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Research Article

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Adsorption isotherm and kinetics studies of cadmium (II) ions removal using various activated carbons derived from agriculture bark wastes: A comparative study

M. Syed Meera[*] and T. K. Ganesan[@#]

[*] *Department of Chemistry, S. L. S. M. A. V. M. Ayira Vaisyer College, Madurai, Tamil Nadu, India*
[@#] *Post-Graduate and Research Department of Chemistry, The American College, Madurai, Tamil Nadu, India*

ABSTRACT

This paper reports the feasibility of using various indigenously prepared activated carbons (IPACs) derived from agricultural residues viz., Eucalyptus Bark (Eucalyptus Globules), Neem Bark (Azadirachta Andica), Tamarind Bark (Tamarindus indica), Mango bark (Mangifera indica), Emblica Bark (Phyllanthus emblica) for the removal of Cd(II) from aqueous solution under different experimental conditions. Effect of various process parameters, viz., initial metal ion concentration, agitation time, initial solution pH and adsorbent dose has been studied for the removal of cadmium. The applicability of Langmuir and Freundlich isotherm suggests the formation of monolayer of Cd(II) ions onto the outer surface of the adsorbents. Moreover, the adsorption data are modeled with various first order kinetic equations like Natarajan-Khalaf, Lagergren and Bhattacharya-Venkobachar equations. Order of Cd(II) removal by various adsorbents is CAC>>EGBC >NBC>TBC>MBC>EOBC.

Keywords: Adsorption, Cadmium ions, kinetic studies, activated carbons, agriculture wastes

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INTRODUCTION

Cadmium (Cd) is one of the heavy metals considered to be toxic to humans and aquatic life. Over the last two decades there has been a sharp rise in the global use of Cd for batteries and a steady decline in its use for other applications, such as pigments, polyvinyl chloride stabilizers, and plating. This trend in the use of Cd products and compounds has inspired a number of international agreements to manage and control the release of Cd to the environment and limit human and environmental exposure. Chronic exposure to Cd can cause kidney damage in mammals and humans. One of the major sources of surface water contamination by heavy metals, such as Cd, is urban and agricultural storm water runoff. There is a great need for new and cost-effective processes for preventing excess concentrations of toxins from accumulating in streams, ponds, and lakes [1].

Among the various treatment processes of wastewater, adsorption is considered as superior to other conventional treatment processes due to the flexibility, easy operation and no/lesser sludge disposal problems, high efficiency and low working cost. Activated Carbon (AC) adsorption is widely employed for the removal of trace inorganics. However, the commercial activated carbon (CAC) has disadvantages like, high cost, difficulty in procurement, and high cost of regeneration and recharging [2-4].

In recent years, a great emphasis is being placed on the use of abundant low cost agricultural wastes/ by products as raw materials for the preparation of ACs. Apart from CAC, adsorbents like, fly ash, waste tea, coffee nut shell, metal oxides of Fe and Mn, bituminous coal, oxidised anthracite, peat, ACs, prepared from agricultural by-products/wastes like, rice, soya bean hull, sugarcane, bagasse, peanut shell and walnut shell, modified ground nut husks, iron oxy hydroxide, biosorbents like marine algae, clay minerals like montmorillonite *etc.*, have been used for the removal of metal ions. Efficient and environment friendly adsorbents are still needed to reduce heavy metal content in wastewaters to acceptable level at affordable costs [5-7].

In the present study, removal of Cd(II) ions by adsorption on CAC and indigenously prepared ACs such as Eucalyptus Globules Bark Carbon (EGBC), Neem bark carbon (NBC), Tamarind Bark carbon (TBC), Mango bark carbon (MBC), Embolica Officinalis Bark (EOBC) has been investigated. The influence of various process parameters like, initial concentration, contact time, dose, initial pH and particle size of IPACs on adsorption of Cd(II) ions has also been studied and the results are compared.

EXPERIMENTAL SECTION

2.1 Chemicals and Reagents

CAC and cadmium(II) sulphate are procured from E. Merck, India. All the other chemicals and reagents are analytical grade used as received.

2.2 Collection, Preparation and activations of adsorbents

Raw materials for the preparation of IPACs such as various agricultural bark residues *viz.*, Eucalyptus Globules *Bark (Eucalyptus Globules)*, Neem bark *(Azadirachta indica)*, Tamarind Bark (*Tamarindus Indica*), Mango bark (*Mangifera Indica*), Embolica Bark (*Embolica Officinalis*) were collected locally, washed, dried, cut into small pieces, carbonised (at 300°C) and thermally activated (at 800°C), acid digested (2N HNO_3) and washed [8]. The materials were then sieved to discrete particle size using mechanical sieve shaker.

