



Experimental studies on removal of microcystin-LR by peat

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ARTICLE INFO

Article history:

Received 29 March 2010

Received in revised form 7 July 2010

Accepted 15 August 2010

Available online 21 August 2010

Keywords:

Peat
Microcystin-LR
Biosorption
pH effect
Desorption

ABSTRACT

Cyanotoxins have caused worldwide concerns for their eclectic occurrence and toxic effects, which led to an intensive search of cost-effective techniques for their removal from contaminated waters. A range of biomaterials was tested for their efficacy to adsorb a potent cyanotoxin, microcystin-LR (MCLR). Among these sorbents, peat showed the maximum efficacy to sequester MCLR. The BET (Brunauer–Emmett–Teller) surface area of peat was found to be 12.134 m²/g. The pH of the reaction media played a significant role in removal of MCLR; maximum adsorption occurred at pH 3. Kinetic studies showed that the adsorption of MCLR onto peat was a rapid process. The adsorption capacity (Q_{\max}) from the Langmuir model was found to be 255.7 μg/g at pH 3. Among various desorption media studied, strong alkali (2N NaOH) showed highest desorption (94%).

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1. Introduction

Microcystins (MCs) are a family of cyanobacterial toxins produced by at least six genera of cyanobacteria including *Microcystis*, *Oscillatoria*, *Nostoc* and *Anabaena*, which are monocyclic heptapeptides composed of seven amino acids including an unusual amino acid (2S, 3S, 8S, 9S)-3-amino-9-methoxy-2,6,8-trimethyl-10-phenyldeca-4,6-dienoic acid (Adda) that is essential for the expression of their biological activity [1,2]. MCs are produced intracellularly, and their occurrence in natural water bodies has been reported worldwide [3–5]. These toxins get released into water bodies due to both natural toxin release caused by natural biological process of cell lysis and by artificial induction through cell destruction in treatment processes [6]. MCs are known for their rapid activity and acute lethal toxicity [7], and damage liver and induce tumour promoting activity through the inhibition of protein phosphatases [8]. Multiple human deaths in Brazil after haemodialysis using water containing microcystins were reported in Ref. [9]. Among 60 molecular variants of MCs isolated till date, MCLR, a most hydrophobic variant containing leucine and arginine, is considered to be the most commonly occurring and most lethal toxin [10]. A provisional safety guideline of 1.0 μg/L MCLR in drinking water was recommended by WHO [11]. Toxicity of MCLR based on intraperi-

toneal LD₅₀ in laboratory mouse or rat injections was found to be 50 μg/kg [12].

Generally, MCLR is a very stable toxin in the water bodies and resistant to be removed from drinking water by traditional water treatment technology [11,13]. Several strategies for the removal of MCLR from water have been investigated. Water treatment technologies including chemical coagulation, flocculation and sand filtration may not only be inefficient but may also enhance the release of cyanotoxins including MCLR contained within the producer-cells, thus requiring further treatment of the water for drinking purposes [14]. Chlorination has been shown in several studies to be effective in deactivating the producer-cells and partially effective in removing the toxin as such. However, chlorination has a disadvantage of generating toxic by-products of toxins such as trihalomethanes [15]. Pre-ozonation followed by rapid sand filtration showed a satisfactory removal of the toxin in a full-scale drinking water treatment [16]. The major disadvantage of this technology is that the cost-factor is too high which precludes its use on a regular basis in a huge city-water supply from a reservoir. Photo-irradiation using UV radiation proved to be an effective treatment technology but its installation and maintenance costs are very high [17]. Adsorption seems to be an effective and cheaper technology, comparatively. Some researchers have reported the possibility of using activated carbon for removal of MCLR and related toxins [18–21]. Even though activated carbon adsorption poses to be an attractive and cheaper technology available, the need to replenish the column with fresh carbon after its saturation makes it still economically not feasible. Thus a natural and environment-friendly sorbent could provide a cost-effective solution. There are only two

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reports available on successful adsorption of MCLR onto natural materials which include clay particles and pumice [22,15].

Peat is a natural material containing lignin, cellulose and humic acid as its major constituents [23]. Peat is generally defined as young coal, organogenic sedimentary rock in the first stage of coalification and ranks as one of the lowest grades of solid carbonaceous fuels [24]. According to the incomplete list of peat resources, ~77% of peat deposits occur in Canada and the USA and 7.5% in Scandinavia, where as in southern hemisphere, the richest deposits are in Indonesia [25]. This natural material is known to have excellent ion-exchange properties similar to natural zeolites [26]. Thus, the use of peat as a sorbent has received increasing attention. Apart from being naturally abundant and inexpensive, peat possesses several characteristics that make it effective for adsorption or ion-exchange operations [26]. To date, the use of peat as sorbent for various metal ions and dyes has been well documented [24,26,27]. However, its effectiveness for removal of cyanotoxins has never been evaluated.

The objective of this work was to assess the uptake capacity of various naturally occurring materials and to optimize the experimental conditions for achieving the maximum uptake of MCLR. Specifically, crab shell, sugarcane baggase, marine algae, chitin and peat were tested for their uptake efficacy of MCLR. Out of the tested materials, peat showed the best performance for the adsorptive removal of MCLR. The influence of operating parameters such as pH and contact on the adsorption capacity of peat was studied, followed by the optimization of these parameters in order to obtain a maximum removal of MCLR from the aqueous phase. The possibility of regeneration of used peat was also examined.

