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Adsorption of Heavy Metals from Matured Leachate by *Gracilaria.Sp* Extract.

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Abstract

Municipal Solid Waste (MSW) landfill leachate is a serious environmental issue and treated using various methods, mostly involving biological treatment. In the present study, *Gracilaria.sp* extract was used for the treatment of matured landfill leachate containing heavy metals (As, Fe, Ni, and Cd) and Formaldehyde (FA). Specifically, this study was carried out to investigate the adsorption rate of heavy metals and formaldehyde by *Gracilaria.sp* extract. Four variants of *Gracilaria.sp* extract were used in the present investigation; 10, 20, 50, and 100 mg/L. The process performance of the treatment was characterized in terms of pollutant removal before and after the treatment process. Results showed that high adsorption of heavy metals were observed compared to the FA compound. Fe was absorbed at the fastest rate as it was not detected in the leachate sample after day one. The FA was removed completely after ten days at a gel concentration of 100 mg/L. Similar trend was also observed for the Cd where it was completely removed after ten days (at 50 mg/L *Gracilaria.sp* extract). However, Ni was not removed even after ten days, suggesting more time was required for the treatment process. As was removed in five days at a gel concentration of 50 mg/L.

Keywords: *Gracilaria.sp* extract, Jar-test, Heavy metals, Formaldehyde

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INTRODUCTION

Landfills are important infrastructure along urban development and the generation of leachate is an unavoidable condition. The actual landfills' function is to store and manage solid waste effectively. The operations involving landfill leachate has grown to be a threat to the natural environment [1]. The leachate made by the rain along with exterior normal water movement in the landfill, through the time interval, and percolated and collected at the bottom of the landfill. The leachate can be a probable hazard to the good quality of groundwater. It can also be toxic to aquatic life. At the moment, leachate generated in Malaysia is treated by biological processes such as using the aerobic ponds.

Leachates are viscous black or brownish liquid rich in organic matter. The landfill leachate contains many chemicals, for instance, excessive phosphate, nitrates along with other metal salts, also with major precious metals or heavy metals [1]. A typical leachate contains Chemical Oxygen Demand (COD) of 4,000 – 20,000 mgL^{-1} depending on the maturity of the leachate. The permissible level of COD in wastewater as per Standard A and B are from 50-100 mgL^{-1} (Environmental Quality Regulations-Industrial Effluents, 2009). Since leachate contains relatively complex substances, a combination of treatment method is required. The major constraint is the heavy metals found in leachate that can cause toxicity to the environment, flora and fauna.

Gracillaria.sp belongs to the phylum rhodophyta or red seaweed group, and the taxonomy of the species are as follow; Kingdom: Plantae; Phylum: Rhodophyta; Class: Florideophyceae; Order: Gracilariales; Family: Gracilariaceae; Genus: *Gracilaria* and Species: *changgi* [2]. It can absorb heavy metals because it contains alginate and carrageenan. Glycoside bond in alginate have a higher capacity to bind or absorb metals than any other derivatives of seaweed [2]. The sulfide in carageenan group in *Gracillaria.sp* is responsible to attract and bond with positively charged metal ions [3]. *Gracillaria.sp extract* also contains polyphenols which aids in the adsorption of formaldehyde [4].

The aim of this study was to treat the heavy metals and FA containing matured leachate by *Gracilaria.sp* extract. The treatment performance of was characterized in terms of As, Fe, Ni, and Cd and FA removal efficiency.

MATERIALS AND METHODS

Matured Landfill Leachate

The matured leachate was obtained from an ageing leachate treatment pond in Jinjang Transfer Station, Selayang, Selangor and had the following characteristics: pH=8.0, COD=2500mgL^{-1}, Arsenic=9.40mgL^{-1}, Iron=12.8mgL^{-1}, Nickel=0.50mgL^{-1}, Cadmium=0.43mgL^{-1} and Formaldehyde=8.6mgL^{-1}.

