ORIGINAL ARTICLE

Removal of Cadmium from aqueous solution using agriculture waste as biosorbent

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Abstract:

The use of agriculture waste for the removal of different pollutants including heavy metals has proved to be efficient. This research intentions was to investigate the feasibility of selected agriculture waste (Rubber wood Sawdust- RWSD, Banana Peel- BP, Mangosteen Peel- MP) in removal of Cadmium (Cd) ion from aqueous solution. The factors that could influence the experimental conditions such as pH, amount of adsorbent, initial concentration of Cd, adsorption isotherm and adsorption kinetics of biosorbent were studied. As for RWSD and MP, the adsorption of Cd was more efficient in the basic pH region (pH 9), while BP prefer the neutral pH condition. The adsorption of Cd achieved its dynamic equilibrium within 20 min of contact times for all of the adsorbent. Pseudo second-order model fits better than the pseudo first-order model for adsorption kinetic data and indicates the adsorption process is based on chemisorptions. The equilibrium isotherm data were fitted well to Freundlich isotherm with maximum adsorption capacity of 4.01, 3.16 and 6.90 mg/g for RWSD, BP and MP respectively. From the study, it showed that RWSD, BP and MP have the potential to be utilized as a cost effective and high capability adsorbent for the removal of Cd from aqueous solutions.

Keywords: Adsorbent, agriculture waste, cadmium, heavy metals

1. INTRODUCTION

Rapid industrialization generates huge amounts of wastes which greatly affect the environment. The increasing amounts of industrial wastes require a larger space of landfill and expensive treatment for disposal. This causes a detrimental pollution effect on the soil, water and air [1]. In Malaysia, several industries have discharged their effluents into water bodies that contains various type of pollutants including heavy metals. These pollutants could be accumulated and magnify in the food chain and affect human health. Chronic exposure towards heavy metals such as Cadmium (Cd) can lead to renal toxicity, lung disease, hepatotoxicity and damage to human respiratory system [2]. Thus, the removal of these heavy metals such is necessary before discharging the effluent into the surrounding environment.

Various techniques has been utilized to reduce heavy metal concentration from the wastewater such as ion exchange, chemical precipitation, solvent extraction, electroplating, reverse osmosis and membrane filtration [3]. However, the expensive cost of the treatment limit the applicability of these technique. Hence, the alternative method for low-cost effective technique is needed. Recent research has indicated that some natural biomaterials including agricultural product including the waste (by-product) can adsorb high concentration of heavy metals [4]. The technique has been proved to be a powerful, effective and low cost for removal of heavy metals especially form the wastewater [5]. This technique can sometimes be used in combination with other treatment or it can be stand-alone treatment without any combination or pre-treatment [6].Various agricultural wastes has been utilized for removal of heavy metals such as rice husk, rice bran, tea waste, orange peel, durian peel, banana peel, palm press fiber and coconut shells [6].

Malaysia is well known through it agricultural sector that can be seen by more than 80 million tons of fresh fruits being produce yearly [7]. This scenario creates a huge amount of agricultural waste and by-product that require to be disposed in landfill. These wastes could be used as alternative absorbent to remove the heavy metal contamination from wastewater effluent and consequently reduce the burden of landfill disposal.

In this study, selected agriculture waste; RWSD, BP and MP were tested to determine its maximum absorption capacity of Cd ion removal from aqueous solution. The RWSD contain cellulose (45-50%) and lignin (23-30%), BP contain lignin (6%-12%), pectin (10%-21%), cellulose (7.6%-9.6%) and hemicellulose (6.4%-9.4%), and MP contain cellulose, lignin, pectin and several others compounds. The presence of these compound the adsorbent indicate the potential functional groups such as hydroxyl, carbonyl, amino carboxylic and alkoxy that has great affinity for the metal ions absorption [8].

2. MATERIALS AND METHODS

2.1 Preparation of adsorbents

RWSD, BP and MP were first crushed mechanically with a jaw crusher before shaken for 24 hours with distilled water to remove soluble impurities. The adsorbent was then dried in an oven at 110°C for 24 hours, and then crushed mechanically once again to produce smaller particles in order to increase the surface area. Samples were sieved following mechanical crushing to obtain a particle size smaller than 500 µm and store in the desiccators.

2.2 Stock preparation

Artificial Cd standard solutions were used throughout the adsorption test. A stock solution of 1000 mg/L was obtained using Perkin Elmer Atomic Spectroscopy Standard Solution. An aliquot of stock solution was further diluted with ultrapure water to prepare the desire experimental concentration.

2.3 Batch adsorption study

The batch experiment was carried out with a defined amount of adsorbent sample in a 30 mL bottle sample. A defined volume of the Cd concentration was prepared from a stock solution by adding ultrapure water. The pH of the Cd solution was then adjusted to the desired value and added to the bottle container. The mixture was stirred at 200 rpm for a defined period. After a certain period of stirring, filtering process was applied to separate solid from liquid. The supernatant then subjected to ion Atomic Absorption Spectroscopy (AAS) for analysis. The percentage of Cd removal and the adsorption capacity were calculated in equation 1 and 2.