2. Materials and methods

2.1. Peat preparation and characterization

Peat was collected from Sungai Sembilan peat deposit; a sub-province located 200 km away from the city of Dumai in Sumatra, Indonesia. The sub-surface layer of the peat collected from the site was dried in sunlight for 3 days and further dried in an oven at 60 °C for 2 days. The dried peat material was then ground and sieved through a 150 µm sieve, prior to its usage in experimental studies. Specific surface area and total pore size distribution were determined using the nitrogen adsorption technique using a Brunauer–Emmett–Teller (BET) NOVA-3000 version 6.07 micropore analyzer. The surface area and total pore volume were calculated by BET and Barret–Joyner–Hallenda (BJH) methods, respectively [24]. Elemental composition analysis of peat was performed using a Perkin–Elmer PE 2400 series II CHNS/O micro-analyzer. pH_{zpc} (pH zero point charge) of peat was determined as follows: 50 mL of a 0.01 M NaCl was placed in a closed Erlenmeyer flask and its pH was adjusted to a value between 2 and 12 using 0.1 M HCl or NaOH. Then, 0.15 g of each peat sample was added and the final pH was measured after 2 days under agitation at 25 °C. The pH_{zpc} is the point where the curve pH_{final} versus $pH_{initial}$ crosses the line $pH_{initial} = pH_{final}$ [24].

2.2. MCLR preparation and quantification

MCLR standard was purchased from Alexis Biochemicals (Switzerland). HPLC grade methanol and formic acid were obtained from Tedia (OH, USA) and Merck (Germany), respectively. Milli-Q water (18 MΩ) used in all experiments was obtained through a Milli-Q (Millipore, Bedford, MA) water purification system. A stock solution of 1000 mg/L of MCLR was prepared using methanol. A standard curve was prepared for concentrations ranging from 5 to 1000 µg/L. The standard curve was obtained before every set of experiments to ensure minimal system error. The determination of

MCLR was carried out on a LC–MS–MS system which comprised of Agilent 1100 series HPLC system (Agilent Technologies, Germany) with a vacuum degasser, quaternary pump, autosampler and thermostated column compartment, coupled to a Micromass (Manchester, UK) Quattro Micro triple quadrupole mass spectrometer, equipped with an electrospray interface. The separation was achieved on a Zorbax Extend-C18 5 µm, 2.1 mm × 150 mm (Agilent technologies, Germany). Injection volumes were 10 µL. The mobile phase consisted of 0.1% formic acid (solvent A) and methanol (solvent B). A gradient elution was used: starting with water:methanol at 90:10 from 0 to 6 min, and to 5:95 up to 10 min before returning to the original conditions to re-equilibrate the system.

The capillary voltage was set at 89.00 V and the cone voltage at 4.00 V. The desolvation gas (nitrogen) temperature and flow-rate were set at 350 °C and 6151/h, respectively. The ion source temperature was set at 120 °C. The instrument was operated in the positive ion mode. MCLR was monitored by using the instrument in the MRM mode (m/z 995.6 and fragment ion at 135.1).

2.3. MCLR sequestration studies

MCLR sequestration experiments were carried out by agitating 50 mg of peat with 10 mL of 100 µg/L MCLR solution under various pH (1–7) at 200 rpm, 30 °C in a thermostated rotary shaker for 12 h. The MCLR solutions were separated from the adsorbent by centrifugation at 5000 rpm for 5 min and quantified for MCLR concentrations. The solution pH was measured using a pH meter (Eutech, cyberscan PCD6500). Kinetic experiments were conducted at various concentrations of MCLR ranging from 100 to 500 µg/L and pH at 3 with adsorbent dosage fixed at 50 mg/10 mL. The samples were collected at different pre-determined time intervals and the remaining MCLR estimation was conducted as describe above. Similarly, adsorption isotherm experiments were conducted at various initial concentrations of MCLR (100–1000 µg/L) at pH 3 with peat dosage, 50 mg/10 mL.

2.3.1. Adsorption isotherm and kinetic modelling

The experimental adsorption kinetic data were modelled using pseudo-first- and pseudo-second-order kinetics. The non-linear forms of pseudo-first- and pseudo-second-order models are shown as Eqs. (1) and (2), respectively [28]:

$$Q_t = Q_e(1 - \exp(-k_1 t)) \quad (1)$$

$$Q_t = \frac{Q_e^2 k t}{1 + Q_e k t} \quad (2)$$

where Q_e is the amount of MCLR sorbed at equilibrium (µg/g), Q_t is the amount of MCLR sorbed at time t (µg/g), k_1 is the first-order equilibrium rate constant (1/min) and k_2 is the second-order equilibrium rate constant (g/mg min).

Langmuir model was used to describe the non-linear equilibrium relationship between the solute sorbed onto the sorbent (Q) and that left in solution (C_f). The model equations can be represented as:

Langmuir model:

$$Q = \frac{Q_{max} b C_f}{1 + b C_f} \quad (3)$$

Freundlich model:

$$Q = K_F C_f^{1/n} \quad (4)$$

where Q_{max} is the maximum MCLR uptake (µg/g) and b_L is the Langmuir equilibrium constant (L/mg), K_F is the Freundlich constant (1/g) and n is the Freundlich constant.

