TREATABILITY OF SA SURFACE WATERS BY ACTIVATED CARBON

K.P. Lobanga, J. Haarhoff and S.J. van Staden

Department of Civil Engineering Science, University of Johannesburg, PO Box 524, Auckland Park, 2006, South Africa
E-mails: (lobanga1@hotmail.com; jhaarhoff@uj.ac.za; samvs@uj.ac.za)

Natural organic matter (NOM) in water can be removed by different methods including the use of activated carbon. Due to the variability of NOM in natural waters, both in terms of its nature and its concentration, a study was undertaken to investigate the NOM removal for a large range of South African surface waters, sampled at different periods, by the use of granular activated carbon. NOM removal was assessed by measuring the ultraviolet absorbance at 254 nm (UV_{254}). It was found that the Freundlich parameters K and n are related. For some waters the two parameters cluster regardless of season, while others do not. Two treatment targets, namely 65% initial UV_{254} removal and absolute level of 6 /m, were considered. It was observed that when the initial UV_{254} is less than about 17 /m, the absolute limit of 6 /m is reached before the 65% removal of initial UV_{254}. If it is more, the situation is reversed. Some waters have the same carbon usage rate for different initial UV_{254} concentrations whilst others have different usage rates for the same initial UV_{254}. This suggests that the activated carbon usage rate is not only a function of the value of the initial UV_{254} but also of the nature and concentration of the NOM, indicating a need for better characterization.

Keywords: Activated Carbon, Adsorption, Freundlich Isotherm, Natural Organic Matter, Surface Water, Ultraviolet Absorbance

INTRODUCTION

Natural Organic Matter (NOM) is a complex mixture of organic compounds such as humic and fulvic acids, proteins, amino acids and carbohydrates resulting from the degradation of plants animals and microorganisms (1, 2). Based on its origin, NOM can be classified in two different categories including the autochthonous organic matter that is the NOM formed within the water body while the allochthonous organic matter is the NOM produced elsewhere and transported to the water body (3). NOM in water affects the organoleptic aspects of the drinking water, promotes bacterial regrowth in the drinking water distribution systems and reacts with disinfectants and oxidants producing disinfection by-products and other products (3, 4, 5, 6). NOM removal by granular activated carbon (GAC) is a function of the NOM composition (nature and concentration), pH of the water, water temperature, GAC size and concentrations of some ions such as magnesium and calcium (7).

The aim of this paper is to investigate NOM removal for a large range of South African surface waters by the use of granular activated carbon (GAC). The removal is assessed by measuring the UV absorbance at 254, 272 and 300 nm.

MATERIALS AND METHODS

Source water

Eight surface waters were sampled. As shown in Figure 1, the sampling sites were chosen from different geographic region in South Africa in order to account for differences in NOM composition. The surface waters were also chosen to account for the five main surface water types of South Africa (8). The different categories of waters are summarized in Table 1. The raw waters were collected at five different periods to capture the seasonal variations in NOM composition (9, 10).

