

# REMOVAL OF CADMIUM IONS FROM INDUSTRIAL EFFLUENT USING BCPW: EQUILIBRIUM AND ISOTHERM STUDIES

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## ABSTRACT

In the present research work, adsorptive capacity of Bone China Pottery Waste (BCPW) for the removal of Cd(II) ions from industrial effluent has been studied. Batch method has been employed to investigate the effects of various adsorption controlling parameters such as contact time (5-180 min), pH (1-8) of solution, metal ions concentration (10-200 mg/L) and adsorbent dose (0.1-1.0 g) on adsorption of Cd(II) ions onto BCPW. The optimum set of conditions for maximum adsorption of Cd(II) ions were found to be initial concentration 50 mg/L, dosage 0.5 g and pH 6.0. The maximum adsorption of Cd(II) ions by BCPW was found to be 52.3 %. The adsorption data was fitted best to the Freundlich model ( $R^2 = 0.969$ ). Langmuir monolayer adsorption capacity of BCPW for Cd(II) was found to be 3.695 mg/g. These results suggested that BCPW could be employed as efficient adsorbent for the removal of Cd(II) from contaminated water sources.

**Key words:** Adsorption, Bone China Pottery Waste (BCPW), monolayer, Langmuir, Freundlich, etc.

## I. INTRODUCTION

The term heavy metal refers to the metals which are toxic at low quantity and cause risks to human health and the environment. Mining, electroplating, metal processing, textiles and battery manufacturing industries are the main sources of heavy metals [1, 2]. Cadmium is a non-essential and highly toxic element which can accumulate along the food chain resulting in serious ecological imbalance and cause hazards to plants and animals [3]. Therefore, elimination of Cd(II) from wastewater is important to protect public health. Commonly used methods to treat metal contaminated effluent are chemical precipitation, ion-exchange, membrane filtration, coagulation and adsorption. All other conventional methods have proved to be less effective and much expensive [4] than adsorption which is technically simple with sludge free environment and involve low investments in terms of both initial cost and land requirement [5, 6]. In recent years, tea waste [7], red mud [8], saw dust [9], ulmus leaves and their ash [10], roasted china clay [11], mixtures of hydrous ferric oxide, quartz and kaolinite [12] and Turkish kaolinite clay [13] have been employed to remove heavy metals from waste water. In this study, BCPW was utilized for the removal of Cd(II) ions from industrial effluent.

## II. METHODOLOGY

### 2.1 Collection and Preparation of adsorbent

In ceramic industries during manufacturing of bone china pots, toys and other decorative articles, the semi-solid paste first moulded into various shapes of articles and then subjected to heating called firing to provide rigidity. But during the process of firing, some of the articles breaks or get deshaped which are thrown away as waste. some of these breaks or get deshaped which are thrown away as waste. This thrown away waste was collected, grinded into fine particles and sieved through 300 $\mu$  mesh size and used as adsorbent to remove Cd(II) ions from aqueous solutions without giving any pre-chemical treatment.

### 2.2 Adsorbate solution

The stock solution of 200 mg/L of Cd(II) was prepared by dissolving required amount of cadmium nitrate tetrahydrate, Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O in DDW in 1L standard flask. This stock solution was used to prepare working solutions of desired concentrations for all experiments. The pH values of the solutions was adjusted by adding 0.1N NaOH or 0.1N HCl.

