APPLICABILITY OF CRUSHED CLAY BRICK AND MUNICIPAL SOLID WASTE SLAG AS LOW-COST ADSORBENTS TO REFINE HIGH CONCENTRATE Cd (II) AND Pb (II) CONTAMINATED WASTEWATER

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ABSTRACT: Along with population growth, rapid urbanization, and industrialization, the generation of waste and industrial by-products is increasing enormously and causing many environmental and social issues. In order to examine effective applications of waste and industrial by-products, this study aimed to investigate the effective use of crushed waste clay bricks (CCB) and municipal solid waste slag (MSWS) as low-cost adsorbents to treat high concentrated wastewater. A series of batch adsorption experiments were carried out to investigate the effects of contact time, initial concentration, pH, ionic strength, and competitive metals on Cd^{2+} and Pb^{2+} adsorption onto the tested adsorbents. The Langmuir model performed well by the fitting Cd^{2+} and Pb^{2+} adsorption isotherms. The maximum adsorption capacity of Pb^{2+} (3.4-5.5 mg/g) was higher than the Cd^{2+} (2.3-3.2 mg/g) for both adsorbents. CCB showed high removal of metals, but a higher dependency on the metal system (single, binary, or multi-metals). Interestingly, MSWS showed lower removal of metals but less dependency on the metal system for Cd^{2+} and Pb^{2+}. Adsorption of tested adsorbents was mainly controlled by deprotonation or ion exchange at the natural pH, and at the higher pH (>9 for Cd^{2+} and >7 for Pb^{2+}), surface precipitation was the predominant mechanism for Cd^{2+} and Pb^{2+} removal (>60%). Overall, tested adsorbents were showed comparatively good performance in treating high concentrated wastewater, but future studies under different conditions and with modification to apply CCB and MSWS fines as better low-cost adsorbents to treat wastewater are essential.

Keywords: Added value, Deprotonation, Desorption, Metal systems, MSW slag

1. INTRODUCTION

Industrialization and economic development in the nineteenth and twentieth century caused rapid population growth worldwide. Simultaneously, urbanization triggered the use of natural resources as building materials for a better standard of living. Traditionally, clay brick was the most popular building material in the construction industry, and at present, it is replaced by the technically developed cement blocks and aerated auto-calved concrete as economical and user-friendly materials. However, renovation and demolition of old infrastructures are causing high amounts of construction and demolition waste (CDW) to be dumped in the environment, creating numerous environmental and social issues [1]. According to statistics, waste clay bricks account for 50-70% of the construction waste produced by urban redevelopment and 30-50% by building operations [2]. Furthermore, around 20000 million m^3 clay bricks have been produced in the past 50 years in China, most of which will be demolished in the next 50 years [3]. Therefore, scientist and researchers are giving more attention to the effective use of waste clay bricks. For example, waste bricks are introducing use as road and pavement sub-base materials and an alternative filler in asphalt mixtures [3,4]. On the other hand, population growth and urbanization are increasing the generation of municipal solid waste (MSW) each year. Conventionally, MSW is managed by landfilling or open dumping. However, incineration has been accepted as an indispensable disposal method for MSW in the twenty-first century, and it reduces the material volume up to 98% [5]. In Japan, >75%, and in China, 34.3% of MSW was incinerated in 2015, and the proportion is increasing year by year [6,7]. However, ultimate products, such as municipal solid waste slag (MSWS) and fly ash (industrial by-products), still moving to the final disposal sites. Thus, it is important to introduce effective methods to manage these marginalized materials for sustainable development.

Surface and ground water are highly vulnerable due to the increasing frequency of discharges of Cd^{2+} and Pb^{2+} like common heavy metals (HMs) from various sources, intensifying the environmental degradation [8]. Recently, numerous approaches have been studied for the development of cheaper and more effective technologies. Among these methods, adsorption has received a great deal of attention because of its low cost, high efficiency, and easy operating conditions [9,10]. Hence, small scale industries in developing countries are keen to use adsorption technology to treat HM-

contaminated wastewater. However, currently, the adsorption method is used to treat mostly low concentrated HMs (<200 mg/L) in wastewater [11,12]. Therefore, it is well-timed to expand treatment of water with metal concentrations ranging from low to high because of some industries are producing high concentrated wastewater. Thus, this study focused mainly on an effective application, and to set an added value for the waste clay bricks and MSWS as low-cost adsorbents to refine high concentrate industrial wastewater.

2. MATERIALS AND METHODS

2.1 Preparation of Adsorbents and Physicochemical Characterization

Waste clay bricks from Sri Lanka and MSWS collected from an incineration plant located in Saitama, Japan was crushed by hand and sieved, and the 0.105-2 mm fraction of crushed clay bricks (CCB) and MSWS fines was prepared for adsorption experiments. Basic physical and chemical properties such as pH, electrical conductivity (EC), loss of ignition, water content, specific gravity and BET surface area (ASAP2020, Micromeritics, USA) of the two adsorbents were determined. In addition, to identify the main chemical composition of the tested adsorbents, energy-dispersive X-ray spectroscopy (EDX; X-Max Extreme, Oxford Instruments, UK) experiments were performed using adsorbent powder particles.