The adsorbate stock solution of 1000 mg/l Cd(II) was prepared from cadmium sulfate ($CdSO_4.8H_2O$) in distilled water containing a few drops of nitric acid to prevent hydrolysis. Cadmium(II) ion concentration was estimated spectrophotometrically (UV–visible spectrophotometer) using pyronine G reagent. A suitable aliquot of the sample solution containing not more than 15 μg of Cd(II) ions was transferred into a 25 mL volumetric flask. Citrate buffer, 10% (w/v) potassium iodide and 0.024% (w/v) pyronine G solutions (each 2.5 mL) were added with mixing followed by 1 mL of 1% (w/v) gelatin solution. The solution was diluted upto mark with DD water and mixed well. Absorbance reading was measured at 575 nm (λ_{max}) against a reagent blank.

RESULTS AND DISCUSSION

Adsorption experiments were carried out at room temperature ($30 \pm 1^{\circ}$C) under batch mode. The experimental conditions are given in Table 1.

Table 1 Experimental Conditions for the removal of Cd(II) ions by adsorption on CAC and IPACs

Parameter	Cd(II) ions (mg/L)	Time[@] (min.)	Dose (g/L)	Particle size (micron/μ)	Initial pH
Cd (II) ions (mg/L)	100-1000 (CAC) 40-220 (EGBC) 25-250 (NBC) 25-70 (TBC) 10-100 (MBC) 20-110 (EOBC)	30 (CAC & IPACs)	4 (CAC) 12 (IPACs)	90	Solution pH
Time[@] (min.)	Optimum # 600 (CAC) 140 (EGBC) 125 (NBC) 50 (TBC) 60 (MBC) 60 (EOBC)	5-50 (CAC & IPACs)	4 (CAC) 12 (IPACs)	90	Solution pH
Dose (g/L)	Optimum #	Optimum # 45 (CAC) 40 (EGBC & NBC) 35 (TBC, MBC & EOBC	3.0-5.0 (CAC) 2-20 (IPACs)	90	Solution pH
Initial pH	Optimum #	Optimum #	Optimum #	Optimum #	2-8

 # Fixed as optimum conditions at which maximum removal was observed.

[@] Contact time.

3.1 Effect of initial concentration on the extent removal of Cd(II) ions

Figure 1 showed the effect of initial concentration of Cd(II) ions on the percentage removal on various adsorbents *viz.*, CAC and IPACs were studied at $30 \pm 1^{\circ}$C. The percentage removal decreased with the increase in initial concentration of Cd(II) ions. This indicates that there exists reduction in immediate solute (Cd(II) ions) adsorption, owing to the lack of active sites required for the high initial concentration of Cd(II) ions [2-5, 7,8]. Optimum concentration is fixed as 600 ppm (CAC), 140 ppm (EGBC), 125 ppm (NBC), 50 (TBC), 60 ppm (MBC) and 60 ppm (EOBC).

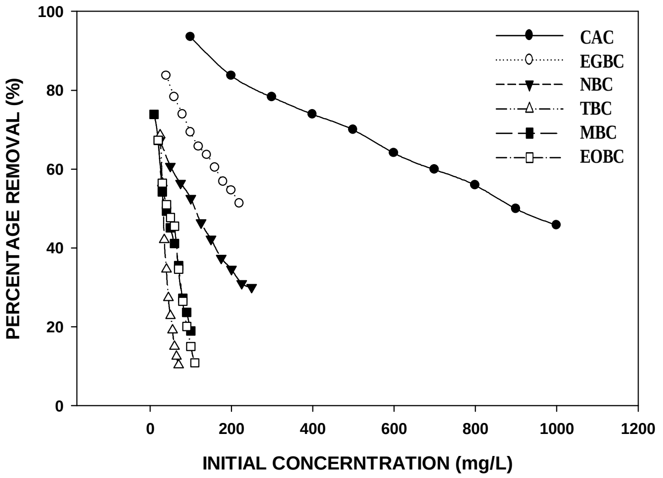

Figure 1 Effect of Initial concentration for the removal of Cd(II) ions by adsorption onto CAC and IPACs

