Kinetics and isotherm of cadmium adsorption onto polyethylene microbeads in artificial seawater

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Abstract. This study investigates the interactions between cadmium (Cd) and microplastic under controlled laboratory conditions using low density polyethylene microbeads as model of plastic particles. Cadmium was added to suspensions of artificial seawater to investigate heavy metal adsorption on microbeads surface in five different concentration. Polyethylene microbeads proved to have affinity in providing surface area for cadmium. Microbeads served as an effective sorption surface and concentrated cadmium amount in seawater through adsorption process. The maximum adsorption was monitored for 96 hours. Maximum adsorption capacity determined to be 0.0101 mg/g occurring within 12-48 hours in test concentration. While, kinetic study was performed according to pseudo-first-order kinetic with k_d at 0.011 L/g. Using data from pseudo first order, isotherm study was performed in nonlinear regression and dataset was in good agreement with Langmuir, Freundlich and Redlich Petterson with coefficient of determination at 0.865, 0.964 and 0.962 respectively. Adsorption of cadmium to polyethylene microbeads has important implications for the potential role of microplastics, in this case microbeads-cadmium contaminated act as a quantified link in aquatic food webs.

1. Introduction

Plastic particle with size range less than 5 mm to 333 μm is defined as 'microplastic'. The lower limit is defined as a practical lower limit when neuston nets was used for sampling [1,2]. Previous researchers demonstrated that, plastic particles that have size between 200 μm to 500 μm are generally found in seawater [3,4].

Microplastics have been found in the water column and marine sediments worldwide [5-8]. According to previous researchers, microplastics are suggested to be long-term sink in sediments [6,9,10]. Density of seawater is around 1.020 to 1.029 gcm^{-3}. If plastic with density exceeds the seawater density, then it will sink and potentially accumulate in sediment.

However, if the plastic density is lower than seawater density, it tends to float in surface or water column [11]. Alarming numbers of microplastic have been found within sediments of estuaries, freshwater and intertidal or coastal ecosystems [12-16]. Microplastic cause negative impact to the environment due to their small size and ability to carry contaminants, thus eventually effects the aquatic life through ingestion [19-24].

One of primary microplastic is microbeads. Microbeads associated with industrial spillages [25] and cosmetics usage such as facial cleanser [1] as well as plastic form ship breaking industries and industrial abrasives in synthetic 'sandblasting' media such as beads of acrylic plastics and polyester, enter seawater directly via runoff [26].

Microbeads are virtually indestructible, often perfectly spherical, multi-colored, buoyant, and typically much smaller than 5 mm making them quite distinct from other plastic found in the environment [1,17]. Once a product containing microbeads is washed off a person's hands or face, the cleaning agents plus the microbeads are rinsed down the drain and will enter wastewater systems.

The products contained microbeads were usually disposed into municipal sewer systems without proper treatment. Because of their small size and buoyancy, many microbeads escape from filtration by wastewater treatment plants. Subsequently, microbeads in the treated water are discharged to rivers, lakes, or oceans, where they accumulate and persist [18].

The interaction of microplastic to metals became primary concerned in marine ecosystem in current research. Holmes and colleagues concluded that addressing metal (Cr, Co, Ni, Cu, Zn, Cd and Pb) sorption kinetics to virgin and beached polyethylene pellets could reach equilibrium within 25 to 100 h [27]. While, Brennecke and co-workers studied the interaction between two types of known polymers (virgin polystyrene plastic beads; PS and aged polyvinylchloride fragments; PVC) with heavy metals (antifouling paint) [28]. The study was performed by exposing different types of microplastics to heavy metal pollution under controlled laboratory conditions and mimicked anthropogenic environment [28].

Boucher and colleagues reported the microcosm study for microbeads from cosmetic cleanser [20]. It was suggested that, the microbeads provided sorption sites for lead (Pb) and cadmium (Cd). Recent study by Zon and colleagues concluded that, virgin microbeads was able to absorb heavy metal in synthetic seawater tested in laboratory [29]. The study was performed by exposing virgin polyethylene microbeads to chromium for 96 hours and reach equilibrium rapidly within 24 hours.

Based on those study mentioned, this ability could be considered as an action of vector for heavy metals to enter the food chain with ingested microbeads [14]. The purpose of this study is to assess the interactions between heavy metals and microbeads under controlled laboratory condition. Using polyethylene microbeads as plastic particles, the sorptive ability of polyethylene microbeads for different concentration of cadmium were evaluated by kinetic and isotherm study.