Sampling and Analysis

The FA was analyzed using a High-Performance Liquid Chromatography (HPLC) 1220 Infinity LC by Agilent Technologies with the following conditions: Column = Zorbax, C18, 4.6 mm x 250 mm ID, 5 µm particle size; Mobile phase = 70/30 acetonitrile/water (v/v); Flow rate = 1.2 $mLmin^{-1}$; Detector = Ultraviolet, operated at 360 nm; and Injection Volume = 20 µL. The heavy metals were analyzed using an Atomic Absorption Spectroscopy (AAS) model AA-7700 Shimadzu according to the Environmental Protection Agency (EPA) manual SW-846.

Jar-Test

The dried local seaweed species of *Gracilaria.sp* was made into gels of different concentrations. This was made by adding various mass (4g, 8g, 20g and 40g) of dried seaweed into 0.4 L of water, and the mixture was boiled and cooled in a cylindrical shaped mould. The gels of different concentrations (10, 20, 50 and 100mg/L) was placed into 1 L of matured leachate before the jar-test for ten days. The change in concentrations of heavy metal and formaldehyde were measured every 24 hours using the AAS and HPLC.

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RESULT AND DISCUSSION

According to the Environmental Quality Act, 1974, under the Malaysia Environmental Quality (Sewage and Industrial Effluents) Regulations (2000), the following standards (Standard B) are required for the discharge of effluent; As=0.10, Fe=5.0, Ni=1.0, Cd=0.02 and FA=2.0 mg/L (Table 1). Any concentrations above the prescribed standard are regarded as illegal and considered harmful to the environment. Table 1 illustrates the initial concentrations and removal efficiency of the heavy metals and FA in the matured landfill leachate.

Table 1: *Gracilaria.sp* extracts jar-test results

Parameters (mg/L)	Standard B (mg/L)	Initial Conc. (mg/L)	*Gracilaria* Gel Conc. (mg/L)	Jar-test			Max Removal (%)
				1d	5d	10d	
As	0.10	**9.4**	10	6.83	4.04	ND	100 in 10d
			20	3.00	2.22	ND	100 in 10d
			50	8.23	ND	ND	100 in 5d
			100	1.28	ND	ND	100 in 5d
FA	2.0	**8.6**	10	7.69	5.23	4.92	42.8 in 10d
			20	6.90	6.59	5.44	36.7 in 10d
			50	6.19	4.02	2.72	68.4 in 10d
			100	5.48	0.73	ND	100 in 10d
Fe	5.0	**12.8**	10	ND	ND	ND	100 in 1d
			20	ND	ND	ND	100 in 1d
			50	ND	ND	ND	100 in 1d
			100	ND	ND	ND	100 in 1d
Ni	1.0	**0.50**	10	0.13	0.11	0.09	82 in 10d
			20	0.13	0.10	0.05	90 in 10d
			50	0.13	0.08	0.01	98 in 10d
			100	0.13	0.08	0.05	90 in 10d
Cd	0.02	**0.43**	10	0.14	0.08	0.04	90.7 in 10d
			20	0.12	0.03	0.01	97.6 in 10d
			50	0.02	<0.01	ND	100 in 10d
			100	0.08	ND	ND	100 in 5d