The residual root mean square error (RMSE) and the Chi-square test were also used to measure the goodness-of-fit. RMSE can be defined as:

$$\text{RMSE} = \sqrt{\frac{1}{m-2} \sum_{i=1}^m (Q_i - q_i)^2} \quad (5)$$

where Q_i is the observation from the batch experiment, q_i is the estimate from the isotherm for corresponding Q_i and m is the number of observations in the experimental isotherm. The smaller RMSE value indicates the better curve fitting.

The Chi-square test can be defined as:

$$\chi^2 = \sum_{i=1}^m \frac{(Q_i - q_i)^2}{q_i} \quad (6)$$

If data from model are similar to the experimental data, χ^2 will be a small number.

2.4. Peat regeneration studies

Peat regeneration studies were carried out with MCLR-laden peat obtained from MCLR uptake studies using 500 $\mu\text{g/L}$ MCLR in 100 mL and 500 mg of peat agitated at 200 rpm for 12 h at pH 3. MCLR-laden peat was removed from MCLR solution by vacuum filtration, gently washed with deionized water to remove un-adsorbed MCLR and dried at room temperature for 24 h. After drying, one set each of MCLR-laden peat sample was resuspended in series of Erlenmeyer flasks containing 10 mL of deionized water adjusted to pH 2–13 using 1N HCl or NaOH and agitated for 12 h. In a similar manner, desorption of MCLR from peat was also carried out using 100% ethanol, methanol, acetonitrile and 1N NaOH.

Milli-Q water (18 M Ω) obtained through Milli-Q (Millipore, Bedford, MA) water purification system was used in all the experiments.

2.5. SEM and FT-IR analysis

Scanning electron microscopy (SEM) of peat before and after adsorption was carried out using JEOL, JSM-5200 (Japan) scanning electron microscope. The images of the peat were then captured at various magnifications using an electron beam high voltage of 15 kV at a 45° tilt on left side. To obtain the IR spectra the peat samples were dried overnight at 60 °C before and after adsorption. Approximately 0.1 g of the peat was mixed with 0.9 g of KBr and pressed into a tablet form by pressing the ground mixed material with the aid of a bench press. The resulting pellet was transparent and was used to test the surface functional groups by IR spectroscopy (Bio-Rad, USA) where it was scanned between 4000 and 400 cm^{-1} at a resolution of 4 cm^{-1} .

3. Results and discussion

3.1. Screening of sorbents

We studied the MCLR sequestration efficacy of a range of natural materials (crab-shell, chitin, sugarcane bagasse, marine alga *Ulva* and *Sargassum* and peat). In addition, two ion-exchange resins (ALXD 4 and ALX 47) were also evaluated. Among the sorbents studied, peat showed the maximum sequestration of MCLR (Fig. 1). Interestingly, the sequestration efficacy of peat was even higher than the ion-exchange resins studied. This can be attributed to the inimitable nature of peat. Peat is rich in organic content which in turn is rich in surface functional groups [29]. In addition, peat is also porous compared to other adsorbents used in the present study,

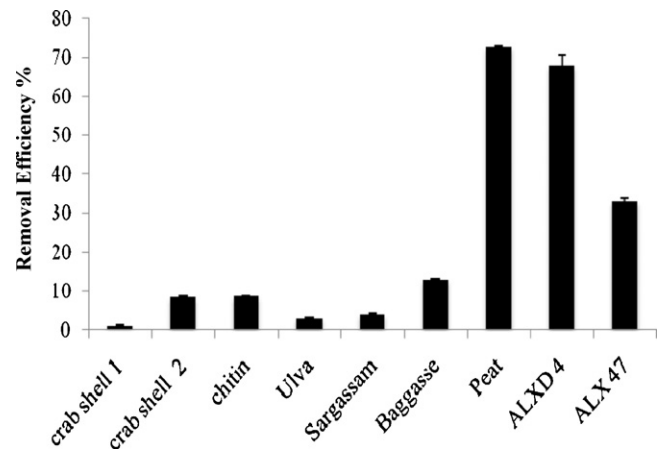


Fig. 1. Screening of various biomaterials to remove MCLR.

thus ion pairing mechanism coupled with pore-diffusion makes peat a more efficient material for sequestering MCLR.

3.2. Characterization of peat

The surface area, pore volume and percent organic matter are listed in Table 1. The surface area was 12.134 m^2/g , which is comparable to peat of various other origins [27,30]. However, Ip et al. [31] reported a very low surface area for the peat studied. The average micropore size of the peat used in the present study was 1.8 nm. Thus, a careful interpretation of MCLR molecule and the average pore size of peat revealed that MCLR has the capability to enter the micropores of peat. The maximum possible length of MCLR molecule at any angle is 2.94 nm (Fig. 2) and the smallest is around 1.4 nm, which confirms the possibility of MCLR entering the micropores of peat. As described earlier, this is one major reason for peat to pose as an efficient candidate for MCLR sequestration. The morphology of peat before and after MCLR sequestration was studied using SEM images. High porous nature of the peat was very evident from the SEM micrograph (Fig. 3).