2.2 Batch Adsorption Experiments

A standard batch method recommended by the Organization of Economic Cooperation and Development [13] was used for all batch adsorption experiments with 0.105-2 mm particles and a 1:10 solid to liquid ratio. All the following batch experiments and test conditions are summarized in Table 1. The solution HMs concentration was determined by flame atomic absorption spectrophotometer (AAS; AA 6200, Shimadzu, JP),

and the exact pH and EC values for each metal solution were measured before the experiment and their changes were observed during the experiments using a pH/EC meter.

2.3 Effect of Contact Time on Cd^{2+} and Pb^{2+} Adsorption

Triplicate samples of CCB and MSWS fines for each metal were sequentially collected from the shaker after 1, 3, 6, 12, 24, 48, 96, and 192 h. The amount of Cd^{2+} and Pb^{2+} adsorbed was calculated based on Eq. (1). Pseudo-first order, Eq. (2), and pseudo-second-order, Eq. (3), kinetics models were used to characterize the adsorption kinetics.

$$Q_t = \frac{V(C_i - C_t)}{m} \tag{1}$$

$$\ln(Q_e - Q_t) = \ln(Q_e) - k_1 t \tag{2}$$

$$\frac{1}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \tag{3}$$

where Q_t (mg/g) is the amount of metal adsorbed at each time t (min), C_i (mg/L) is the initial metal concentration, C_t (mg/L) is the instantaneous concentration of adsorbate at time t, V (L) is the sample volume, m (g) is the mass of the adsorbent, Q_e is the amount of adsorption at equilibrium (mg/g), k_1 is the pseudo-first order rate constant (1/min), and k_2 is the pseudo-second-order rate constant (g/mg/min).

2.4 Effect of Initial Metal Concentration on Cd^{2+} and Pb^{2+} Adsorption

Triplicate samples were shaken for 24 h, as determined by the kinetic experiments for Cd^{2+} and Pb^{2+} adsorption onto CCB and MSWS fines. To estimate the maximum adsorption capacity, and to assess the adsorption intensity of metals onto adsorbents, the Langmuir model [Eq. (4)] and the Freundlich model [Eq. (5)] was used with observed

Table 1: Summary of the followed batch experiments and testing conditions for CCB and MSWS fines.

Metal solution	Type of experiment	C_i (mg/L)	pH_i	Background solution
Single metal solution (Cd^{2+} or Pb^{2+})	1. Kinetics	1000	Natural pH*	Deionized water
	2. Isotherm	0-2000	Natural pH*	Deionized water
	3. pH	1000	3-11	$NaNO_3$ (0-0.1 M)
	4. Ionic strength	1000	3-11	$NaNO_3$ (0-0.1 M)
	5. Desorption	1000	Natural pH*	Deionized water
Binary metal solution ($Cd^{2+}+Pb^{2+}$)	6. Competitive metal	1000	Natural pH*	Deionized water
Multi-metals solution ($Cd^{2+}+Pb^{2+}+Cu^{2+}+Ni^{2+}+Zn^{2+}$)	7. Competitive metal	1000	Natural pH*	Deionized water

Note: *observed adsorbent pH when it dissolved in deionized water.

experimental data.

$$\frac{C_e}{Q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m} \qquad (4)$$

$$\text{Log } Q_e = \text{Log } K_f + \frac{1}{n} \text{Log } C_e \qquad (5)$$

where C_e (mg/L) is the equilibrium concentration of metals, b (g/L) is the Langmuir constant related to binding strength, Q_m (mg/g) is the maximum adsorption capacity, K_f (L/g) is the Freundlich adsorption capacity, and 1/n is the adsorption intensity.

2.5 Reversibility and Irreversibility of the Adsorption Process

Desorption experiments were done based on the sequential decant-refill technique introduced by Mon et al. [14]. After the adsorption experiments, the solution remaining in the tubes was immediately decanted, tubes were refilled with 10 mL of the filtrate, and deionized water was added to achieve the 1:10 solid-liquid ratio. Desorption process was repeated more than five successive times to obtain complete desorption isotherm, and modeled by the Freundlich model [Eq. (5)]. The adsorption-desorption hysteresis was quantified for each adsorbent-adsorbate system using the hysteresis index [Eq. (6)] defined in previous studies [14-16].

$$\omega = \left[\left(\frac{n_a}{n_d} \right) - 1 \right] \times 100 \qquad (6)$$

where ω is the hysteresis index (%), n_a is the adsorption intensity, and n_d is the desorption intensity based on the Freundlich isotherm model [Eq. (5)] was determined. A higher ω indicates greater difficulty in detachment of the adsorbed metals from the adsorbent. Theoretically, irreversible and reversible metal adsorption should follow $n_a > n_d$ and $n_a = n_d$ or $n_a < n_d$, respectively.