% of Removal = (Initial Concentration – Final Concentration)/ Initial Concentration x 100 (1)

Adsorption Capacity = (Initial Concentration – Final Concentration) x Volume (L) / Weight of adsorbent (2)

2.4 Adsorption isotherm

In this study, two isotherm model namely Langmuir and Freundlich were used to determine the maximum adsorption capacity of the adsorbent. Linearized form of Langmuir isotherm was shown in equation 3;

$$1/Q_e = 1/b.Q_m.C_e + 1/Q_m \qquad (3)$$

Where; Qe (mg/g) is the amount of metal adsorbed, Ce (mg/L) is concentration at equilibrium, Q_m (mg/g) is the maximum adsorption capacity of adsorbent, b (L/g) is the Langmuir constant.

The linearized form of Freundlich isotherm models were expressed in equation 4 as follow:

$$\text{Log } Q_e = \text{Log } K_f + 1/n \log C_e \qquad (4)$$

Where, Q_e (mg/g) is the amount of metal adsorbed, Ce (mg/L) is concentration at equilibrium, K_f is the adsorption capacity, n is adsorption intensity.

3. RESULTS AND DISCUSSION

3.1 Effect of pH

The influence of pH on removal of Cd ion by RWSD, MP and BP were examined and the results were presented in Figure 1. The results showed that the biosorption process of Cd ions was pH dependent. Generally, the removal of Cd was increased with the increased of pH condition. The optimal pH condition for RWSD and MP were at pH 9, while BP achieved its optimum Cd removal in neutral condition. At low pH condition, the binding of Cd ions is not efficient due to protonated adsorbents surface which cause electrostatic repulsion [9]. As the pH level goes up, adsorbents surface become deprotonated and lead to Cd sorption by attracting the positively charged ions [10]. This is due to the functional group of the adsorbents and the compound presence in each of it such as cellulose, lignin, pectin, pentosan and tannins that has the ability to bind metals ions [11].

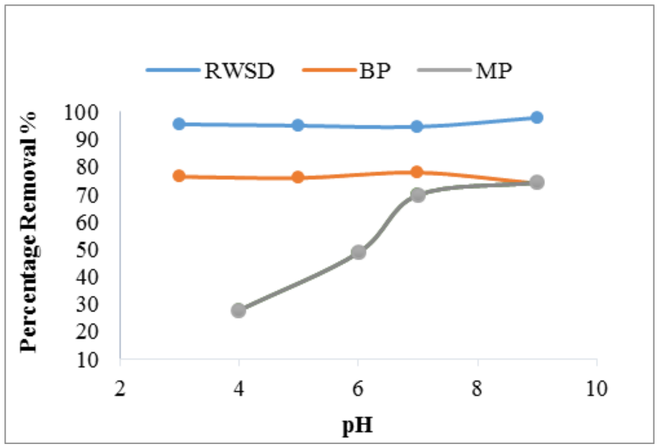

Figure 1: Effect of pH condition on Cd ion removal (1 g of adsorbent dosage; 10 mg/L initial concentration; 30 min contact time)

3.2 Effect of contact time

Figure 2 showed the removal of Cd ion with respect to contact time of RWSD, MP and BP adsorbents. The result indicated that the Cd removal was increased significantly for the first 20 min of reaction. No significant Cd removal was observed following 20 min of exposure. When the reaction time was increased from 20 to 120 min, the Cd removal remained constant. Therefore, 20 min of reaction time was selected for further study. The larger removal rate occurred during initial phase was due to the availability of pores that can bind the Cd ions [9]. In the end phase after the adsorption become constant, the surface pores of adsorbent has been covered and it became difficult for Cd ion to enter the pores [11]. This is due to the adsorbents surface is in a state of dynamic equilibrium with the amount of Cd that is being adsorbed from the solution. This constant value is known as equilibrium point which shows the maximum capacity of Cd ion that can be adsorbed by the adsorbents.

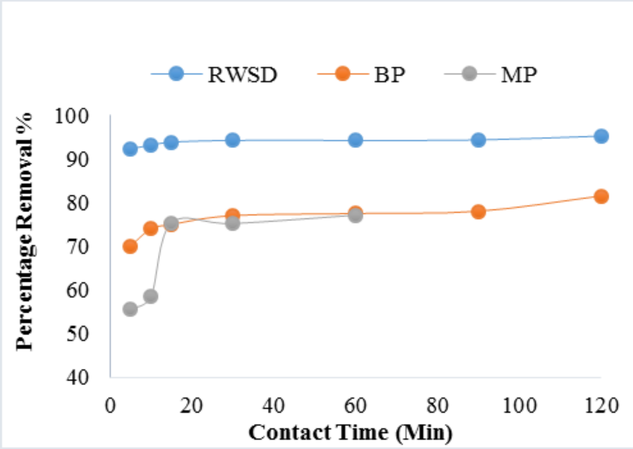

Figure 2: Effect of reaction time on Cd ion removal (1 g of dosage and 10 mg/L of initial Cd concentration.