### 2.3 Determination of point of zero charge

The point of zero charge (pH<sub>pzc</sub>) of the BCPW was determined by solid addition method with DDW and 0.1 N KNO<sub>3</sub> solutions [14]. The 50 ml DDW (Double distilled water) was transferred into a series of conical flasks and the initial pH (pH<sub>i</sub>) of these solutions were roughly adjusted between 2 to 10 by adding either 0.1 N HCl or 0.1 N NaOH solutions. The initial pH (pH<sub>i</sub>) of these solutions was than measured accurately by using pH meter. After that 0.5 gm of adsorbent was added into each flask and allowed to equilibrate for 24 hours with intermittent manual shaking. After attaining equilibrium solution was filtered and the final pH (pH<sub>f</sub>) of the supernatant liquid was then noted. The difference between initial and final values ( $\Delta$ pH = pH<sub>i</sub> – pH<sub>f</sub>) were plotted against pH<sub>i</sub>, the point of intersection of resulting curve with abscissa at which  $\Delta$ pH is zero, gave the point of zero charge (pH<sub>pzc</sub>). The same procedure was repeated using 0.1 N KNO<sub>3</sub> solutions.

### 2.4 Adsorption studies

Batch experiments for adsorption of Cd(II) ions on BCPW were conducted by varying pH, contact time, adsorbent dose and adsorbate concentration. The experiments were carried out by contacting 0.5g of the adsorbent with 50 ml solution of 50 mg/L concentration of Cd(II) ions except for the effects of contact time in which concentration range from 10 mg/L to 200 mg/L were used. The flasks were shaken for the required time period on a rotary shaker at 120 rpm at room temperature at pH 6. The effect of contact time was studied for the time period of 5 to 180 minutes. At predetermined times, the flasks were withdrawn from the shaker and the reaction mixtures were filter and filtrate samples were analyzed for residual concentration of Cd(II) ions by AAS. The amount of metal adsorbed (mg/g), q<sub>e</sub> and removal efficiency, R % was calculated using the formula given below:

$$q_e = \frac{(C_i - C_e)}{W} \times V \qquad R\% = \frac{(C_i - C_e)}{C_i} \times 100$$

where  $q_e$  is the amount of metal adsorbed (mg/g),  $R\%$  is the adsorption percentage of metal ions,  $V$  is the volume of the adsorbate solution (L),  $C_i$  is the initial metal ions concentration (mg/L),  $C_e$  is the metal ions concentration at equilibrium (mg/L) and  $W$  is the weight of the adsorbent in gram (g).

## 2.5 Adsorption isotherms

The analysis of isotherm data by fitting them to different isotherm models is an important step in finding a suitable model that can be used for design purpose. The adsorption capacity of the system was studied with the Langmuir [15] and Freundlich [16] isotherm models. The equilibrium sorption of Cd(II) ions was carried out by contacting 0.5g of the BCPW with 50 ml solutions of Cd(II) ions of concentrations ranging from 10 – 200 mg/L in 100 ml conical flasks with intermittent shaking for 2 hours on the rotary shaker.

## III. RESULTS AND DISCUSSION

### 3.1 Adsorption studies

#### 3.1.1 Effect of pH

The pH of the solution affects the surface charge of the adsorbents as well as the degree of ionization and speciation of adsorbate particles [17]. It is known that metal species  $[M(II)=Cd(II)]$  are present in deionized water in the form of  $M^{+2}$ ,  $M(OH)(s)$ ,  $M(OH)_2(s)$  etc. [18]. It is obvious that adsorption of M(II) must be higher in alkaline medium. But at higher pH, precipitation of metal ions as  $M(OH)_2(s)$  plays an important role in removing M(II) ions. Therefore, all the experiments were conducted at  $pH \leq 8$ . The optimization of pH of Cd(II) ions solution and its influence on the extent of adsorption onto BCPW was studied by varying pH in the range of 1-8 which is shown in “Fig. 1”. It was observed that adsorption of Cd(II) ions increased with an increase in pH and reaches maximum, 52.30 % at pH 6. The increase in adsorption with increasing pH is gradual as increase in pH reduces the competition of  $H^+$  ions present in the solution with Cd(II) ions for adsorption sites. It may be due to the fact that increase in pH makes the adsorbent surface more negatively charged due to protonation of adsorbent and thus become more accessible for the adsorption of metal ions (positively charged) through electrostatic force of attraction [19, 20]. At higher pH, ( $pH > 6.0$ ) Cd(II) ion adsorption decreased and became nearly constant when it reached 8.