2.6 Effect of Initial pH and Background Electrolytes on Adsorption

Batch adsorption experiments were conducted for Cd^{2+} and Pb^{2+} adsorption by CCB and MSWS fines at the 0.1, 0.01, 0.001, and 0 M $NaNO_3$ ionic strength levels with pH ranges of 3, 5, 7, 9, and 11. Solution pH was adjusted by adding either 1 N HCl or 1 N NaOH. The removal percentage of metals (R, %) was calculated using Eq. (7).

$$R = \frac{C_i - C_e}{C_i} \times 100 \qquad (7)$$

2.7 Effects of Competitive Metal Ions on Adsorption

Effects of competitive metal ions on the adsorption process of test adsorbents were examined using binary and multi-metals solutions. The binary metal solution of Cd^{2+} and Pb^{2+} with each metal concentration at 1000 mg/L was mixed at a molar ratio of 1:1 to investigate the competitive behavior of Cd^{2+} and Pb^{2+} during the adsorption process. As well, each metal concentrations of 1,000 mg/L, Cd^{2+}, Pb^{2+}, Cu^{2+}, Ni^{2+}, and Zn^{2+}, was mixed at molar ratios of 1:1:1:1:1 to examine the effects of multi-metals solution on Cd^{2+} and Pb^{2+} adsorption onto each adsorbent.

3. RESULTS AND DISCUSSION

3.1 Physicochemical Characterization of Adsorbents

Adsorption of metals from the liquid phase to the solid phase is affected by the fundamental characteristics of the adsorbents. The basic physical and chemical properties of CCB and MSWS fines are shown in Table 2. According to the results, CCB had an almost neutral pH, and MSWS exhibited a slightly alkaline pH. Thus, negatively charged adsorbent surfaces are potential to adsorb cations from wastewater and might be able to neutralize acidic waste water during the adsorption process [17]. The comparatively higher BET surface area of CCB might be increased the chance of contact between CCB particles and metal ions and it facilitate higher adsorption. As shown in Table 3, EDX analysis before adsorption distinguished a relatively higher SiO_2 content in CCB (>50%) and MSWS (>35%). In contrast, a higher CaO content was observed in MSWS fines (>29%), indicating the possibility for ion exchange (Ca^{2+}) reactions with HMs, as calcium silicate materials [18,19]. Interestingly both adsorbents were showed a sufficient amount of metal oxides such as Al_2O_3 and Fe_2O_3, indicating its potential for the ion exchange and surface complexation reactions with HMs.

Table 2: Basic physical and chemical properties of the CCB and MSWS fines.

Properties	Adsorbent	
	CCB	MSWS
Particle size (mm)	0.105-2	0.105-2
Air-dried water content (%)	1.72	1.50
Natural pH (Deionized water)	6.40	9.10
EC(mS/cm)	0.12	0.36
Loss of ignition (%)	1.10	0.00
Specific gravity	2.77	2.79
BET surface area (m^2/g)	15.9	-

Table 3: Chemical composition of the CCB and MSWS fines (wt%).

Chemical composition (%)	Adsorbent	
	CCB	MSWS
SiO_2	57.6	36.8
CaO	1.25	29.6
Al_2O_3	24.4	14.7
Fe_2O_3	11.1	6.14
K_2O	1.17	1.01
TiO_2	1.58	2.03
MgO	0.78	1.93
H_2O	1.49	0.29
Other	0.63	7.5

3.2 Effect of Contact Time on Cd^{2+} and Pb^{2+} Adsorption

As shown in Fig. 1, all adsorbents, Q_t [Eq. (1)], increased with increasing contact time and reached to equilibrium within 12 to 24 h (720-1440 min). Also, the rates of Cd^{2+} and Pb^{2+} adsorption onto both adsorbents were almost identical. It was observed that, under all the experimental conditions, no significant adsorption was seen after 24 h onto each adsorbent. For subsequent experiments, the contact time was thus maintained as 24 h to ensure that equilibrium could be achieved.
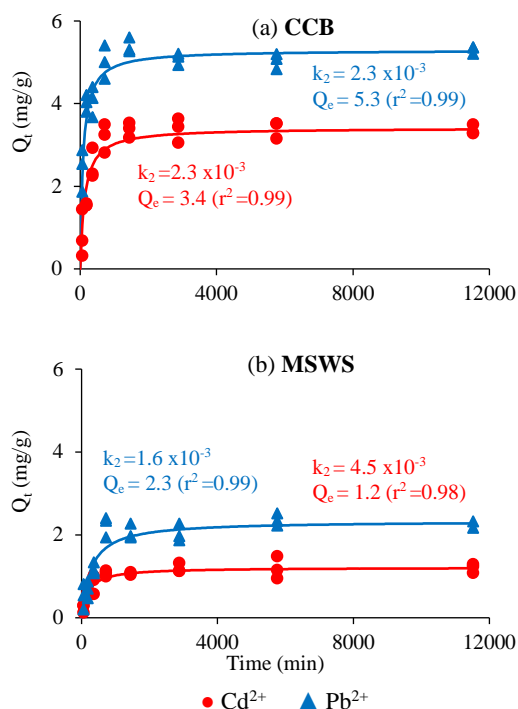

Fig. 1: Observed and fitted pseudo-second order model data for Cd^{2+} and Pb^{2+} adsorption onto 0.105-2 mm particle size of (a) CCB and (b) MSWS fines.