The FT-IR spectra of peat before and after sorption of MCLR are shown in Fig. 4. No major difference in adsorption bands was noticed before and after sorption. The strong adsorption bands at 1629.5 and 1540.2 cm^{-1} are characteristic of the amide I and II [32], respectively. The adsorption bands at 2846.9 and 2916.4 cm^{-1} show the presence of fatty acids/wax in peat samples. The absorption bands between 1200 and 900 cm^{-1} could be assigned to the complex stretching vibrations of polysaccharides [32,33]. The adsorption bands at 1719.9 and 1260.72 cm^{-1} represent the C=O stretch of COOH or COOR from carboxylic acids and C–O stretching indicative of lignin backbone [34]. Artz et al. [32] illustrated that the adsorption band at 1427 cm^{-1} is a clear representation of symmetric C–O stretch of a carboxylate/carboxylic structure (humic acids). These absorption bands showed a typical FT-IR spectrum of a peat sample.

Table 1
Physico-chemical properties of peat.

Parameter	Value
pH _{ZPC}	6.56
Organic matter (%)	92.5
C (%)	50.7
H (%)	6.3
N (%)	1.5
BET surface area (m^2/g)	12.134
Average pore dia (nm)	13.13
Average micropore dia (nm)	1.8

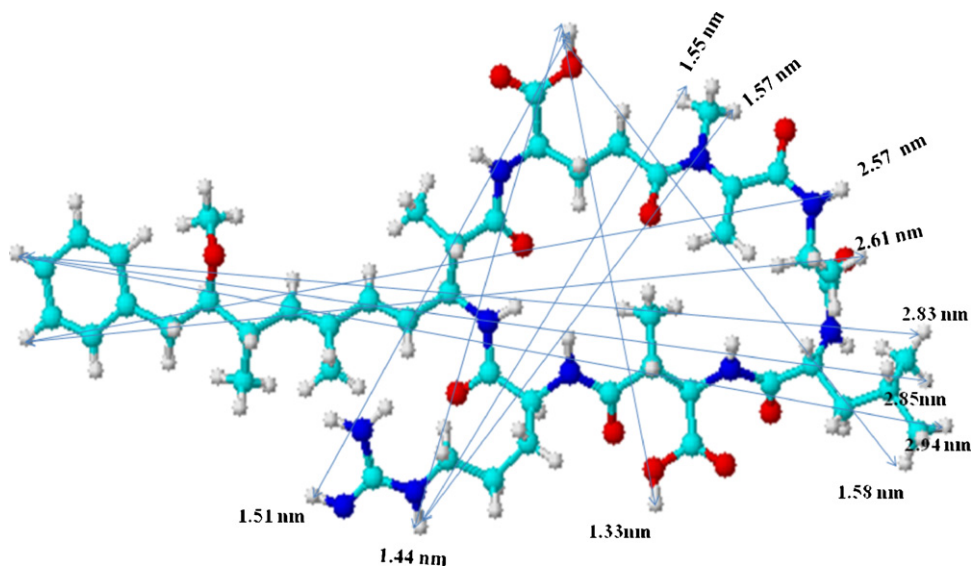


Fig. 2. Three-dimensional structure of MCLR molecule.

3.3. Effect of pH

Batch equilibrium adsorption experiments were performed at different pH values ranging between 1 and 9. A maximum adsorption was noticed at pH 3. Below pH 3, there was a rapid decrease in adsorption whereas above pH 3, adsorption gradually decreased (Fig. 5). Huang et al. [21] reported that an electrostatic repulsion between neighbouring negatively charged sites that cause stretch-

ing out of the molecules of MCLR is decreased with decreasing pH. As a result, MCLR molecules may become smaller in size due to the tendency to coil that reduces overall molecular dimensions [21]. Furthermore, the hydrogen bonds can also be formed between the coiled molecules and carbon surface charges at low pH, which lead to increased adsorption of MCLR.

Since the structure of microcystins contains numerous ionizable groups, the overall charge on the toxin is pH dependent. Maagd et al.