2. Materials and Methods
The experiment was performed in order to investigates the interactions between cadmium and polyethylene microbeads under controlled laboratory conditions using virgin polyethylene microbeads as plastic model.

2.1. Chemicals and apparatus
Milli-Q deionized (18.2 MΩ) water, was used in all experimental work. Polyethylene microbeads with size 200-300 μm was obtained from a local plastic company. Instant Ocean synthetic sea salt (Aquarium Systems Inc., Sarreboug, France) was used to prepare artificial sea water (ASW).

Analytical grade concentrated nitric acid (Merck 98% and 65%) was used throughout the study. Stock solution of Cd (Perkin Elmer, USA) were prepared from 1000 μg/mL by several step dilution. All experimental apparatus such as glass tank, volumetric flask, beakers, syringes, and bottle samples were soaked for 24 hours in diluted nitric acid (10%) and later double-rinsed with deionized water to avoid possible contamination.

2.2. Sorptive study of polyethylene microbeads
Batch experiments were conducted for heavy metals Cd with five different concentrations added to 10 litre artificial seawater in order to produce 0.2, 0.4, 0.6, 0.8 and 1.0 μg/ml solution. The sorptive test was conducted for 96 hours in presence of oxygen. 0.3 g of microbeads were sampled at 12 hours subsequently [27, 29]. The batch tank was observed frequently to maintain its original condition.

Samples was then placed into 10 mL test tubes and preserved. The experiment was repeated in triplicates.

2.3. Microwave acid digestion for polyethylene microbeads
Samples were weighted at 300 mg and mixed with 6 mL of 65% of nitric acid. Samples were then placed in oven vessel, capped and put in digestor (Milestones SK-10, USA) and heated at 110°C for 4 minutes. Then, the sampled was cooled in ice-cold water for 15 minutes and heated again at 200°C. The resulting solution was diluted to 25 mL in volumetric flask and filtered. Sample solution then analysed with atomic absorption spectrophotometer (Perkin Elmer PinAAcle 900T).

3. Results and Discussion
In this study, it was proven that cadmium was able to be adsorbed onto microbeads surface. All results shown were calculated based on non-linear regression by solver data analysis using Microsoft Excel 2010. Previously, result was presented using linear regression for adsorption of chromium [29]. However, due to uncertainty of result and inconsiderable of error, non-linear regression used for pseudo first order analysis in this study [29].

Adsorption occurred rapidly in most cases due to the high availability surface sites of microbeads and concentration gradient, presumably approach equilibrium subsequently. Maximum adsorption capacity occurred approximately 12-48 hours. The value of adsorption capacity is considerably low, indicated that polyethylene microbeads only have few sites available for adsorption. Thus, giving minimal associations of cadmium with polyethylene microbeads.

The abundance of cadmium in 1.0 μg/ml exposed to polyethylene microbeads higher than other concentration due to its high molecules availability in solution making it easier to interact to microbeads surface. The rate interaction of cadmium-microbeads in term of kinetic is discussed further in kinetic adsorption study. The result might differ for different types of microbead-heavy metals combination [28]. Adsorption occurrence was also determined based on its surface area and reactivity or affinity to specific heavy metals-plastic type [27]. Ashton and others also found that, the adsorption mechanism for metal adsorption might be because of direct adsorption of cations/anions or complexes onto charged sites or neutral region of plastic surface [15,30].

3.1. Adsorption Kinetics
Rate of adsorption cadmium-polyethylene microbeads was modelled by non-linear regression of pseudo-first-order reversible kinetic model [31].

$$q_t = q_e(1 - e^{-k_t t}) \tag{1}$$

where q_e (mg/g) represent as metal adsorbed to microbeads surface at equilibrium and k_t (hour⁻¹) is pseudo-first-rate constant.

Figure 1 shows the time dependant of adsorption in aqueous solution which correspond to kinetic study. Investigation of kinetic analysis found that, data were satisfied with regression coefficient close to unity, small sum-of-squared errors and comparable q_e values with the experimental ones. Table 1 summarizes constant from pseudo-first-order kinetics model obtained from kinetic observation where q_e is relatively small subject to initial concentration.
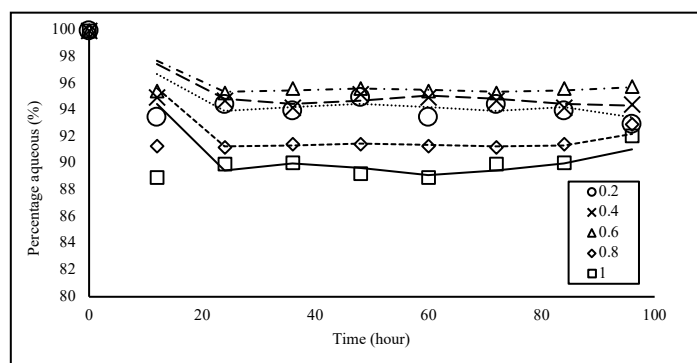
Figure 1. Time dependent of cadmium adsorption.