3.1.1 Adsorption isotherms

The adsorption data were analysed with the help of Freundlich [9] and Langmuir isotherms [10]. The adsorption data were fitted with these isotherms by carrying out correlation analysis between the values of: log q *vs* log C_e and (C_e/q) *vs* C_e. Figure 2 showed the Langmuir and Freundlich isotherm plots on the adsorption of Cd(II) ions by various carbons. The adsorption isotherm parameters along with the r-values are given in Table 2. The observed linear relationships are found to be statistically significant, which indicates the applicability of these isotherms. Langmuir isotherm indicates the monolayer coverage of Cd(II) species on the surface of AC and also gives the monolayer adsorption capacities (Q_0-values). The adsorption capacity of various ACs (as evidenced from values) is found to be of the order: **EOBC<MBC<TBC < NBC < EGBC << CAC.** Among the IPACs, EGBC was found to possess high adsorption capacity than the other carbons.

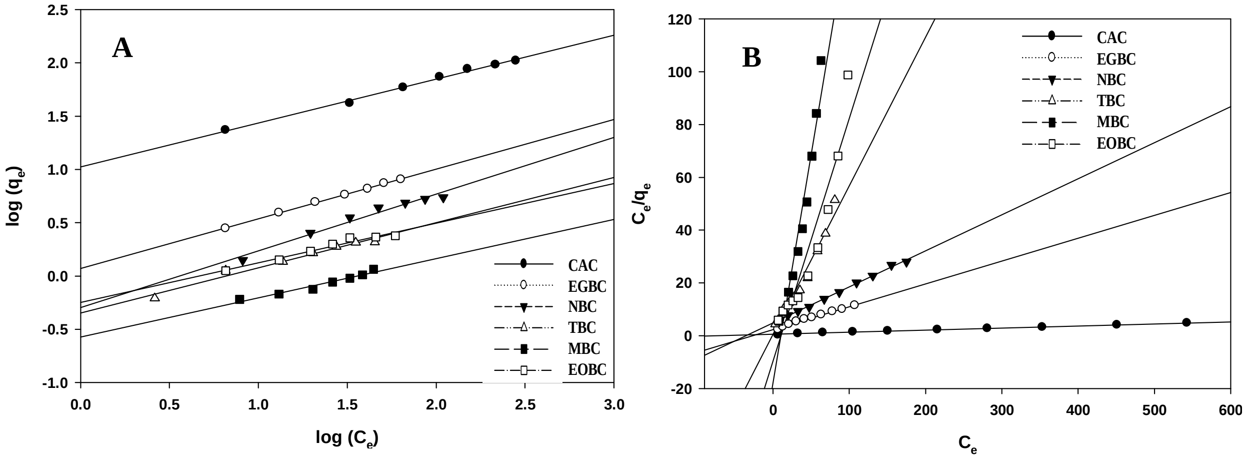

Figure 2 (A) Freundlich and (B) Langmuir adsorption isotherm plots for the removal of Cd(II) ions onto CAC and IPACs

Table 2 Isotherm Constants for the adsorption of Cd(II) ions by ACs

Parameters	CAC	EGBC	NPC	TBC	MBC	EOBC
Langmuir isotherm						
10^2 b value (Lmg^{-1})	0.018	0.045	0.029	0.178	0.109	0.351
Q_o (mg/g)	12.11	10.464	7.729	2.502	2.019	0.813
R_L-Value	0.157	0.204	0.303	0.179	0.231	0.064
r-value	0.989	0.992	0.999	0.992	0.995	0.976
Δq (%)	1.435	0.168	0.286	0.624	0.195	0.936
Freundlich isotherm						
Slope (1/n)	0.412	0.466	0.533	0.289	0.424	0.264
Intercept (log K)	1.024	0.069	0.298	0.447	0.345	0.128
r-value	0.998	0.999	0.985	0.955	0.986	0.928
Δq (%)	0.051	0.005	0.024	0.120	0.095	0.077

3.2 Effect of contact time on the removal of Cd(II) ions

Effect of contact time on the extent removal of Cd(II) ions by CAC and IPACs were showed in Figure 3. The percentage removal of Cd(II) ions increases with increase in contact time and reaches almost constant after equilibrium time. The increase in the relative extent of removal of Cd(II) ions after 45 min., of contact time for the adsorbents CAC and 40 min., for EGBC and NBC; 35 min., for TBC, MBC and EOBC and hence 35/40/45 min., is fixed as the optimum contact time. The adsorbate normally forms a surface layer, which is only one molecule thick; *i.e.,* a monolayer on the surface of the adsorbent. Although the adsorption capacities of IPACs were less, but still they could be considered as low cost alternatives to CAC for the removal of metal ions [2-5,8].