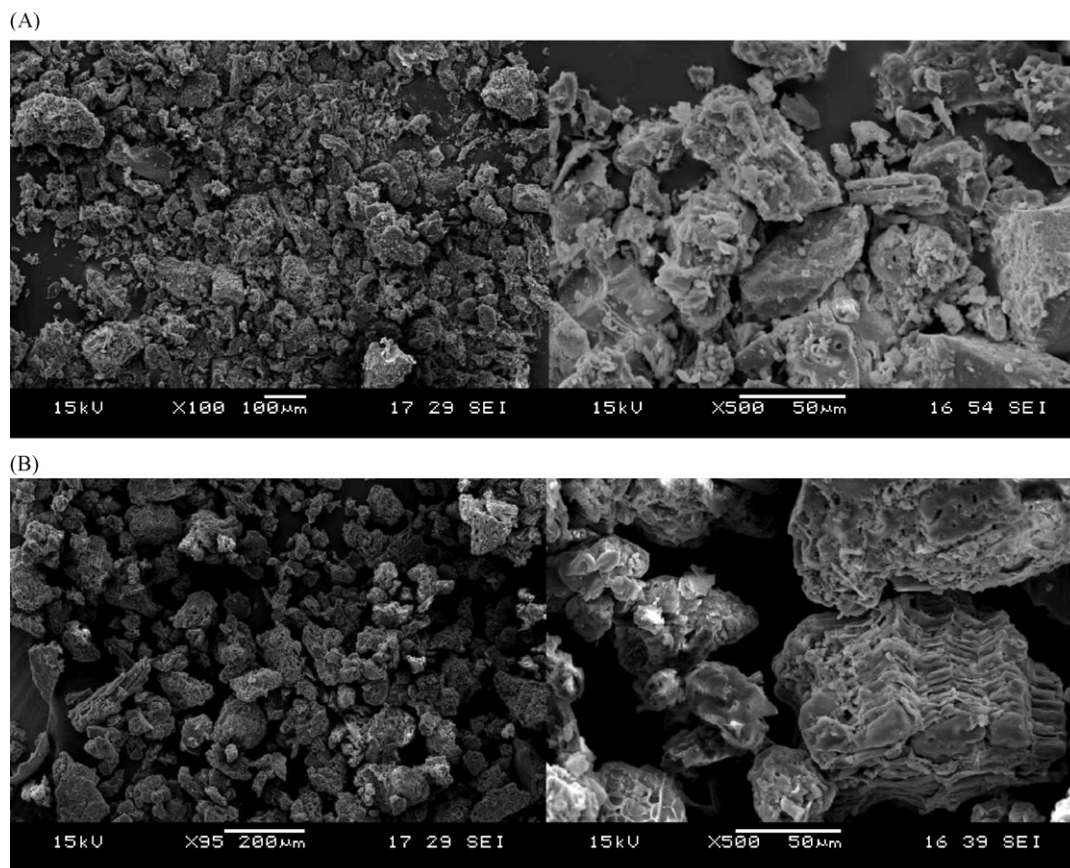


Fig. 3. SEM image of peat before (A) and after (B) MCLR adsorption.

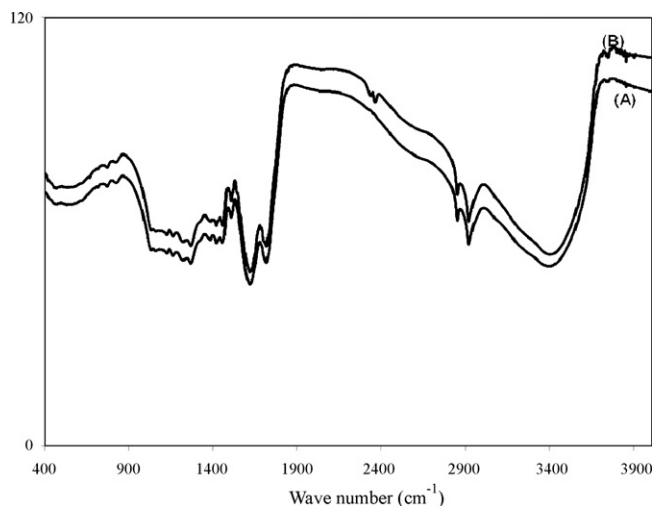


Fig. 4. FT-IR spectra of peat before and after MCLR adsorption.

[35] demonstrated that the MCLR species remain neutral at the narrow pH range of 2.09–2.19; the cationic species $[(\text{COOH})_2(\text{NH}_2^+)]$ are produced at $\text{pH} < 2.09$ and anionic species $[(\text{COO}^-)_2(\text{NH}_2^+)]$ and $[(\text{COO}^-)_2(\text{NH})]$ are produced at $\text{pH} > 2.19$. Better adsorption capacities are expected at pH values where both peat and MCLR carry opposite charges to explain the adsorption by ion pairing effect. The pH_{zpc} of peat is at 6.56 which would mean that it would carry cationic charges at pH 1–6.55 and carry anionic charges from pH 6.57 to 14. In our experiments, the maximum adsorption capacity was observed at pH 3. At pH 3, MCLR is essentially in anionic form and peat would be carrying cationic charges so there could be possible ion pairing effect leading to higher adsorption at that pH. As the pH of the system increases, the cationic charges carried by peat tend to decrease till the pH_{zpc} (6.56) where it exists as a neutral compound with zero charges. At the same time, even though the cationic charges carried by peat below pH 3 are higher than at pH 3 (due to higher protonation occurring as pH decreases), the degree of adsorption would be less which is due to cationic charges on MCLR below 2.19 as described by Maagd et al. [35]. This would result in repulsion of the MCLR molecule from the sorbent.

Another analogy to explain the decreased adsorption of MCLR at higher pH could be attributed to partitioning effect of charged MCLR. Partitioning is the measure of differential solubility of a compound between two immiscible solvents at equilibrium. Normally, one of the solvents chosen is water and the second one is hydrophobic like octanol. It correlates with the tendency of a molecule to concentrate in the lipids of organisms and the organic carbon of sediments and soils [36,37]. Maagd et al. [35] demon-

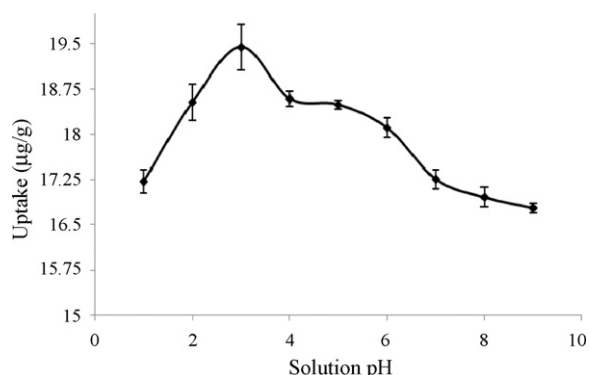


Fig. 5. Effect of pH on adsorption of MCLR by peat.