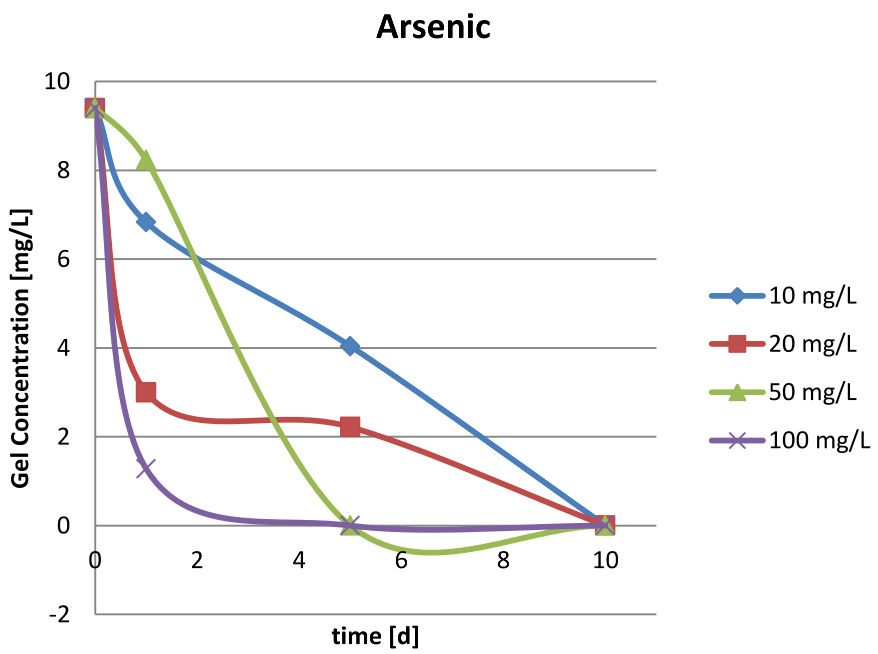

Figure1. Arsenic removal by *Gracilaria.sp* extract

It can be seen that, Fe was completely removed in the treatment system when the *Gracilaria.sp* extract concentrations were 10, 20, 50, and 100 mg/L. There was no detection of the Fe even at 24hr experimental period. The adsorption capacity of the heavy metals were in the following order; As > Ni > Cd > Fe. In addition, alkaline condition also contributed to the high adsorptive property of the heavy metals (pH of leachate =8.0) [4]. Fourier Transform Infra-Red (FTIR) Spectroscopy result reveals (result not given) that *Gracilaria.sp* extract contains high amount of Glycoside bond (C=O), hydroxide (O-H) and sulfide bonds (R-S) [4]. Fe is also capable of forming bonds with various chelating agents such as sulfides, glycosides, and hydroxide. The high availability of metal chelating bond and high competitiveness of Fe (reactivity) explains the efficiency of the adsorption process.

Figure 1 illustrates the As removal profile by *Gracilaria.sp* extract and can be seen that high removal efficiency was noted at a gel concentration of 100 mg/L (87.2%) followed by 50 mg/L > 20 mg/L > 10 mg/L. On day five, 100 and 50 mg/L of gel concentration achieved 100% removal of As whereas in 20 and 10 mg/L, it was below 80%. However, on the tenth day, the removal efficiency was 100% at a gel concentration of 20 and 10 mg/L. As is very toxic heavy metal which are normally found in ground water sources and mercury mines [5]. Despite being the least reactive, As could be adsorbed due to the presence of sulfide bonds in the *Gracillaria.sp extract* [6].