Moreover, the pH of point of zero charge,  $pH_{zpc}$  has an important influence on adsorption processes. The surface of adsorbent was positive when  $pH < pH_{zpc}$ , neutral when  $pH = pH_{zpc}$  and negative at  $pH > pH_{zpc}$ [21]. The data plotted in “Fig. 5” indicated that the  $pH_{zpc}$  value of BCPW was 5.4, showing that the surface was negatively charged above this pH and hence fairly large amount of Cd(II) ions (52.30% at pH 6) were adsorbed.

#### 3.1.2 Effect of contact time

In order to optimize the contact time for the maximum uptake of Cd(II) ions, contact time was varied between 5-180 minutes for the removal of Cd(II) ions from aqueous solutions of 50 mg/L of Cd(II) ions with adsorbent dose of 0.5 g at optimum pH 6.0. The effect of contact time on adsorption of Cd(II) ions is shown in “Fig. 2”. It can be seen that adsorption of Cd(II) ions increases with increase of contact time until it reaches equilibrium. The rate of Cd(II) ions removal was very rapid during initial 15 minutes (48.54%) which may be due to the availability of large number of vacant sites on the adsorbent surface during initial stages of adsorption.

Thereafter, the rate of adsorption of Cd(II) ions increased slowly and reached maximum (52.30%) in 120 minutes and then became almost constant. This showed that equilibrium was established in 120 minutes.

### 3.1.3 Effect of concentration

The effect of initial Cd(II) ions concentration ( $C_i$ ) from 10 – 200 mg/L on the removal of Cd(II) ions with adsorbent dose of 0.5 g and optimum pH 6.0 was investigated and shown in “Fig. 3”. It was observed that an increase in the initial Cd(II) ion concentration, decreased cadmium ions uptake from 98.36% to 26.45%. The adsorption capacity ( $q_e$ ) of adsorbent at initial Cd(II) ions concentration of 10, 25, 50, 75, 100, 125, 150, 175 and 200 mg/L observed were 0.98, 1.96, 2.62, 3.62, 4.18, 4.69, 5.0, 5.05, 5.29 mg/g, respectively.

### 3.1.4 Effect of adsorbent dose

The effect of adsorbent dosage from 0.1 to 1.0 g on the uptake of cadmium ions onto BCPW was studied and is shown in “Fig. 4”. The figure reveals that the removal efficiency of metal ions increased from 16.36% to 89.372% with an increase in the adsorbent dosage from 0.1 g to 1.0 g. Increase in adsorption by increase in adsorbent dose is because of increase in ion exchange sites, surface area and number of available adsorption sites [22]. Adsorption of Cd(II) reaches its saturation at adsorption capacity of 2.615 mg/g and then decrease gradually to 2.234 mg/g with increase of adsorbent dose up to 1 g. It may happen due to the overlapping of adsorption sites as result of adsorbent particles overcrowding [23].