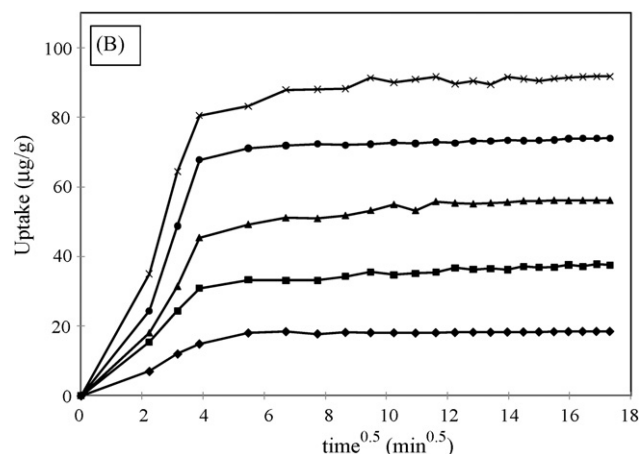
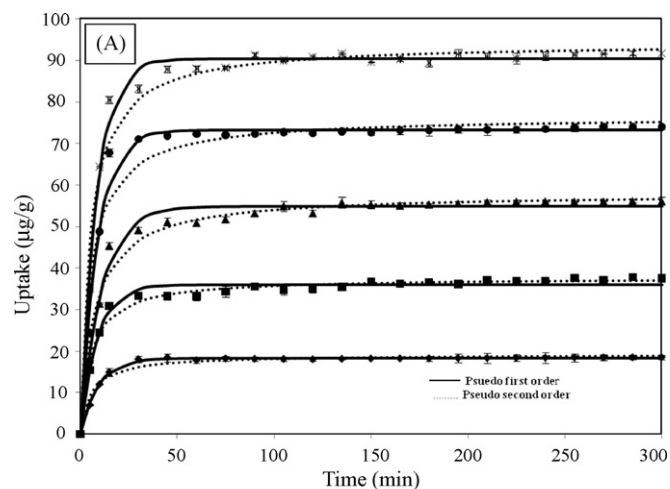


Fig. 6. Effect of contact time (A) and intraparticle diffusion plot (B) for adsorption of MCLR by peat (♦) 100 µg/L, (■) 200 µg/L, (▲) 300 µg/L, (●) 400 µg/L, (×) 500 µg/L.

strated the *n*-octanol/water distribution ratio D_{ow} for MCLR which decreased from 2.18 at $\text{pH} = 1$ to -1.76 at $\text{pH} = 10$, suggesting that with the increase in pH MCLR exhibits increased hydrophilicity and consequent decreased partitioning in octanol. Therefore, with the increase in pH, MCLR has more tendency to remain in aqueous phase rather than getting adsorbed. As adsorption was high at pH 3 compared to other pH values examined, all further adsorption isotherm and kinetic studies were conducted only at pH 3.

3.4. Effects of contact time and initial MCLR concentrations

The effect of initial MCLR concentration on the rate of adsorption onto peat was studied. The experiments were carried out at a fixed adsorbent dose (50 mg/10 mL) with different initial concentrations of MCLR (100–500 µg/L) for different time intervals at pH 3 and 30 °C. The sorption kinetics plays a very important role in the treatment of water and wastewater, as it provides valuable insights into the reaction pathways and mechanisms of sorption reactions. Since biosorption is a metabolism-independent process, it would be expected to be a very fast reaction. Experimental kinetic data at different initial MCLR concentrations concurred with this expectation; around 90% removal was achieved by 30 min with the initial concentration of 100 µg/L, whereas 90% of MCLR removed by 90 min for the other concentrations studied (Fig. 6A). This initial quick phase was followed by a slow attainment of equilibrium. Equilibrium time for MCLR sequestration was 480 min for carbon nanotubes [38], 960 min for carbon from coconut shell and bitu-

Table 2
Kinetic parameters for MCLR sequestration by peat.

MCLR concentration	q_e (exp) ($\mu\text{g/g}$)	First-order kinetic model		Second-order kinetic model	
		q_e (cal) ($\mu\text{g/g}$)	r^2	q_e (cal) ($\mu\text{g/g}$)	r^2
100	18.46	18.27	0.999	19.08	0.999
200	37.56	35.99	0.999	37.70	0.999
300	56.12	54.81	0.999	57.99	0.999
400	74.04	73.29	0.999	76.51	0.997
500	91.78	90.43	0.999	94.29	0.998