3.3 Effect on adsorbent dosage

In this study, the adsorbent dosage were determined at optimum pH by varying the mass of adsorbent at shaking time of 20 min at room temperature and 10 mg/L of initial Cd ion concentration. Results of this experiment was illustrated in Figure 3. RWSD shows a greater adsorption with 0.2 g of adsorbent at 91.5% removal rate as compared to BP and MP that remove 71.2% and 75% by using 0.4 g and 1 g of adsorbents. Generally, the percentage of Cd removal increase with the increase of the adsorbent dosage. This condition was due to the greater availability of surface area and thus provided higher exchangeable sites for Cd binding [11]. However, after certain dosage, the RWSD, BP and MP adsorbent showed the decrease of Cd removal due to the presence of more sorption sites on surface which become saturated with the fixed concentration of Cd solution [10].

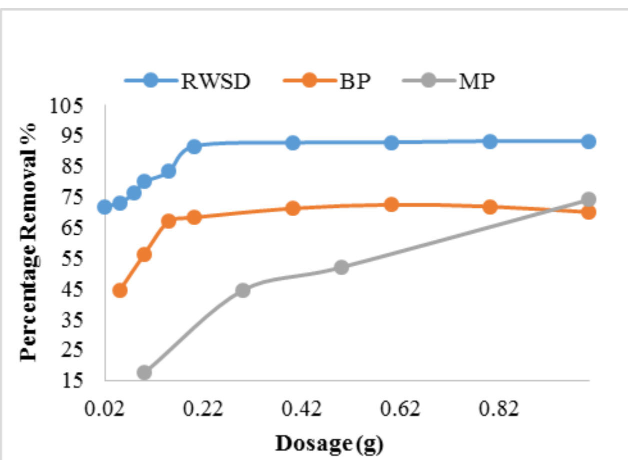

Figure 3: Effect of adsorbent dosage alteration towards percentage removal by fixing 10 mg/L of initial metal concentration.

3.4 Adsorption isotherm study

Adsorption isotherm data is used to study the mechanism of Cd sorption onto adsorbent surface. This study will identify the adsorbents surface properties and affinity towards the adsorbate uptake. Based on the result presented in Table 1, All RWSD, BP and MP better fit with Freundlich isotherm with K_f value 4.01, 3.16 and 6.90 mg/g respectively. The selection of model was determined through the higher correlation coefficient and the maximum adsorption capacity.

Table 1: Langmuir and Freundlich isotherm (Q_m and K_f is the maximum adsorption; r^2 is correlation coefficient)

Adsorbent	Langmuir		Freundlich	
	Q_m	r^2	K_f	r^2
RWSD	0.67	0.81	4.02	0.995
BP	0.36	0.83	3.16	0.992
MP	0.13	0.76	6.90	0.998

3.5 Adsorption kinetic study

Adsorption kinetic data is used to determine the rate-controlling mechanisms of Cd sorption onto the adsorbents which help in modelling the best process for the adsorbents. The experimental data as depicted in Table 2 were tested with two kinetic models which is pseudo-first order and pseudo-second order. All the tested adsorbents was better fit with pseudo-second order. Based on the analysis made, these three adsorbent adsorption processes are controlled by chemical sorption. The process of chemical sorption involved the electron exchange between the adsorbent and Cd ion.

Table 2: Correlation coefficient of kinetic models

Kinetic Model	r^2		
	RWSD	BP	MP
Pseudo-first	0.95	0.94	0.92
Pseudo-second	0.98	0.97	0.98

4. CONCLUSION

The removal of Cd from aqueous solution is influenced by a number of factors such as pH, contact time, adsorbent dosage and initial metal concentration. The adsorption of Cd was more effective in the basic pH region (pH 9) for RWSD and BP, meanwhile the optimum pH condition for MP is at neutral pH condition. Only 20 min reaction times was required for all the three adsorbent to achieve equilibrium. Pseudo second-order model fits better than the pseudo first-order model for adsorption kinetic data and indicates the adsorption process is based on chemisorptions. The equilibrium isotherm data were fitted well to Freundlich isotherm with maximum adsorption capacity of 4.01, 3.16 and 6.90 mg/g for RWSD, BP and MP respectively. Our findings suggests that RWSD, BP and MP have the potential to be an effective, economical and environ-mental friendly bio sorbent for Cd adsorption in aqueous solution. These adsorbents can act as an alternative wastewater containing metal ions that could be used to replace the current expensive materials such as activated carbon and ion exchange.

ACKNOWLEDGEMENT

The authors are grateful to the all the staff in Environmental Analytical Laboratory for giving the permission and their kind cooperation to conduct this study successfully.

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