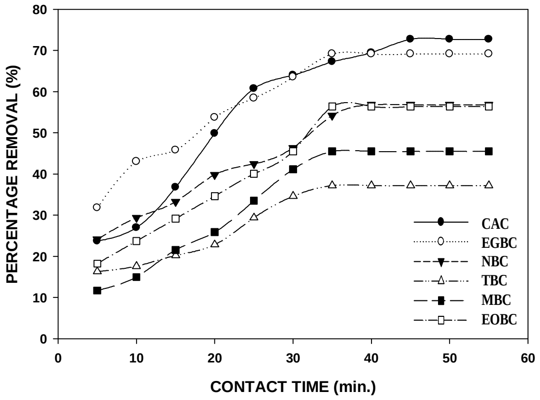

Figure 3 Effect of contact time for the removal of Cd(II) ions by adsorption onto CAC and IPACs

3.2.1 Kinetics Studies

The kinetics of adsorption of Cd(II) ions by various ACs have been studied by applying various first order kinetic equations proposed by (i) Natarajan and Khalaf [11], (ii) Lagergren [12] and (iii) Bhattacharya and Venkobachar [13] equations and the plots are shown in Figure 4. The values of (i) log (C_i/C_t) vs. time, (ii) log (q_e-q_t) vs. time and (iii) $(3+(1/(q_e-q_t))$ Vs. time were linearly correlated were linearly correlated. The values of order rate constant (k in min.$^{-1}$) along with the correlation coefficients are given in Table 3.

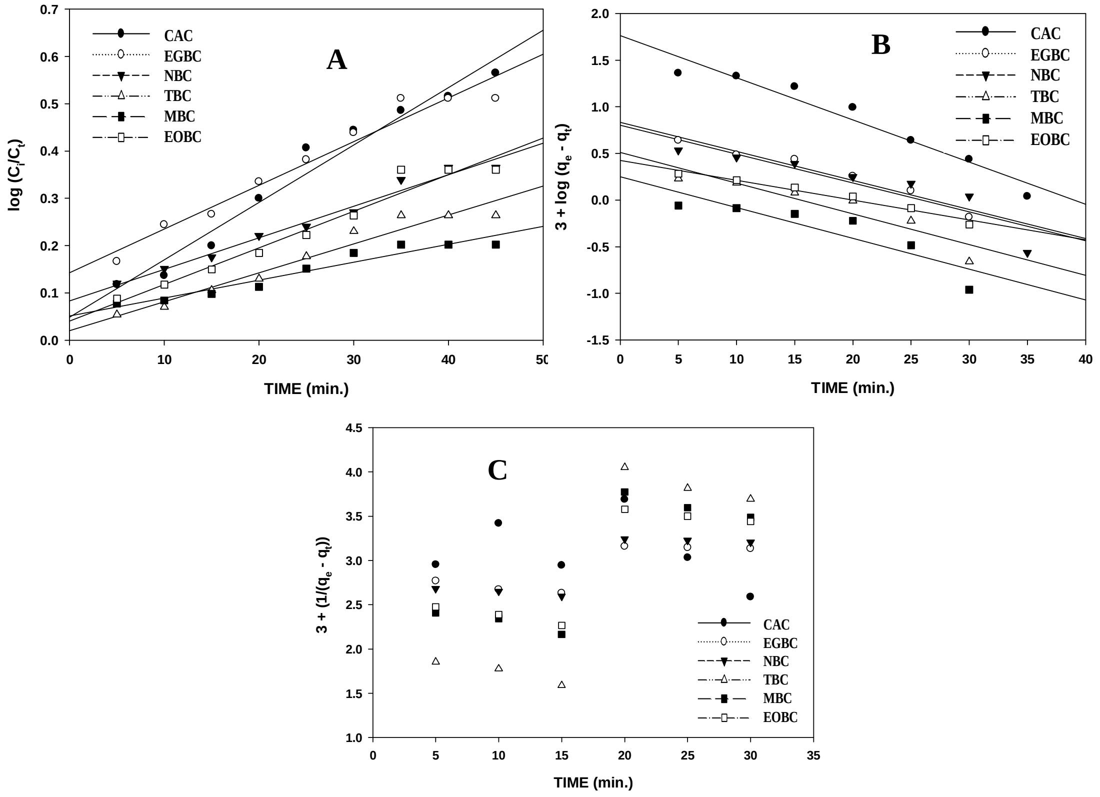

Figure 4 (A) Natarajan-Khalaf; (B) Lagergren and (C) Bhattacharya-Venkobachar equations for the removal of Cd(II) ions onto CAC and IPACs

All the linear correlations were found to be statistically significant at 95% confidence level, and indicate the applicability of these kinetic equations and first order nature of the adsorption process of Cd(II) ions on ACs. Among the IPACs, EGBC is found to possess a higher rate constant of adsorption (5.541 min.$^{-1}$) compared to other IPACs.