minous coal [21]. Equilibrium time reported for these adsorbents for MCLR sequestration was much higher than the present report, which indicates the potential use of peat in industrial scale. Equilibrium time is one of the important considerations in the design of water and wastewater treatment systems because it influences the size of the reactor thereby the plant economics [39]. On changing the initial MCLR concentration from 100 to 500 $\mu\text{g/L}$, the uptake increased from 18.46 to 92.3 $\mu\text{g/g}$, whereas the removal efficiency decreased from 93 to 89%. This anomaly can be attributed to the fact that the ratio of the initial moles of adsorbate (MCLR) to the available surface area was low, and subsequently the fractional sorption became independent of initial concentration of adsorbate. However, at higher concentrations the available surface area becomes less compared to the moles of MCLR present. Hence, the percentage of MCLR removal is dependent upon the initial MCLR concentration [40]. It was also observed that for an initial MCLR concentration of 100 $\mu\text{g/L}$, the maximum amount of MCLR adsorbed by peat for the first 5, 10, 15, 30 and 45 min was at an average adsorption rate of 1.4, 1.0, 0.58, 0.21 and 0.03 $\mu\text{g/g min}$, respectively and thereafter the adsorption rate seemed to decline and proceed at an average adsorption rate of 0.005 $\mu\text{g/g min}$. A similar trend was observed for other initial MCLR concentrations (100–500 $\mu\text{g/L}$) studied. The initial rapid uptake may be due to availability of more number of adsorption/vacant sites and easy diffusion into the pores of the particles. As a result, there exists an increased concentration gradient between adsorbate in solution and adsorbate in the adsorbent [41]. Asfour et al. [42] explained that this might be due to strong attractive forces between the adsorbate molecules and the sorbent and fast diffusion into the intraparticle matrix to attain rapid equilibrium.

3.5. Kinetic modelling

The experimental kinetic data were described using pseudo-first and -second-order models. Application of both models resulted in very high correlation coefficients and low % error and low RMSE values (Table 2). The pseudo-first-order model slightly under-predicted the equilibrium uptake values at all initial concentrations examined. The reason for these differences in the Q_e values is that there is a time lag, possibly due to a boundary layer, or external resistance controlling the initiation of the sorption process [43]. In most cases in the literature, the pseudo-first-order model does not fit the kinetic data well for the whole range of contact time and generally underestimates the Q_e values [41,44]. The pseudo-second-order model is based on the sorption capacity on the solid phase. Contrary to other well established models, the latter model predicts the behavior over the whole range of studies, and it is in agreement with a chemisorption mechanism being the rate controlling step [44]. However, the equilibrium uptake values were slightly over-predicted by the pseudo-second-order model. The curves predicted by the pseudo-second-order model are shown in Fig. 6A.

Sorption is a multi-step process involving four consecutive elementary steps in the case of porous sorbents [45]: (1) transfer of solute from the bulk of solution to the liquid film surrounding the

sorbent, (2) transport of the solute from the boundary liquid film to the surface of the sorbent (external diffusion), (3) transfer of solute from the surface to the internal active binding sites (intraparticle diffusion) and (4) interaction of the solute with the active binding sites. In general, the first two steps are usually fast provided sufficient agitation to avoid concentration gradients in solution. If the fourth step is assumed to be a rapid step, then intraparticle diffusion is therefore the rate-limiting step. The most commonly used technique for identifying the mechanism involved in the sorption process is by fitting the experimental data in an intraparticle diffusion plot as early mentioned by Weber and Morris [46]:

$$q_t = k_i t^{1/2} \quad (7)$$

Thus the intraparticle diffusion constant k_i ($\mu\text{g/g min}$) can be obtained from the slope of the plot of q_t versus $t^{1/2}$. The calculated values of k_i were 1.14, 9.47, 16.62, 26.48 and 28.01 $\mu\text{g/g min}$ at 100, 200, 300, 400 and 500 $\mu\text{g MCLR/L}$, respectively. According to the Weber–Morris model, the plot of q_t versus $t^{1/2}$ should be linear if intraparticle diffusion is involved in the sorption process; if this line passes through the origin then intraparticle diffusion is the rate controlling step. It can be clearly observed from the trend of the plots shown in Fig. 6B that peat adsorption showed multi-linearity. This occurrence implies that the process involves more than one kinetic stage (or sorption rates) [45]. The first one could be attributed to sorption of MCLR over the surface of biomass, and hence it is the fastest sorption stage. The second one, which ascribed to the intraparticle diffusion, was also relatively fast. The third stage may be regarded as the diffusion through smaller pores and this stage is followed by the establishment of equilibrium. Thus, it was inferred that the intraparticle diffusion is not the sole rate controlling step.

3.6. Isotherm modelling

Isotherms pertaining to the sorption of MCLR onto peat were determined at different initial MCLR concentrations ranging from 100 to 1000 $\mu\text{g/L}$ (Fig. 7). A critical analysis of the shape of isotherms revealed that the isotherm was favourable and can be classified as “L-shaped” [47]. This means the ratio between the MCLR concentration in the solution and that sorbed onto the biosorbent (peat) decreases with increase in the MCLR concentration, providing a concave curve without a plateau.