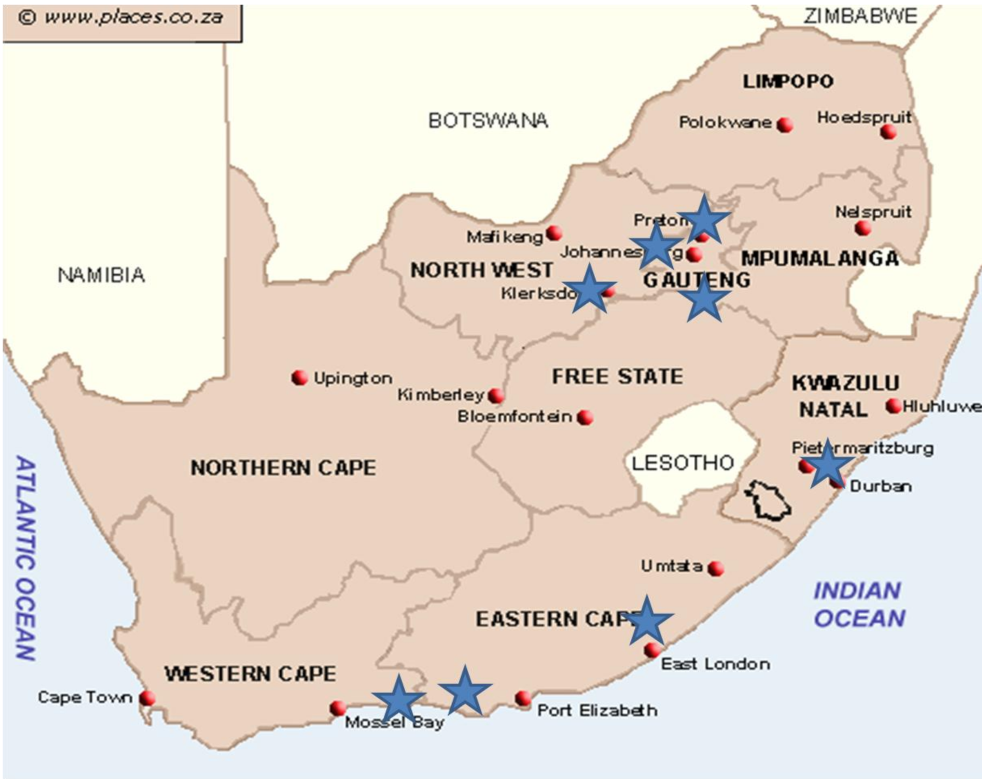


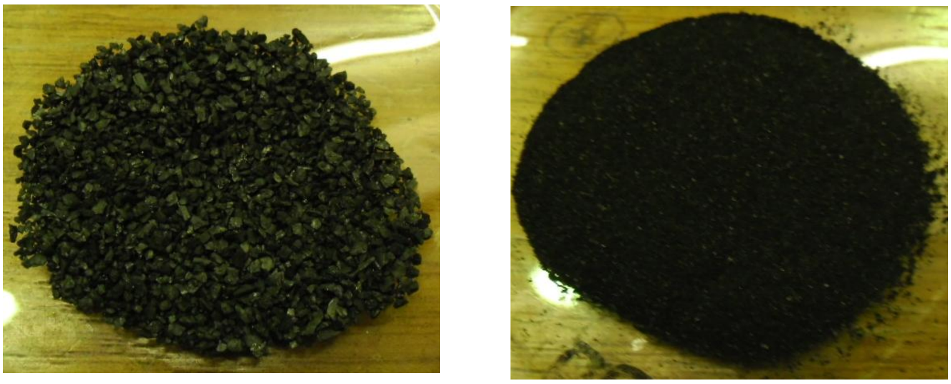
Figure 1. Sample sites (11)

Table 1. Surface water categories

Plant names	Categories
Loerie (Water Treatment Plant)	Low-alkalinity low-colour water
Olifantsvlei (Wastewater Treatment Plant)	Sewage effluent
Plettenberg Bay (Water Treatment Plant)	Very soft, highly coloured water
Rietvlei (Water Treatment Plant)	Eutrophic reservoir water
Stilfontein (Water Treatment Plant)	Eutrophic river water
Umzoniana (Water Treatment Plant)	Moderate-alkalinity low-colour
Vereeniging (Water Treatment Plant)	Oligotrophic reservoir water
Wiggins (Water Treatment Plant)	Low-alkalinity reservoir water

Granular Activated Carbon (GAC)

The GAC used, carbsorb, was supplied by the Rietvlei Water Treatment Plant. Carbsorb is a bituminous coal-based GAC used in liquid phase applications to remove organic compounds. Figure 2 shows a picture of GAC as supplied (a) and after crushing (b).



(a) (b)

Figure 2. Granular Activated carbon, (a) before and (b) after crushing and sieving

The activated carbon used in this study was prepared by crushing the GAC and passing it through a 300 µm sieve.

Batch adsorption tests

Batch tests were conducted for the equilibrium isotherms at room temperature. The experimental method consisted of adding different masses of carbon (blank, 6.25, 8.25, 12.50, 16.50, 25.00, 33.25 and 50.00 mg) to 250 mL of raw water in 500 mL Erlenmeyer flasks. The samples were stirred with a shaker table at 140 rpm for 72 hours (3 days) at room temperature of about 22 °C. After 3 days, the samples were filtered through a 0.45 µm membrane filter before the ultraviolet absorbance was measured at 254 nm (UV_{254}), 272 nm (UV_{272}) and 300 nm (UV_{300}).