According to Arrhenius theory, rate of adsorption is high at low concentration because of less repulsion between molecules in system, thus resulting in rapid adsorption. However, this is not related in this system because of minimum changes in k_t value in different concentration. The low adsorption occurred because the low availability of sites. Low value of equilibrium partition coefficient, k_d L/g indicated that, the contaminants in seawater was in mobility.

The adsorption occurred is considered as rapid and subsequent approach to equilibrium or more protracted period of slower adsorption. Polyethylene microbeads-cadmium was relatively in good agreement for pseudo-first order of kinetic and it was in good agreement to previous study [27, 28].

Pseudo-first-order kinetic specified that desorption is possible in this adsorption type. The model implies the formation of imaginary bonds as a result of the mutual interactions between the cadmium and polyethylene microbeads surface. The bond represents adsorption in multilayer and monolayer occurred with electrostatic, hydrogen bonds, van der waals or dipole-dipole [32]. The bonds are relatively physical weak, and the adsorption is reversible.

Table 1. List of parameters obtained from pseudo-first order for adsorption of microbeads onto cadmium.

| Initial Concentration (μg/ml)	q_e (mg/g)	k_t (hour^{-1})	r^2	k_d (l/g)
0.2	0.0012	1.0	0.914	0.006
0.6	0.0027	1.0	0.988	0.005
1.0	0.0101	1.6	0.928	0.011

3.2. Adsorption Isotherm

Polyethylene microbeads show an affinity towards cadmium ion because microbeads might provide surface area for ion to be adsorbed. High surface area provides high chances for adsorption occurrence. According to previous study, cations might randomly distribute because of weak electrostatic forces. This account has been proved in adsorption kinetic study previously [34].

Thus, we proposed the adsorption occurred in this system might because of pore filling, electro-static interaction or ion exchange of cadmium. Surface of microbeads is considered as neutral or positively charged, resulting the reversible and rapid adsorption. Positive surface might repel away the cadmium ion presumably bivalent cation Cd^{2+}, hydrophobic character, polar or charged microbeads surface which might have weak interaction [27, 30].

Figure 2 shows the adsorption of cadmium onto polyethylene microbeads to concentration of cadmium in solution at equilibrium based on pseudo-first order approach. Freundlich scattering data almost similar and much better fit to experimental data compared to Langmuir. Generally, adsorption is increased with increasing of adsorbate concentration that provides a driving force to overcome

resistance of mass transfer in liquid phase until the surface saturation is achieved at which the adsorption is equilibrium [34].
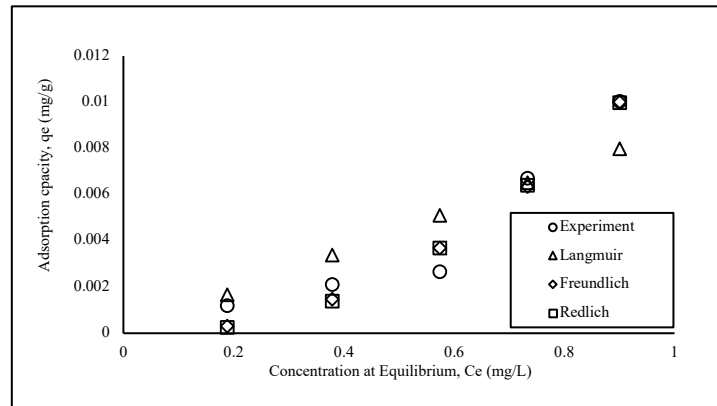
Figure 2. Validity of adsorption isotherm with experimental data.

Langmuir, Freundlich and Redlich-Petterson models were calculated and modelled to the isothermic. Langmuir model was assumed that maximum adsorption occurs when saturated monolayer cadmium is present on homogenous microbeads surface, the energy of adsorption is constant and there is no migration of cadmium molecules in surface plane. The isotherm model was performed using nonlinear regression analysis based on equation (2).

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2}$$

where q_e and q_m represent maximum adsorption capacity for the microbeads loading and energy constant related to heat of adsorption respectively. The value of q_m determined to be 1.582 mg/g respectively.