As shown in Fig. 1, the measured kinetic data were well captured by the pseudo-second-order model [Eq. (2)], but the pseudo-first-order model [Eq. (3)] did not follow the experimental data (results not shown). Thus, results suggest that the rate-limiting factor in adsorption of Cd^{2+} and Pb^{2+} onto CCB and MSWS is chemisorption rather than physisorption [20,21]. Chemisorption, which is a rate-limiting step, may involve valence forces through sharing or exchange of electrons between the adsorbent and the adsorbate [22].

3.3 Effect of Initial Metal Concentration on Cd^{2+} and Pb^{2+} Adsorption

Langmuir and Freundlich isotherm models [Eq. (4) and (5)] were fitted to measure adsorption isotherm data for Cd^{2+} and Pb^{2+} onto CCB and MSWS, and observed, fitted, and measured data are shown in Fig. 2. The Langmuir model fittd well in the entire concentration range ($0<C_i<2000$ mg/L) for Cd^{2+} and Pb^{2+} adsorption onto both adsorbents with a higher regression coefficient ($r^2>0.9$). This indicates that, monolayer adsorption acts as the predominant process, and homogeneous adsorption onto tested adsorbents may be occurred [23]. However, the Freundlich model was closely fitted with MSWS fines at the higher C_i ($C_i>500$ mg/L), indicating the possibility of multi-layer adsorption in high concentrated wastewater. The Q_m values for Pb^{2+} adsorption (3.4-5.5 mg/g) were always higher than for Cd^{2+} adsorption (2.3-3.2) onto both adsorbents. However, CCB showed higher Cd^{2+} and Pb^{2+} adsorption than the MSWS fines. Higher reactivity and low free energy in hydration of Pb^{2+} may be encouraged for higher adsorption [23,24]. The measured Q_m values for CCB and MSWS fines were compared with the adsorption capacities previously reported for different types of low-cost adsorbents, such as CDW, industrial waste, geo-sorbents, bio-sorbents and modified or commercially available sorbents at the higher C_i. The results are tabulated in Table 4. The Q_m values for tested adsorbents showed comparatively better performance, suggesting that both adsorbents have the capacity to treat high concentrated wastewater.

Figure 3 shows the relationship between the amount of adsorbed metals onto CCB and MSWS fines at the equilibrium (Q_e, mg/g) against the difference between equilibrium pH and initial solution pH (ΔpH). The results revealed a good linear relationship between Q_e and ΔpH for both metals. For the CCB, the ΔpH turns out to be mostly negative with increasing Q_e, demonstrating that equilibrium pH was decreasing during the metal adsorption process. This is might be due to the CCB (burned clay) surface whose dominant reactive group is a hydroxyl group (-OH) which reacts with metals, and that releasing H^+ (deprotonation) to the solution, and initiated a decreasing equilibrium pH [34,35]. On the other hand, with MSWS fines, ΔpH
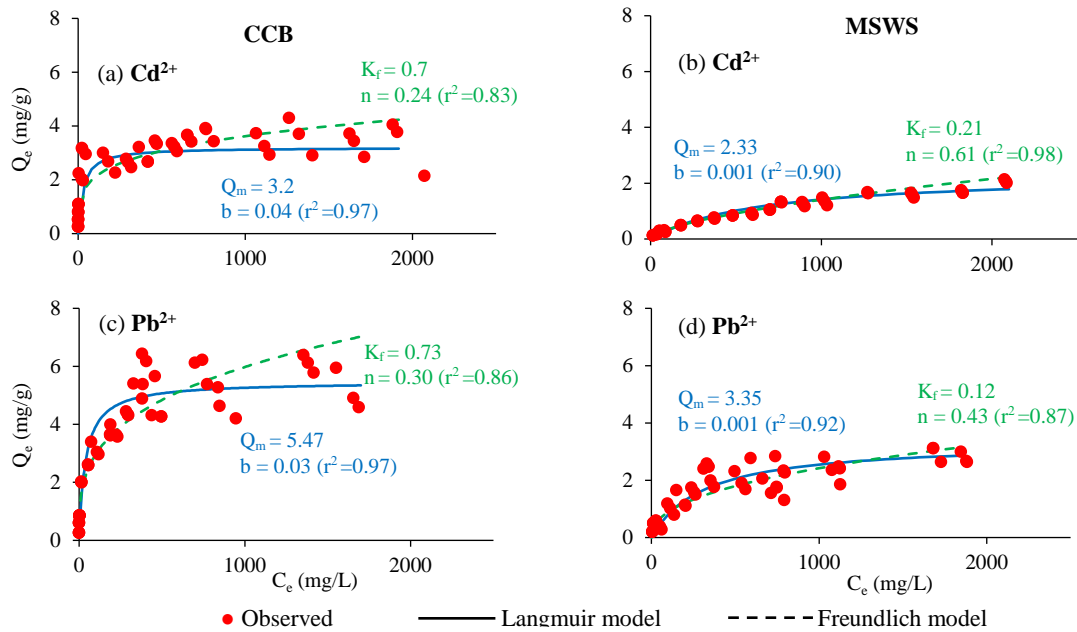
Fig. 2: Measured adsorption isotherms and fitted Langmuir and Freundlich models for Cd^{2+} [(a) and (b)] and Pb^{2+} [(c) and (d)] adsorption onto CCB and MSWS fines. Calculated Langmuir and Freundlich models parameters are also shown.