Freundlich equilibrium isotherm

The Freundlich parameters K and n were determined from the results of UV_{254}. The Freundlich equation is given in equation [1]:

[1]

q_e = equilibrium NOM concentration in the solid phase (UV per mg/L)
C_e = equilibrium NOM concentration in water (/m)
K and n = Freundlich constant and exponent respectively.

The Freundlich parameters K and n are related to the capacity and the affinity of the resin for NOM molecules respectively (1).

Performance criteria indicators

The required GAC dosage for every raw water was determined for two arbitrary treatment goals. They are:

- Absolute level: UV limit of 6 /m
- Percentage removal: 65% removal of initial UV_{254}

The GAC dosage was calculated as follows:

Equation [1] can be developed as follows:

—— [2]

—— [3]

If C_e = 6 /m —— [4]

If C_i is removed by 65% —— [5]

C_i = initial NOM concentration in raw water (/m)
M = GAC dosage (mg/L)

RESULTS AND DISCUSSION

The indicators used and reported in this paper are the UV_{254} (indicative of the double bonds), UV_{272} (which is the best predictor for the THMs formation) and UV_{300} (used by some South African water treatment plants as operational parameter) (12). UV_{254} is the wavelength used internationally to characterize NOM (3). It was found that when plotting the graphs of UV equilibrium in water (C_e) versus the GAC dosage, the removal patterns are the same for all wavelengths, as shown in figures 3 and 4 (Round 5 Stilfontein and Round 3 Umzoniana waters).