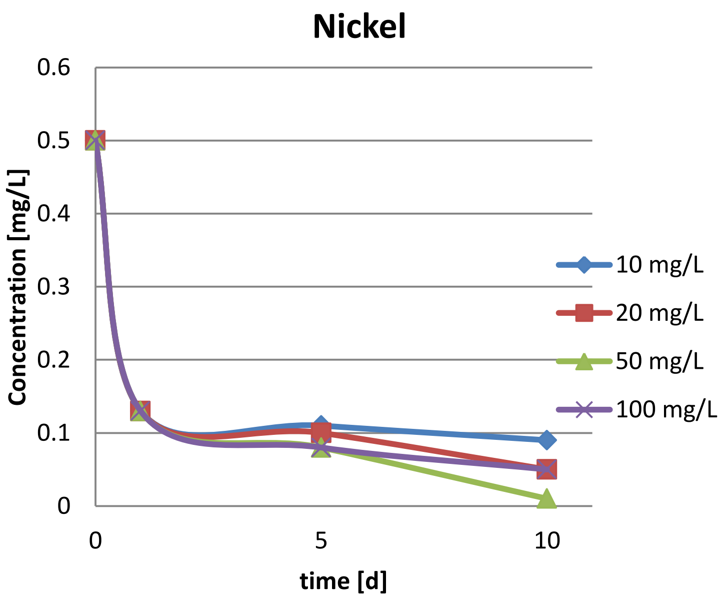

Figure 2: Nickel removal by *Gracilaria.sp* extract

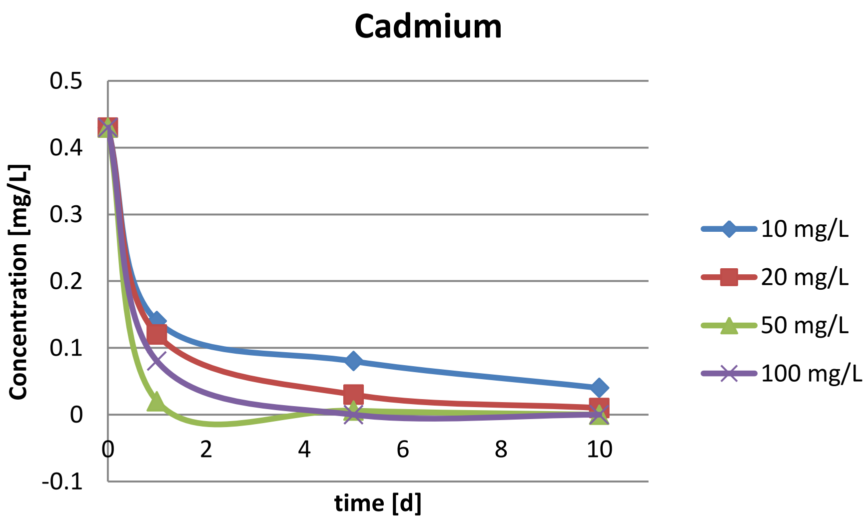

Figure 3: Cadmium removal by *Gracilaria.sp* extract

Figure 2 illustrates Ni removal by *Gracillaria.sp* extract by jar-test at different concentrations. At day one, no significant difference could be observed in the removal efficiency (all were 74% removal). Similar trend was also observed in day five where the removal was 78%, 80%, 84% and 84% for the gel concentration of 10, 20, 50 and 100 mg/L, respectively. On the tenth day, 98% Ni was removed at a gel concentration of 50 mg/L, signifying high removal during this period. Ni in the landfill leachate may have originated from coated metal waste. It may have also originated from Ni/Cd batteries which are not properly disposed [7]. Ni removal by *Gracillaria.sp* extract was possible due to sulfide and hydroxide bond [8].

Figure 3 illustrates the Cd removal profile and showed high removal at a gel concentration of 50 mg/L (95.4%) followed by 100 mg/L (81.4%), 20 mg/L (72.1%), and 10 mg/L (67.4%). On day five, complete removal of Cd was achieved at a concentration of 100 mg/L. The removal efficiency at a concentration of 50, 20, and 10 mg/L was 98.0%, 93.0%, and 81.4%, respectively. Source of origin of the Cd in leachate could be from the textile products, Ni/Cd batteries, and electronic gadgets [9]. As the pH of the leachate was 8, Cd adsorption may have dominated by the hydroxide bonds [2].