Table 4: Comparison of maximum adsorption capacity (Q_m) of Cd^{2+} and Pb^{2+} onto CCB and MSWS fines with the previous studies.

Adsorbent	Q_{max} (mg/g)		Reference
	Cd^{2+}	Pb^{2+}	
CCB	3.2	5.5	This study
MSWS	2.3	3.3	
Grout	1.2	16	[25]
Fly ash	3.8	5.1	[26]
Furnace slag	5.1	4.9	[26]
Coal fly ash	1.4	2.2	[27]
Natural soil	1.1	5.8	[28]
Kaolinite	0.9	2.4	[29]
Zeolite	6.7	10	[30]
Montmorillonite	1.2	3.3	[31]
Rice husks	0.6	2.0	[32]
Fungus	2.0	3.8	[33]
Biochar	2.9	15	[16]
ICZ	10	6.7	[30]

was maintained mostly on the positive side, especially for Cd^{2+}. A possible reason for this might be the presence of a higher amount of CaO (Table 3). The reaction of water with CaO might be released an adequate amount of OH^- and set up a buffering condition during the adsorption process. But the increasing equilibrium pH gradually decreased while Q_e increased, which resulted in a decreasing ΔpH with the increase of Q_e. This is due to higher H^+ release caused by high deprotonation, and adsorption of Cd^{2+} and Pb^{2+} [36,37]. However, further studies are recommended to determine the contributions of CaO, Al_2O_3, and Fe_2O_3 to the metal

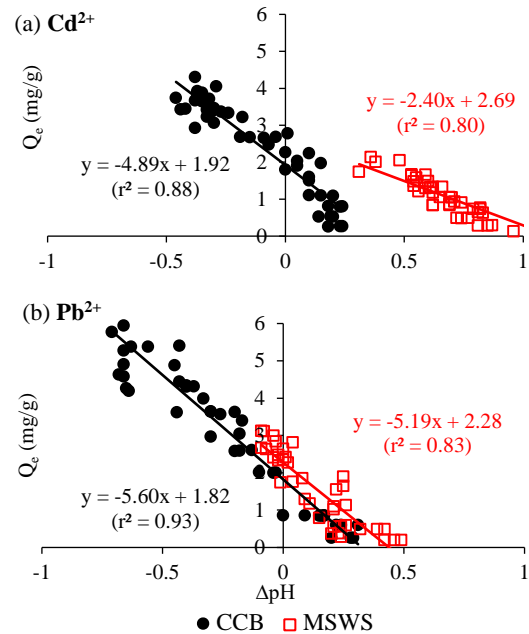adsorption process (potential for ion exchange reactions).

Fig. 3: Relationship between equilibrium adsorption (Q_e) and ΔpH for the Cd^{2+} and Pb^{2+} adsorption onto CCB and MSWS fines; (a) Cd^{2+} and (b) Pb^{2+}.

3.4 Reversibility and Irreversibility of the Adsorption Process

Desorption experiments were conducted to observe reversibility and irreversibility (leaching or non-leaching) of the metal adsorption process by CCB
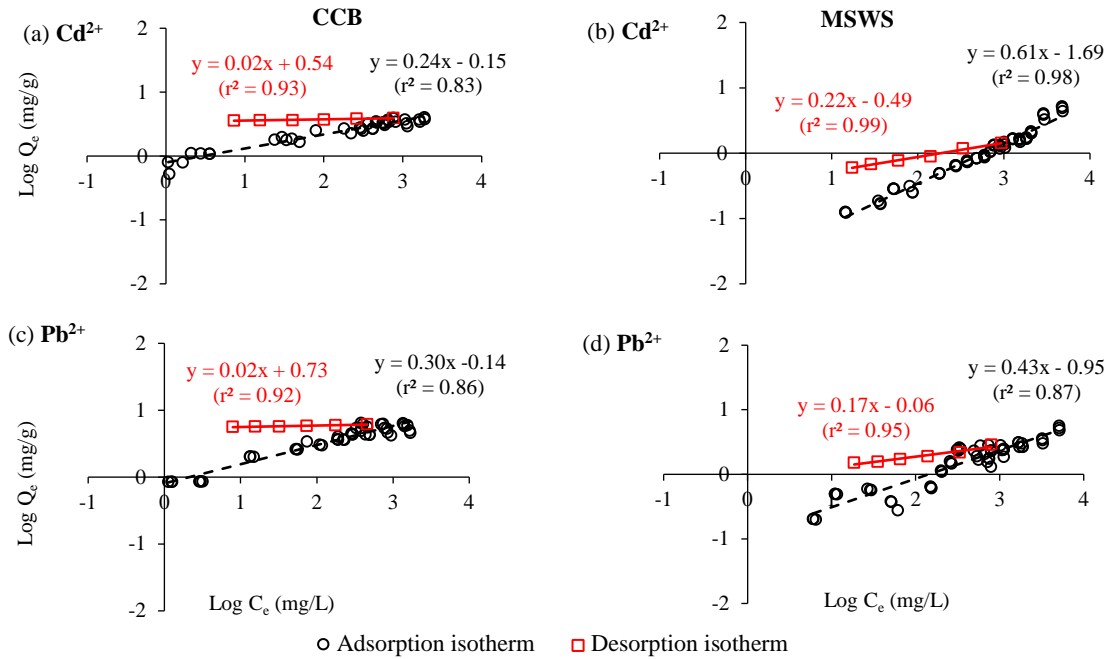
Fig. 4: Adsorption and desorption isotherms fitted with the Freundlich model for 0.105-2 mm particles of (a, c) CCB and (b, d) MSWS fines.