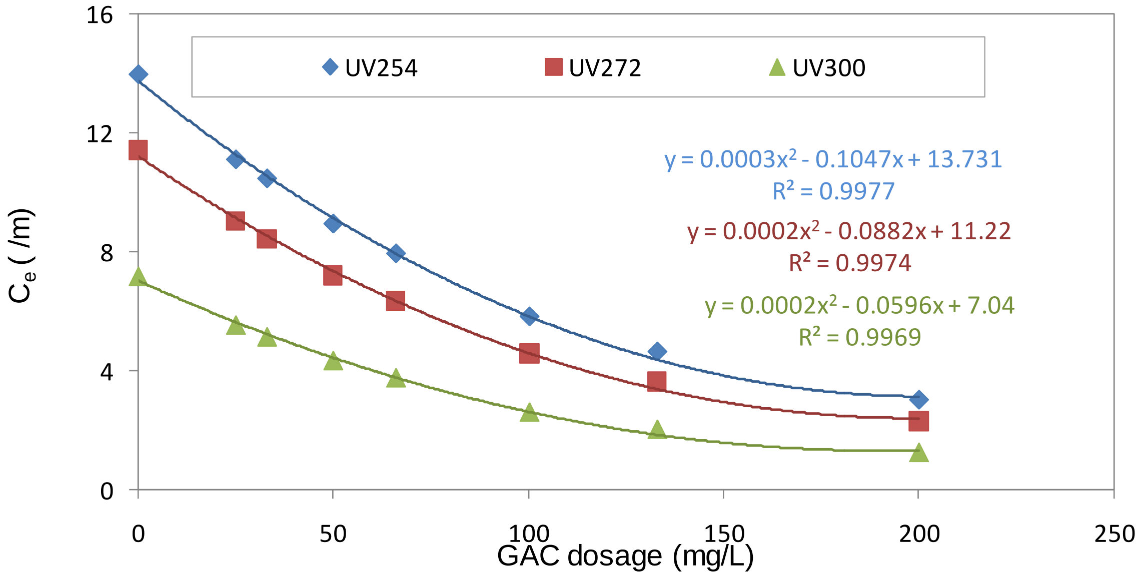


Figure 3. UV equilibrium vs. GAC dosage for the Round 5 Stilfontein water

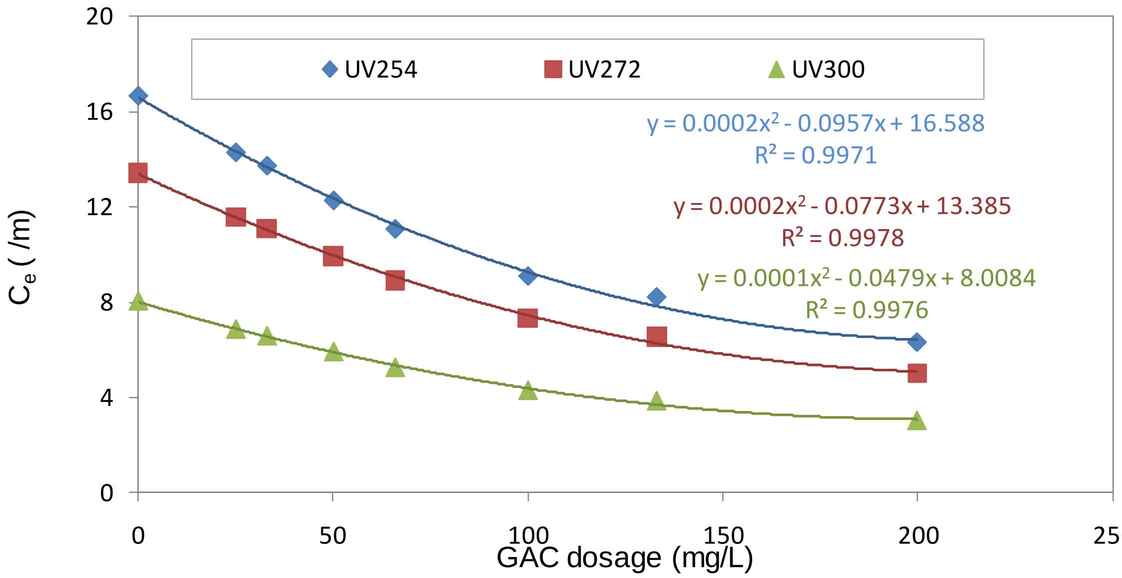


Figure 4. UV equilibrium vs. GAC dosage for the Round 3 Umzoniana water

Table 2 gives the ratios between UV_{254} and UV_{272} and, UV_{254} and UV_{300} for the Round 5 Stilfontein and Round 3 Umzoniana waters.

Table 2. Ratios between UV_{254} and UV_{272} as well as UV_{300}

GAC dosage (mg/L)	Round 5 - Stilfontein water		Round 3 - Umzoniana water	
	UV_{254}/UV_{272}	UV_{254}/UV_{300}	UV_{254}/UV_{272}	UV_{254}/UV_{300}
0	1.22	1.94	1.24	2.07
25	1.23	2.00	1.23	2.08
33	1.24	2.03	1.24	2.09
50	1.24	2.06	1.24	2.07
66	1.25	2.11	1.24	2.11
100	1.27	2.23	1.24	2.12
133	1.28	2.28	1.26	2.13
200	1.31	2.41	1.26	2.08

Table 2 demonstrates that the ratios between UV_{254} and UV_{272} were practically the same for all the GAC dosages for the Round 5 Stilfontein and Round 3 Umzoniana waters. The same conclusion was also found for the ratios between the UV_{254} and UV_{300}. The average value of the ratio between UV_{254} and UV_{272} as well as the ratio between UV_{254} and UV_{300} for all the water samples were about 1.22 (standard deviation = 0.0018) and 1.89 (standard deviation = 0.0545) respectively. Table 3 presents the removal of UV at different wavelengths for some waters. It can be seen that the percentage of UV removal is the same for the same water at the same GAC dosage for the three wavelengths.

Table 3. UV percentage removal

GAC dosage (mg/L)	Percentage initial UV Removal (%)								
	Round 1 – Loerie			Round 2 – Rietvlei			Round 4 – Olifantsvlei		
	UV_{254}	UV_{272}	UV_{300}	UV_{254}	UV_{272}	UV_{300}	UV_{254}	UV_{272}	UV_{300}
25	13	13	12	-	-	-	-	-	-
33	17	17	17	23	24	24	25	26	25
50	19	19	18	30	30	31	31	32	31
66	26	27	26	39	40	40	40	40	39
100	36	35	34	50	51	51	51	52	50
133	44	43	41	60	60	60	57	58	55
200	58	58	55	71	72	71	67	67	64

From the UV data, the Freundlich isotherms were fitted and its parameters (*K* and *n*) determined. The values of the parameters for three waters are presented in Table 4.