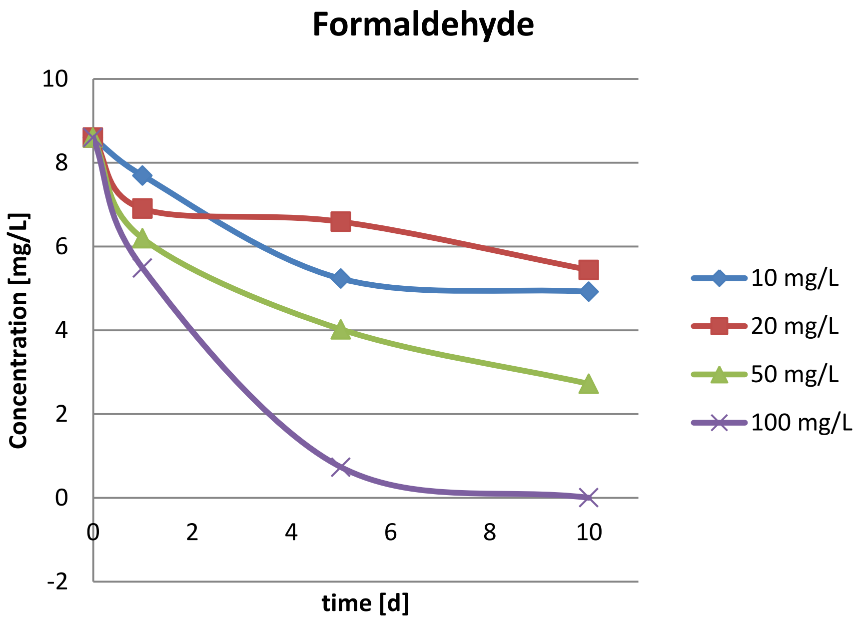

Figure 4: Formaldehyde removal by *Gracilaria.sp* extract

The adsorption of FA by *Gracillaria.sp* extract shows a significant difference throughout the ten days of the jar-test (Figure 4). On day one, FA removal in gel concentrations of 100, 50, 20 and 10 mg/L was 36.3%, 28.0%, 19.8% and 10.6%, respectively. On day five, it was 91.5%, 53.3%, 23.4% and 39.2% and on day ten it was 100.0%, 68.4%, 36.7% and 42.8%. The major source of origin of FA in leachate was makeup items, plastics, and household cleaning products [10]. Compared to the heavy metal removal efficiency, FA showed less successful treatment using the gel (Figure 4). This could be due to the reason that FA is a large molecule, and it is less reactive compared to the other heavy metal species studied in the leachate. Thus, it has to compete with the heavy metal ions to be bound with alginates. Another adsorbent molecule found in *Gracillaria.sp* extract for FA is polyphenols. The less presence of this compound compared to alginate may have affected the adsorption capacity of FA [2].

From the overall observation, *Gracillaria.sp* extract of 100 mg/L was most suitable for the treatment of heavy metal and FA in ten days. However, a gel concentration of 50 mg/L was more effective for the adsorption of heavy metals (Fe, Ni, Cd and As), especially after five days of the jar test. For Cd and As treatment, the optimum adsorption period and gel concentration was five days and 50 mg/L, respectively.

CONCLUSIONS

From this study, it was found that *Gracillaria.sp* extract is the most suitable material for the adsorption of As, Cd, Fe and Ni and FA. The adsorption of heavy metals in leachate was due to the presence of glycoside bonds in alginate, sulfide bonds carrageenan, polyphenols and hydroxide bonds. The optimum *Gracillaria.sp* extract was found at a concentration of 100 mg/L and the ideal adsorption period was ten days.

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REFERENCES

[1] Malyuba AD, Hani AQ, Hatem A. J Environ Prot 2013; 2: 344-352.
[2] Plazinski W. Adv Colloid Interfac 2013; 197-198: 58-67.
[3] Stronach SM, Rudd T, Lester JN. Anaerobic Digestion Processes in Industrial Wastewater Treatment. Springer Verlag, Berlin, 1986.
[4] Gajski G, Orescanin V, Vrhovac VG. Ecotox Environ Safe 2012; 78: 253–259.
[5] Varank G, Demir A, Top S, Sekman E, Akkaya E, Yetilmezsoy K, Bilgilil S. Sci Total Environ 2011; 409: 3183–3196.
[6] Kurniawan AT, Lo WH, Chan GYS. J Hazard Mater 2006; B129: 80–100.
[7] Wiszniowski J, Rober D, Surmacz-Gorska J, Miksch K, Weber JV. Environ Chem Lett 2006; 4: 51–61.
[8] Lopez de Morais J, Peralta Zamora P. J Hazard Mater 2005; B123: 181–186.
[9] Sletten RS, Benjamin MM, Horng JJ, Ferguson JF. Water Res 1995; 29: 2376-2386.
[10] Foo KY, Lee LK, Hameed BH. Chem Eng J 2013; 223: 604-610.