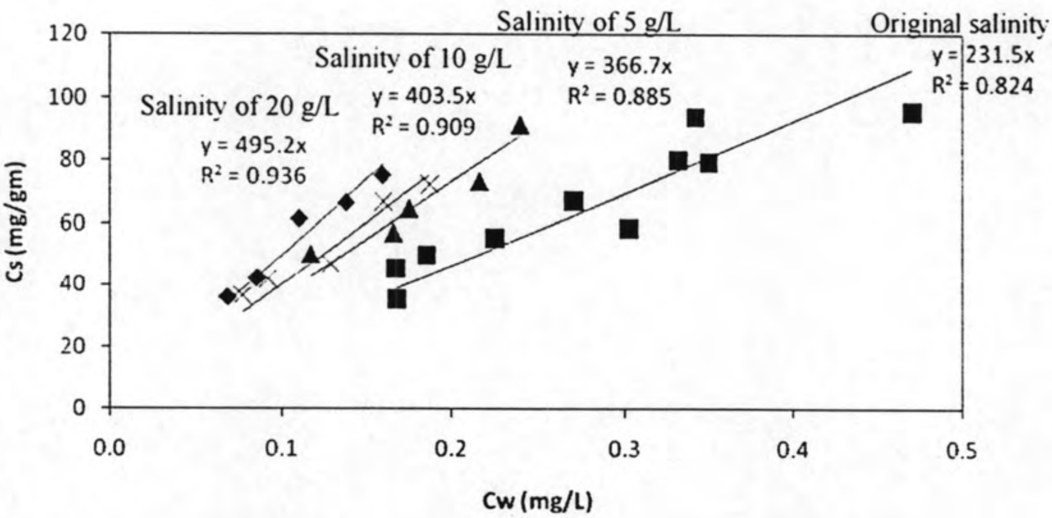

Figure 4.19 17 alpha-methyltestosterone sorption isotherms for sediment: original salinity (lower than 0.5 g/L) (■), salinity of 5 g/L (▲), salinity of 10 g/L (×), salinity of 20 g/L (◆)

Table 4.4 The sorption isotherm for each type of soil

Soil	Percent organic content	Salinity g/L	Linear isotherm		Freundlich isotherm		
			K_d (L/gm)	R^2	K_f	n	R^2
sand	0	0	4.71±1.36	0.95	4.98±0.17	0.77	0.94
		5	4.73±0.78	0.80	4.78±0.54	0.98	0.95
		10	6.08±1.73	0.92	5.93±0.61	1.00	0.89
		20	4.98±2.10	0.80	5.11±0.19	0.67	0.91
Garden soil 1	0.56	0	50.00±7.60	0.82	40.55±0.02	0.79	0.88
		5	78.95±10.79	0.93	57.81±0.04	0.78	0.96
		10	41.47±6.12	0.65	28.91±0.03	0.68	0.90
		20	52.70±7.74	0.81	42.76±0.03	0.83	0.84
Sediment	2.96	0	231.50±29.38	0.82	200.45±0.00	0.87	0.87
		5	366.70±36.12	0.89	257.63±0.01	0.79	0.90
		10	403.50±44.38	0.91	264.24±0.02	0.78	0.94
		20	495.20±34.95	0.94	406.44±0.02	0.90	0.96