Table 5: Fitted Freundlich model parameters for the Cd^{2+} and Pb^{2+} desorption (K_{fd}, n_d), and calculated hysteresis index (ω) for CCB and MSWS fines. Previously reported results are also given.

Adsorbent	Particle size (mm)	Metal	Freundlich desorption parameters			ω %	Reference
			K_{fd} (L/g)	n_d	r^2		
CCB	0.105-2	Cd^{2+}	2.61	2.0×10^{-2}	0.83	11×10^2	This study
		Pb^{2+}	5.34	2.0×10^{-2}	0.92	14×10^2	
MSWS	0.105-2	Cd^{2+}	0.32	22×10^{-2}	0.99	1.8×10^2	This study
		Pb^{2+}	0.88	17×10^{-2}	0.95	1.5×10^2	
Natural soil	<2	Cd^{2+}	2.02	4.2×10^{-2}	0.62	9.7×10^2	[16]
		Pb^{2+}	3.36	2.3×10^{-2}	0.71	29×10^2	
Biochar	<0.075	Cd^{2+}	2.36	1.4×10^{-2}	0.99	14×10^2	[16]
		Pb^{2+}	3.04	3.9×10^{-2}	0.69	21×10^2	
Bentonite	0.05	Cd^{2+}	0.02	112×10^{-2}	0.99	0.00	[38]
		Pb^{2+}	3.63	48×10^{-2}	0.98	0.00	
Zeolite	0.05	Cd^{2+}	0.58	15×10^{-2}	0.99	5.0×10^2	[38]
		Pb^{2+}	49.4	4.4×10^{-2}	0.98	3.9×10^2	

and MSWS fines. As illustrated in Fig. 4, the measured adsorption and desorption data were fitted to the Freundlich model [Eq. (5)] to obtain the adsorption and desorption parameters such as K_{fa}, n_o, K_{fd}, and n_d. Desorption isotherms shadowed the Freundlich model well with a higher regression coefficient ($r^2 > 0.92$), and the calculated parameters are shown in Table 5 with the estimated hysteresis index, ω (%) [Eq. (6)]. The n_d values for CCB and MSWS fines were lower than the n_a values, indicating that, adsorbed metals were strongly bound to the adsorbents. According to Eq. (6), a high ω indicated, higher irreversibility of the adsorption of metal ions. As shown in Table 5, CCB exhibited a higher ω ($>1 \times 10^3$) than the MSWS fines ($\omega < 200$) for both metals, meaning CCB has better

irreversible reactions with adsorbed metals (minimum leaching). Comparison of tested adsorbents with the previously reported ω (%) revealed that, CCB and MSWS fines showed better performance with less metal leaching than the well-known bentonite and zeolite like adsorbents [38].