The Langmuir adsorption isotherm was originally developed to describe the gas–solid phase adsorption. In its formulation, binding to the surface was primarily by physical forces and implicit in its derivation was the assumption that all sites possess equal affinity for the sorbate. Its use was extended to empirically describe equilibrium relationships between a bulk liquid phase and a solid phase [48]. It has produced a good agreement with wide variety of experimental data. The Langmuir model served to estimate the maximum MCLR uptake values where they could not be reached in experiments. The constant b_L represents affinity between the adsorbent and adsorbate. Initially, the Langmuir model was applied to the present system, with the assumptions that adsorption sites are identical, each site retains one molecule of the given com-

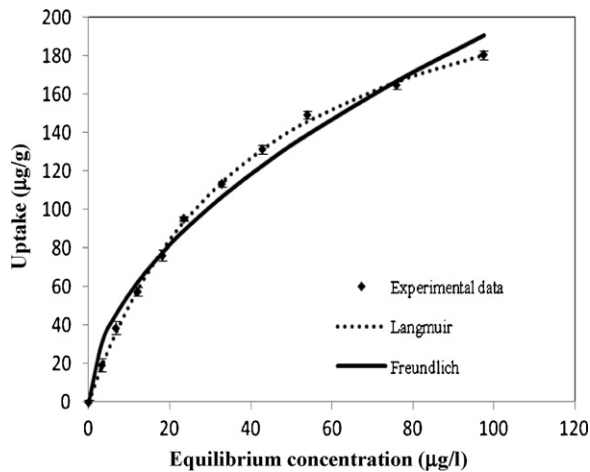


Fig. 7. Sorption isotherm at pH 3.

pound, and all sites are energetically and sterically independent of the adsorbed quantity. Even though these assumptions are not valid for a biomaterial used as sorbent, the model was able to describe the isotherm data with high r^2 and low % error values. A maximum MCLR biosorption capacity of 225.7 $\mu\text{g/g}$ was observed (Table 3). High values of b_L are reflected in the steep initial slope of a sorption isotherm, indicating desirable high affinity. Thus, for good biosorbents in general, high Q_{max} and a steep initial isotherm slope (i.e. high b_L) are desirable. Adsorption capacity of peat used in the present study completely out-performed almost all the wood and coal based powdered carbon reported by Donati et al. [18] except one wood based carbon which had an adsorption capacity of 280 $\mu\text{g/g}$. Similarly, peat's performance was better than all the phosphoric acid- and steam-activated wood based carbons reported by Pendleton et al. [20].

Freundlich model also showed reasonably a better fit with high r^2 and low % error values. However, the curve predicted by this model significantly deviated from the experimental data (Fig. 7). The Freundlich isotherm was originally empirical in nature, but was later interpreted as sorption to heterogeneous surfaces or surfaces supporting sites of varied affinities. It is assumed that the stronger binding sites are occupied first and that the binding strength decreases with the increasing degree of site occupation. High K_F and $1/n$ values indicate that the binding capacity reached its highest value, and the affinity between the biosorbent and MCLR was also high.

3.7. Desorption

Desorption studies help to elucidate the mechanism of adsorption and also help in the recovery of adsorbate and adsorbent, which makes the treatment process more economical [49]. Desorption studies were conducted at different levels of pH ranging from 2 to 12. The results revealed that an increase in pH increased

Table 3
Langmuir and Freundlich isotherm constants for MCLR sequestration by peat.

Langmuir model					
Q_{max}	b	r^2	χ^2	RMSE	ε (%)
255.71	0.0246	0.999	0.39	1.99	0.38
Freundlich model					
K_F	$1/n$	r^2	χ^2	RMSE	ε (%)
16.58	1.87	0.997	8.69	8.49	7.4

the percentage desorption of the MCLR from 0.66% at pH 2 to 62.68% at pH 12 for 410 $\mu\text{g/L}$ MCLR concentration, which is much less than the percentage adsorption. This highlights the strong binding between adsorbate and adsorbent, and also reveals the possibility of a chemisorption mechanism involved in the sequestration of MCLR. Only physisorbed MCLR molecules by weak Vander Waals force could have desorbed from the adsorbent surface [41]. Regeneration and reuse of the adsorbent is a very important issue to be addressed when applied industrially. Since the percentage desorption only about 60%, it is practically impossible to reuse the adsorbent (peat) for the next cycle. Hence desorption was attempted with ethanol, methanol, acetone and strong alkali (2N NaOH). Desorption was also attempted with deionized water for comparison. 50 mg of the MCLR-laden peat was suspended in 10 mL of the above-mentioned desorbing media and agitated in a rotary shaker at 150 rpm for 3 h. Acetone, ethanol, methanol, NaOH and water showed 0.04%, 14.9%, 40.97%, 93.7% and 0.01% desorption, respectively. Thus the adsorbent can be reused for several cycles until the rigidity of the biomass is suitable for adsorption. Since the biomass is easily biodegradable, it can be dumped 'as is' or can be subjected to composting after several cycles of adsorption.

4. Conclusions

Adsorption of MCLR onto peat was pH dependent and was found to be maximum at pH 3 with 90% removal efficiency in 30 min. The maximum adsorption capacity (Q_{max}), as predicted by Langmuir isotherm, was 255.7 $\mu\text{g/g}$. 93.7% of MCLR could be desorbed with 2N NaOH as eluting media. Based on this study, it could be concluded that peat is a promising adsorbent for removal of MCLR. Since peat is readily available, inexpensive, indigenous and environment-friendly, its use as a biosorbent would significantly lower water treatment costs and can be viewed as an effective biomaterial management strategy.

Acknowledgements

The authors gratefully acknowledge the support and contributions of this project to the Singapore-Delft Water Alliance (SDWA). The research presented in this work was carried out as part of the Singapore-Delft Water Alliance (SDWA)'s research programme (R-264-001-013-272).

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