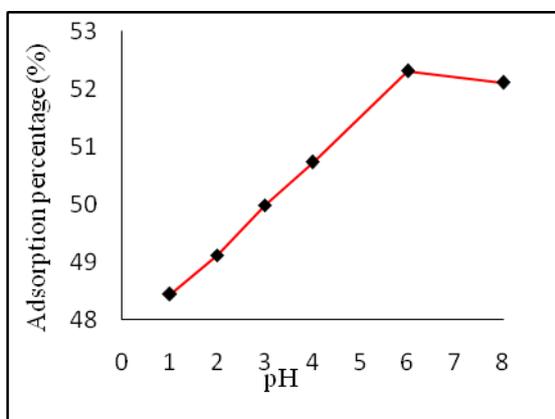


Fig. 1 Effect of pH

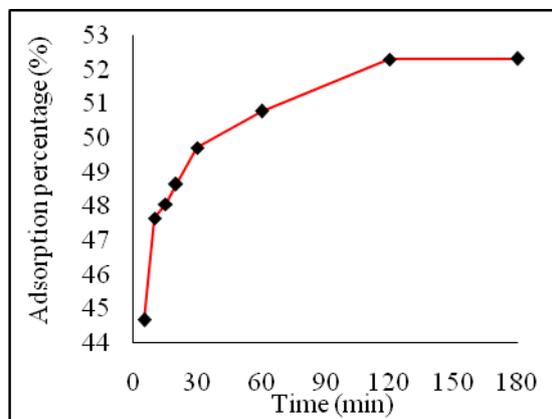


Fig. 2 Effect of contact time

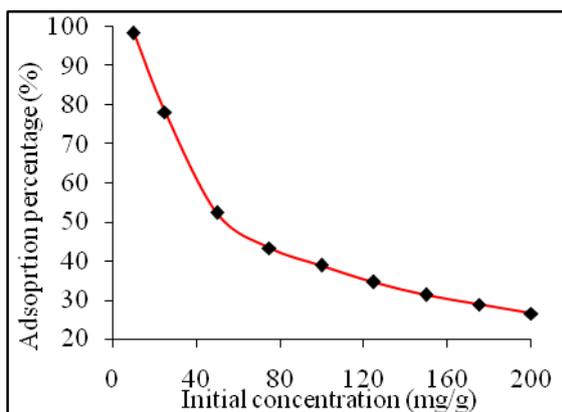


Fig.3 Effect of Cd(II) ions concentration

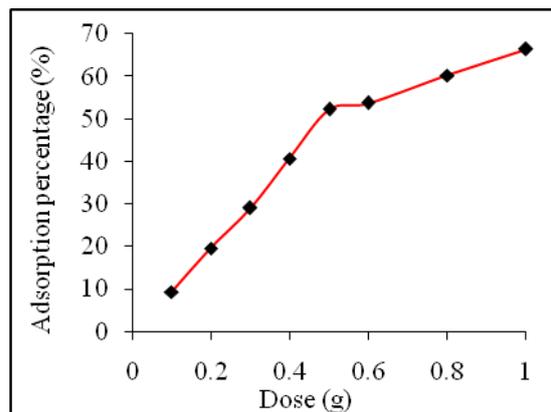


Fig. 4 Effect of adsorbent dose

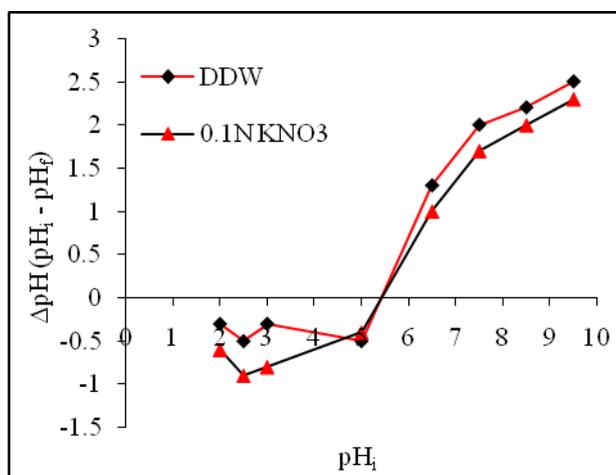


Fig.5 Point of zero charge of BCPW

### 3.2 Adsorption isotherms studies

The distribution of adsorbed molecules between the liquid and solid phase at equilibrium is indicated by adsorption isotherm. The obtained experimental data was analysed with Langmuir and Freundlich adsorption isotherm and shown in “Fig. 6 and 7”. The values of correlation coefficients,  $R^2$  and constants of these isotherms shown in table 2 indicated that Freundlich model dominates with  $R^2 \approx 0.969$  in the applicability of experimental data on isotherm models. The monolayer adsorption capacity,  $q_m$  of BCPW for Cd(II) ions calculated from Langmuir plot of  $1/q_e$  vs  $1/C_e$  shown in “Fig. 6” was found to be 3.695 mg/g. The values of  $K_F$ ,  $1/n$  and  $R^2$  obtained from the graph of  $\log q_e$  vs  $\log C_e$  for Freundlich isotherm shown in “Fig. 7” are listed in “Table 1”. The value of  $n$  was found to be 3.886 which is greater than 1 indicated that the adsorption of Cd(II) ions on BCPW occurred through chemisorption process. Moreover, the values of  $K_F \approx 1.421$  indicated good adsorption capacity of adsorbent.