Redlich-Petterson model represent adsorption equilibria over a wide concentration range, that can be applied either in homogeneous or heterogeneous systems. Isotherm with β value found to be less than zero which is approaches Freundlich at high concentration, whereas β value approaching to one is ideal for Langmuir condition with low concentration [35].

$$q_e = \frac{K C_e}{1 + a C_e^{\beta}} \tag{3}$$

Freundlich model gave highest r^2 which is 0.964 where the adsorption occurred in multilayer onto heterogenous surface. The applicability of these models is supported by the relatively small sum-of-squared errors. Adsorption of cadmium from solution to microbeads surface with assumptions different sites with several adsorption energies involved. The relationship of cadmium adsorbed per unit mass of microbeads Q_e and the concentration of cadmium at equilibrium C_e with logarithmic equation as shown in equation (3).

$$q_e = k_f C_e^{\frac{1}{n}} \tag{4}$$

where k_f and n indicate as adsorption capacity and adsorption intensity respectively. The value was determined to be 0.013 L/mg. The coefficient correlation indicated that Freundlich to be more favourable adsorption than Langmuir. This result also supported by Redlich-Peterson model parameter, β value.

Table 2 summarizes the Langmuir, Freundlich and Redlich-Peterson isotherm constants for cadmium adsorption. The equilibrium data with coefficient of determination, r^2 in range of 0.86-0.96 for Langmuir and Redlich.

Despite that, general assumption that plastics are inert to aqueous metals, polyethylene microbeads suspended in cadmium-amended seawater rapidly and fitted in Langmuir and Freundlich models.

Previous study for beached pellets equilibrium occurred at 25-100 hours [27]. However, other researchers claimed that, all types of plastic tend to accumulate with similar concentration of metals and increased over time without reaching saturation point [1]. From previous perspective, plastic particles were an inert compared to heavy metals due to its impact to physical damage such as ingestion and entanglement rather than sources of contaminants carrier [30]. Duarte and colleagues found that, particles behaviour of adsorption is similar to estuarine sediments [33]. In this context, microbeads might enter the food chain since its behaviour is similar to estuarine sediment and also acted as a vector for heavy metals in environment [28].

Table 2. List of calculated parameters from the Langmuir, Freundlich and Redlich-Petterson adsorption isotherm models.

Langmuir		Freundlich		Redlich-Petterson	
q_m (mg g^{-1})	1.582	K_f (L mg^{-1})	0.013	K (L g^{-1})	0.042
				a	2.366
b (L mg^{-1})	0.006	n	0.451	g	-1.517
r^2	0.865	r^2	0.964	r^2	0.962

4. Conclusion

Through investigation of batch experiment between cadmium and microbeads under controlled laboratory conditions using low density polyethylene microbeads as a model plastic particle, it was revealed that interaction between cadmium and surface polyethylene microbeads are occurred rapidly.

Pseudo-first order was determined with assumption that desorption is possible in this adsorption type. The model implies the formation of imaginary bonds as a result of the mutual interactions between the cadmium and polyethylene microbeads surface. The bond represents adsorption in multilayer and monolayer occurred with electrostatic, hydrogen bonds, van der waals or dipole-dipole. The bonds are relatively physical weak, and the adsorption is reversible. However, the equilibrium constant might underestimate of environmental values.

Adsorption occurred in this system might because of pore filling, electro-static interaction or ion exchange of cadmium. Surface of microbeads is considered as neutral or positively charged, resulting the reversible and rapid adsorption. Positive surface might repel away the cadmium ion presumably bivalent cation Cd^{2+}, hydrophobic character, polar or charged microbeads surface which might have weak interaction. Polyethylene microbeads suspended in cadmium-amended seawater rapidly and fitted in Langmuir and Freundlich models. Freundlich scattering data almost similar and much better fit to experimental data and proved by Redlich model.

Association of cadmium and plastic is considered as general phenomena in term of aquatic environments with respect to different size and types of plastic. Rate of adsorption depends on few factors that need to be considered such as characteristic of microplastic model; surface area, existing charged of microplastic and presence of additives. Evaluation of microplastic-heavy metals also recommended for different types of kinetic and isotherm studies to estimate the interaction precisely. Based on our findings, it was concluded that, microbeads will become vector if ingested in aquatic life. The ability to sorb heavy metals and presumably might desorb in gastrointestinal condition of organism is crucial as an additional path for heavy metals to enter the food chain through ingestion rather than direct intake. Further investigation needs to be considered in term of time of adsorption, specific microbeads-heavy metals combination and contaminated microbeads of heavy metals to aquatic organism.

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