Table 4. Freundlich parameters for the different wavelengths

UV	Round 5 – Wiggins			Round 5 – Olifantsvlei			Round 2 – Plettenberg Bay		
	K	*n*	R^2	*K*	*n*	R^2	*K*	*n*	R^2
UV_{254}	4.1E-2	0.43	0.98	2.4E-2	0.65	0.99	7.2E-3	0.75	0.95
UV_{272}	3.9E-2	0.42	0.97	2.5E-2	0.63	0.99	7.5E-3	0.71	0.95
UV_{300}	3.0E-2	0.42	0.99	2.2E-2	0.65	0.98	5.3E-3	0.78	0.95

Table 4 shows that for each water sample, the values of the Freundlich parameters are practically the same for each of the wavelength. The average *K* values are 3.7E-2, 2.4E-2 and 6.7E-3 for Wiggins Round 5, Olifantsvlei Round 5 and Plettenberg bay Round 2 waters respectively. Similarly the values of the constants *n* are 0.42, 0.64 and 0.75 for Wiggings, Olifantsvlei and Plettenberg bay waters respectively. Based on all the facts presented it appears that the values of any of the three wavelengths can be used. In this paper the rest of the analysis will be done with the UV_{254} values because it gives the biggest number.

The Freundlich parameters of the water samples obtained with UV_{254} are presented in Table 5.

Table 5. Freundlich parameters derived from UV_{254} data

Plant name	Round 1		Round 2		Round 3		Round 4		Round 5	
	K	*n*	*K*	*n*	*K*	*n*	*K*	*n*	*K*	*n*
Umzoniana	1.2E-2	0.86	1.9E-2	0.64	1.5E-2	0.71	9.4E-3	0.88	2.3E-3	1.38
Wiggins	1.4E-2	1.03	2.2E-2	0.95	1.2E-2	1.22	5.0E-3	1.61	4.1E-2	0.43
Loerie	1.2E-2	0.75	1.2E-2	0.88	1.0E-2	0.83	1.5E-2	0.71	3.5E-2	0.32
Rietvlei	2.8E-2	0.51	2.2E-2	0.63	1.2E-3	0.83	2.2E-2	0.57	5.1E-2	0.59
Vereeniging	3.4E-2	0.41	-	-	1.5E-2	1.71	3.4E-4	2.49	1.2E-2	0.85
Olifantsvlei	2.5E-2	0.73	1.8E-2	0.79	1.6E-2	0.78	1.1E-2	0.97	2.4E-2	0.65
Stilfontein	2.8E-2	0.58	1.5E-2	0.80	1.4E-2	0.82	3.4E-2	0.46	3.0E-2	0.55
Plettenberg Bay	-	-	7.2E-3	0.75	-	-	-	-	2.4E-5	2.23

Round 1 waters were collected from February to April 2010, Rounds 2, 3 and 4 were sampled in July 2010, November 2010 and February 2011 respectively. Round 5 waters were sampled in May and June 2011.
The cells with no data mean their R^2 are very poor ($R^2 \leq 0.11$) or there is no data. The non-shaded cells are those which R^2 were very good (R^2 range 0.91 – 1.00). The shaded cells are those which the coefficients of correlation R^2 were less the 0.90. (Round 1 Loerie and Vereeniging had a R^2 of 0.80 and 0.73 respectively while the Round 3 of the Vereeniging water had a R^2 of 0.78. The lowest R^2, 0.61, for Round 4 was found with the Stilfontein water. For Round 5, the Umzoniana, Vereeniging and Plettenberg Bay waters displayed the R^2 values of 0.78, 0.83 and 0.66 respectively).
The graphical representations of *K* and *n* values are shown in Figure 5. Generally their positions show that *K* and *n* seem to be related.