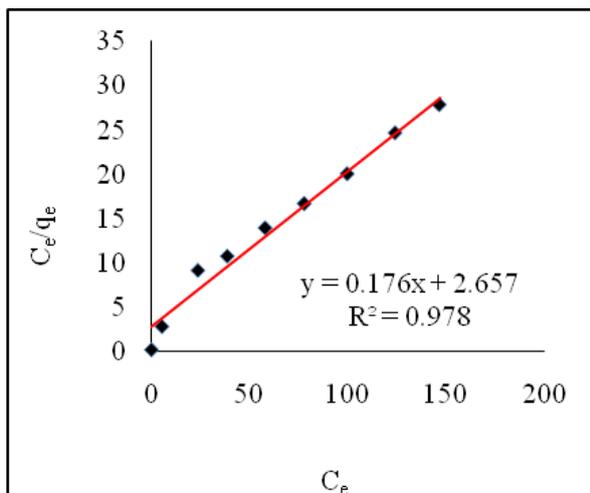


Fig. 6 Langmuir adsorption isotherm

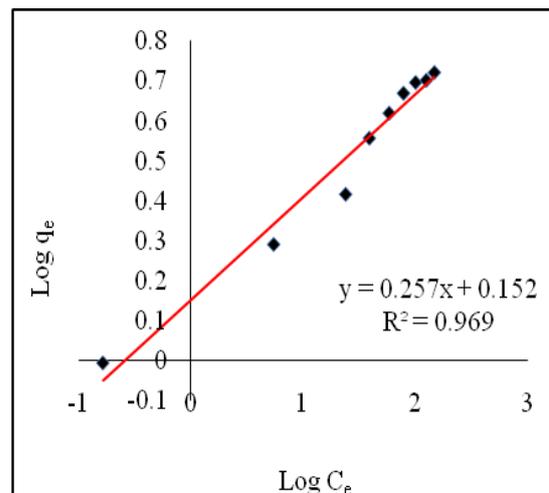


Fig. 7 Freundlich adsorption isotherm

Table: 1 Langmuir and Freundlich isotherm constants for the adsorption of Cd(II)

Metal	Langmuir isotherm				Freundlich isotherm			
	$q_m$	$b$	$R^2$	$R_L$	$1/n$	$n$	$K_F$	$R^2$
$\text{Cd}^{+2}$	3.695	2.217	0.860	0.0089	0.2573	3.886	1.421	0.969

## VI. CONCLUSION

The present investigation reveals that BCPW is an excellent free of cost available adsorbent used for the removal of Cd(II) ions from aqueous solutions. The adsorption parameters such as solution pH, adsorbent dose, initial Cd(II) ions concentration and contact time were studied in the experiment and the maximum adsorption of Cd(II) ions was found 52.3 % at pH 6 using 50 mg/L of Cd(II) ions solution with 0.5 g of adsorbent dose. Adsorption equilibrium data is best fitted to Freundlich model. The maximum adsorption capacity,  $q_m$  obtained from Langmuir model was 3.695 mg/g. The adsorption process was found to be chemical in nature and occurred by forming monolayer of Cd(II) ions. From these observations it can be concluded that BCPW is a potential, inexpensive and non-hazardous industrial waste which could be used as an effective indigenous material for treatment of wastewater stream containing cadmium ions.

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