3.5 Effect of Initial pH and Background Electrolytes on Adsorption

Figure 5 shows the removal efficiencies [Eq. (7)] of Cd^{2+} and Pb^{2+} by the tested adsorbents at the deferent initial pH (pH_i) and ionic strengths. The pH_i of the solution has a great influence on the adsorption process because it alters the nature of the
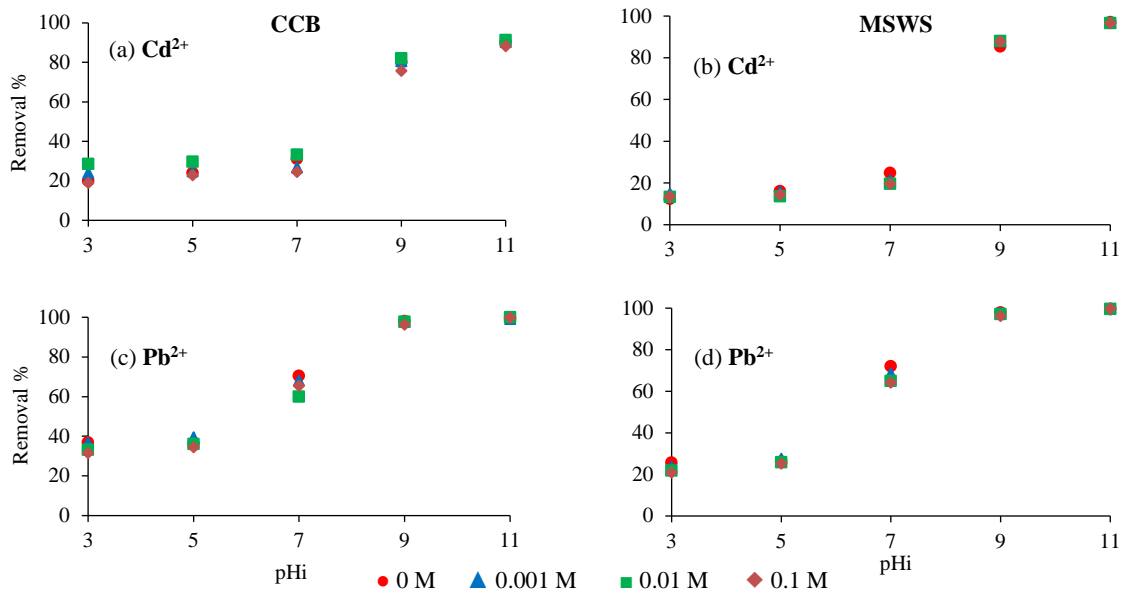
Fig. 5: Effects of initial pH (pH$_i$) and ionic strength on Cd^{2+} and Pb^{2+} adsorption for 0.105-2 mm particle size of (a, c) CCB and (b, d) MSWS fines.

surface charge and degree of ionization [24,39]. CCB and MSWS fines showed the same pattern of removal efficiency and higher dependency of pH$_i$ for each metal. Cd^{2+} removals increased from 20-30% to >90% when pH$_i$ was changed from 3-7 to 9-11. On the other hand Pb^{2+} removals was elevated from 20-40% to >60% when pH$_i$ was changed from 3-5 to 7, and it reached >99% when pH$_i$ was raised to 7-11 for the tested adsorbents. Similar results were reported by [16] for clay bricks.

According to the literature, Cd^{2+} and Pb^{2+} have potential to precipitate as metal hydroxides when the solution pH reaches to 9 for Cd^{2+} and 7 for Pb^{2+} [40,41]. Therefore, deprotonation or ion exchange reactions at lower pH$_i$ (<9 for Cd^{2+} and <7 for Pb^{2+}) might act as a dominant mechanism for Cd^{2+} and Pb^{2+} removal from the system. However, at higher pH$_i$, surface precipitation might be the predominant mechanism for the metal removal (>60%) from the solution along with the deprotonation or ion exchange. However, ionic strength didn't significantly affect the HMs removal process of each adsorbent in the studied pH range.

3.6 Effect of Competitive Metal Ions

Typical wastewater is most probably a mixture of different types of metal ions. Thus, existence of two or more heavy metals had a significant effect on the adsorption of the targeted heavy metals [7,8]. Therefore in this study, competitive behaviors of Cd^{2+} and Pb^{2+} in binary metals and the multi-metals system was studied and compared with the its single-metal system.

The observed results are shown in Fig. 6. Comparatively, CCB showed high metal removal but a higher dependency on the metal system. Interestingly, MSWS showed lower metal removal but less dependency on the metal system for Cd^{2+} and Pb^{2+} adsorption. For CCB, the single metal system resulted in higher Cd^{2+} and Pb^{2+} removal, but it gradually decreased with binary to multi-metals system. For CCB especially, the removal efficiency of Cd^{2+} became <1/2 and <1/4 in the binary and multi-metals solution respectively, when compared with a single metal solution. Overall, Pb^{2+} showed higher adsorption capacity in all three metal systems than the Cd^{2+} for both CCB and MSWS fines.