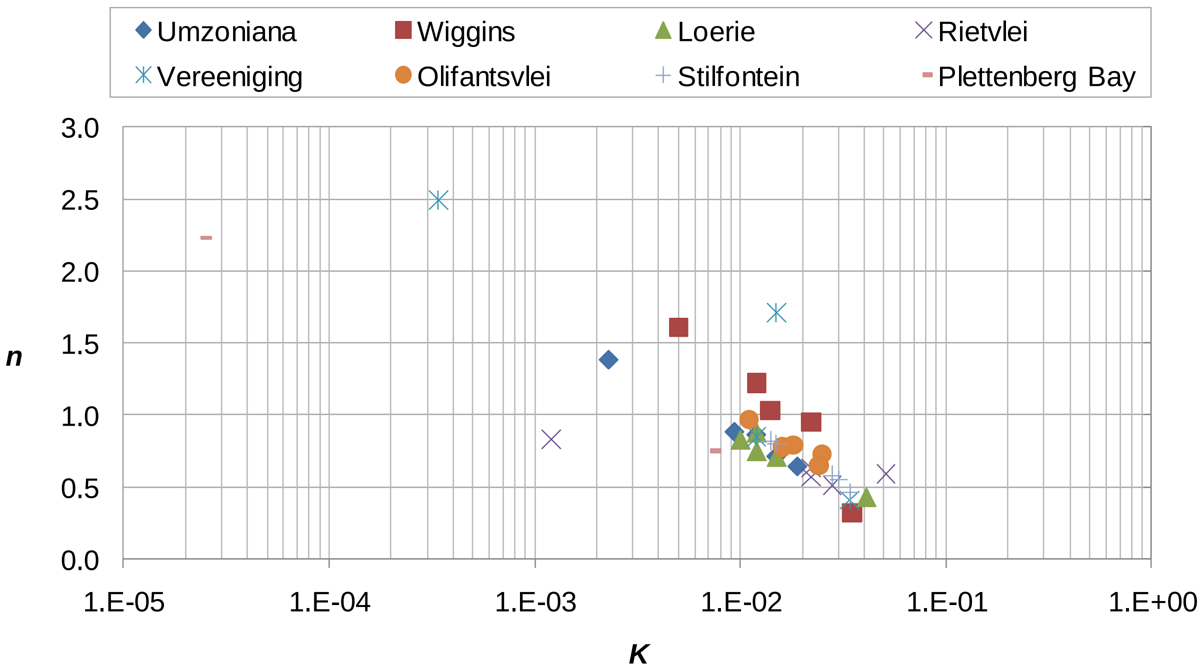


Figure 5. Graph of *n* vs. *K*

Performance criteria

The required activated carbon dosage was calculated next, i.e. the lowest carbon dosage that would meet either of the two adopted treatment goals. Table 6 represents the lowest GAC dosage M (mg/L) to meet the required criteria.

Table 6. Lowest GAC usage rate M (mg/L)

Plant name	Round 1		Round 2		Round 3		Round 4		Round 5	
	C_i	M	C_i	M	C_i	M	C_i	M	C_i	M
Umzoniana	15.8	175	14.8	147	16.7	200	19.0	248	28.2	338
Wiggins	7.0	11	6.3	2	6.1	1	7.6	18	4.9	0
Loerie	25.2	267	17.3	192	6.7	16	15.1	170	13.3	82
Rietvlei	18.4	165	17.2	164	19.2	2140	24.0	211	81.6	144
Vereeniging	19.5	170	25.4	-	20.8	30	86.9	34	28.7	219
Olifantsvlei	13.1	77	16.4	140	15.8	151	15.4	150	14.3	108
Stilfontein	16.4	131	15.3	148	18.5	186	33.7	207	14.0	100
Plettenberg Bay	-	-	30.4	466	43.8	-	74.5	-	49.3	2329

The shaded cells are those where the 6 /m criterion was reached first (i.e. before the 65% removal of initial UV). The non-shaded cells are those where the 65% removal was reached before the 6 /m criterion. The data from Table 6 suggest that when the initial UV (C_i) is less than about 17 /m, the absolute level of 6 /m is reached first but when *Ci* is greater than about 17 /m, the 65% initial UV removal criterion is reached before. It can also be observed that the GAC usage rate does not depend on the initial UV only because some waters (i.e. Round 1 Umzoniana and Round 3 Olifantsvlei waters) with almost the same initial UV_{254} (15.8 /m) have very different GAC usage rates (175 and 157 mg/L respectively).

The graph of initial UV_{254} versus the lowest GAC dosage is presented in Figure 5. It can be concluded from this graph that some waters display a clear relationship between the activated carbon dosage and the initial UV_{254}. It is, therefore, possible to predict the usage rate of some waters but, for others it is difficult to predict.

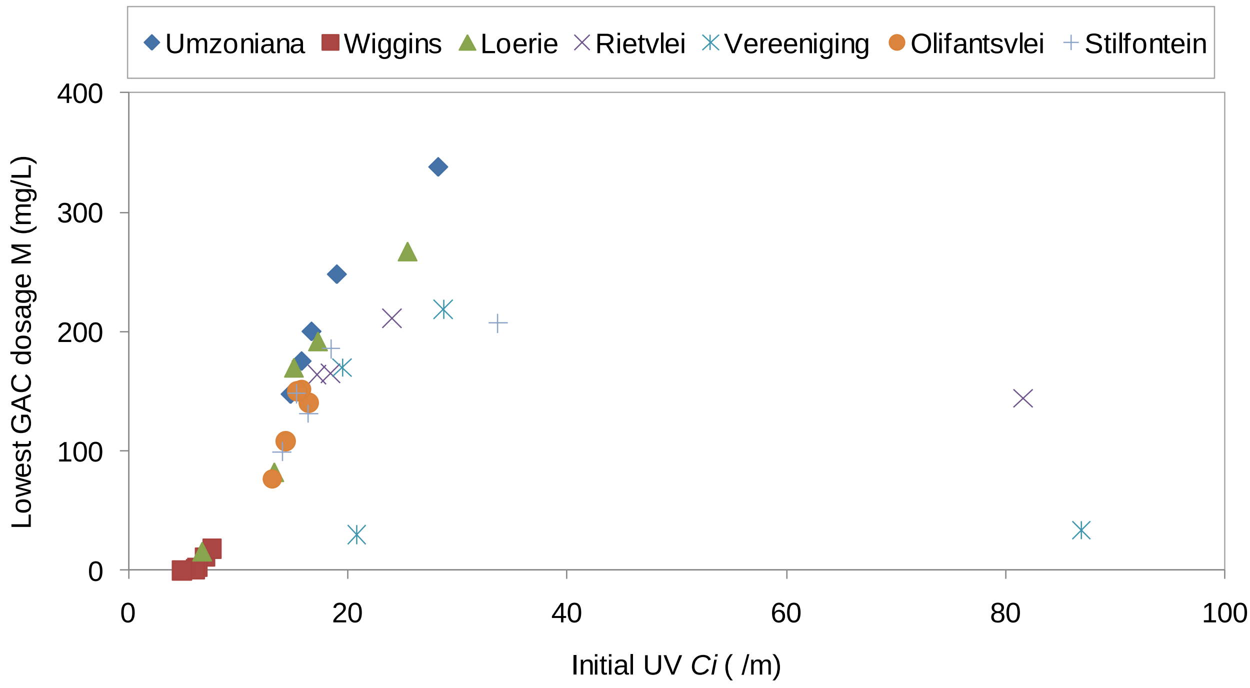


Figure 5. GAC dosage vs. initial UV

CONCLUSION

The aim of the paper was to investigate the removal of NOM by measuring UV_{254}, UV_{272} and UV_{300} for a large range of South African surface waters by the use of granular activated carbon in batch experiments. The performance of activated carbon was considered over a large range of dosages in order to detect some general patterns – not to suggest practical or economical values. The data for the three wavelengths were compared first:

- It was found that at all the three wavelengths the percentage of NOM removal was practically the same. The differences amongst these wavelengths can therefore not be used to characterise the differences in NOM composition of the different sources.
- The UV_{254} values were on average 1.22 and 1.89 times greater than the UV_{272} and UV_{300} data respectively. The UV_{254} data were chosen for the rest of the analysis, as it is the most popular wavelength used in the published literature.

The Freundlich equilibrium equation was then applied to UV_{254} data only and two criteria were also investigated to find the lowest GAC dosage. It was find that:

- The Freundlich parameters *K* and *n* are generally related – higher *K* values correspond to lower *n* values.
- If the initial UV is less than about 17 /m, the criterion of 6 /m limit was reached first, if not then the criterion of 65% UV removal was reached before the 6 /m criterion.
- The GAC usage rate was not only dependent on the initial UV of the water but also on the composition (nature and concentration) of the NOM indicating a need for a better NOM characterization.

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