Characteristics of HMs such as hydrated radius, atomic weight, and hydrolysis constant affect mainly the metal adsorption, and affinity of metals for the adsorption sites [24,42]. Therefore, the smaller hydrated radius of Pb^{2+} (4.01 Å) compared to Cd^{2+} (4.26 Å) produced greater affinity for adsorbents. The selectivity sequences of Cd^{2+} and Pb^{2+} in multi-metals solution by CCB and MSWS fines are shown in Table 6 and compared with the reported selectivity sequences for various kinds of low-cost adsorbents. Remarkably, all types of adsorbents showed a similar type of selectivity sequence for Cd^{2+} and Pb^{2+} adsorption, i.e., Pb^{2+}, Cu^{2+}, and Ni^{2+} always dominated, and the Cd^{2+} adsorption was hampered by the presence of other metals in the solution.
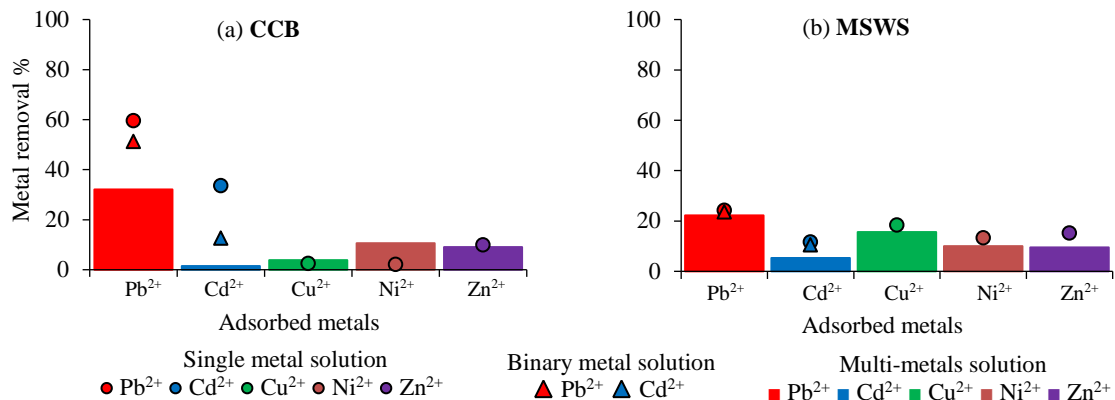
Fig. 6: Percentages of heavy metals removal (%) in (○) single metal (Cd^{2+} or Pb^{2+}), (△) binary metal (Cd^{2+}+ Pb^{2+}), and (□) multi-metals (Cd^{2+}+ Pb^{2+}+ Cu^{2+}+ Ni^{2+}+ Zn^{2+}) system for the tested adsorbents; (a) CCB and (b) MSWS.

Table 6: Selectivity sequence for $Cd^{2+}$and Pb^{2+} adsorption by low-cost adsorbents in multi-metals solution.

Adsorbent	Selectivity sequence	Ref.
CCB	$Pb^{2+}>Ni^{2+}>Zn^{2+}>Cu^{2+}>Cd^{2+}$	This
MSWS	$Pb^{2+}>Cu^{2+}>Zn^{2+}>Ni^{2+}>Cd^{2+}$	study
Fly ash	$Pb^{2+}>Cu^{2+}>Zn^{2+}>Ni^{2+}>Cd^{2+}$	[7]
Soil	$Pb^{2+}>Cu^{2+}>Zn^{2+}>Ni^{2+}>Cd^{2+}$	[16]
Soil	$Pb^{2+}>Cu^{2+}>Zn^{2+}>Cd^{2+}>Ni^{2+}$	[28]
Zeolite	$Pb^{2+}>Cu^{2+}>Cd^{2+}>Cr^{3+}>Zn^{2+}$	[30]
Biochar	$Cu^{2+}>Pb^{2+}>Zn^{2+}>Ni^{2+}>Cd^{2+}$	[16]
Corncobs	$Pb^{2+}>Cu^{2+}>Zn^{2+}>Ni^{2+}>Cd^{2+}$	[43]
Sesame straw	$Pb^{2+}>Cu^{2+}>Cr^{3+}>Zn^{2+}>Cd^{2+}$	[24]
Pepper straw	$Pb^{2+}>Cu^{2+}>Cr^{3+}>Zn^{2+}>Cd^{2+}$	[44]
Duolite GT-73	$Pb^{2+}>Zn^{2+}>Cu^{2+}>Ni^{2+}>Cd^{2+}$	[43]
Amberlite@200	$Pb^{2+}>Zn^{2+}>Ni^{2+}>Cd^{2+}>Cu^{2+}$	[43]
ICZ	$Pb^{2+}>Cu^{2+}>Zn^{2+}>Cd^{2+}>Cr^{3+}$	[30]

4. CONCLUSIONS

A series of Batch adsorption and desorption experiments for CCB and MSWS fines were carried out with high concentrated wastewater. Langmuir model was fitted well for the both adsorbents, and revealed that, dominant monolayer adsorption of Cd^{2+} and Pb^{2+} is occurring in 0-2000 mg/L concentration range. The higher hysteresis index ($>1x10^3$) for CCB revealet that, minimum leaching of adsorbed metal ions when compared to the commercially available adsorbents. CCB showed high metal removal, but it exhibited higher dependency on the metal system. Thus, the removal efficiency of Cd^{2+} became <1/2 and <1/4 in the binary metal and the multi-metals solution respectively, when compared with the its single metal solution. Interestingly, MSWS fines showed lower metal removal, but less dependency on the metal system for Cd^{2+} and Pb^{2+}. The main adsorption mechanism of metals might be the deprotonation or ion exchange at the natural pH, and at the higher pH (>9 for Cd^{2+} and >7 for Pb^{2+}),

surface precipitation was the predominant mechanism for Cd^{2+} and Pb^{2+} removal (>60%) by both adsorbents. Overall, tested adsorbents showed comparatively better performance in high concentrated wastewater, but future studies under different conditions, and with modification to label CCB and MSWS fines as suitable adsorbents to treat high concentrated wastewater are essential.

5. ACKNOWLEDGMENTS

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