Table 3 Kinetic parameters for the removal of Cd(II) ions by adsorption on CAC and IPACs

Parameters	CAC	EGBC	NBC	TBC	MBC	EOBC
Natarajan-Khalaf Equation						
10^2 k (min.$^{-1}$)	3.172	2.535	1.954	1.683	1.580	1.031
r-values	0.985	0.995	0.988	0.986	0.975	0.976
Δq (%)	2.514	13.14	15.94	1.84	13.17	5.47
Lagergren Equation						
10^2 k (min.$^{-1}$)	5.610	5.541	4.23	3.75	2.541	3.724
r-value	0.944	0.980	0.983	0.989	0.983	0.997
Δq (%)	1.682	6.090	8.141	2.175	18.440	5.741
Bhattacharya-Venkobachar Equation						
10^2 k (min.$^{-1}$)	5.610	5.541	4.232	3.752	2.541	3.724
r-value	0.944	0.980	0.983	0.989	0.983	0.997
Δq (%)	19.81	20.06	25.84	28.49	36.81	28.62

The rate constant 'k' calculated from the statistical values of intercept and the constant (l/m) from the slope are shown in Table 3. The significant correlation coefficients obtained for the metal–AC systems (CAC: 0.963; EGBC: 0.980; NBC: 0.994; TBC: 0.979; MBC: 0.991; EOBC: 0.928) clearly evidence the applicability of modified Freundlich equation [8, 14, 15].

3.3 Effect of Dose of adsorbents on the extent removal of Cd(II) ions

The effect of dose of adsorbent (AC) on the extent of adsorption (in terms of percentage removal) was studied by varying the dose by keeping all the other process parameters as constant (Figure 5). As the dose of AC increases, the percentage removal of Cd(II) ions increases and reaches a maximum value. The optimum dose of CAC and IPACs are fixed as 4gL^{-1} and 12 gL^{-1}, respectively. The amount of Cd(II) ions adsorbed was found to vary exponentially with a fractional power term of the dose of adsorbent according to the relationship:

$$\mathbf{q = m\,(dose)^{-n} + c}$$

Where, q = amount adsorbed (mg g^{-1}) ; m = slope; c = intercept and n= power term, which is a fraction. The n value for various ACs (r value): CAC=0.145 (0.994); EGBC=0.137 (0.988); NBC=0.122 (0.971); TBC=0.119 (0.968); MBC=0.094 (0.954) and EOBC = 0.088 (0.949). The plots of log(% removal) *vs* log(dose) are found to be linear (r≈1.0). This suggests that the adsorbent species may either block the access to the internal pores or cause particles to aggregate or conglomeration taking place and thereby resulting in decrease in the availability of active sites for adsorption [8, 16-19].

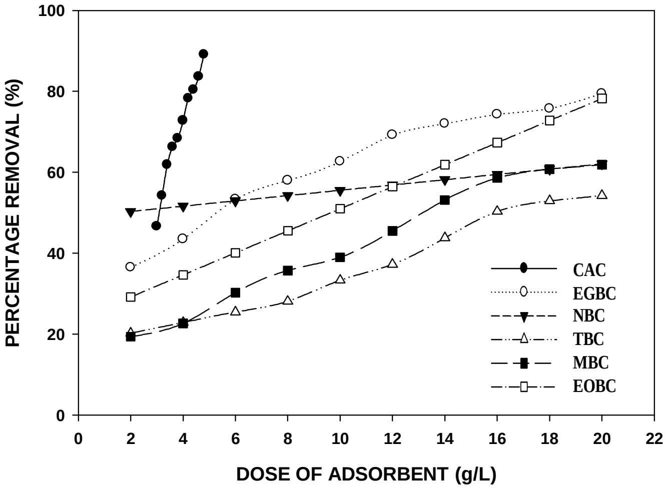

Figure 5 Effect of Dose of adsorbent for the removal of Cd(II) ions by adsorption onto CAC and IPACs

3.4 *Effect of initial pH on the extent removal of Cd(II) ions on IPACs*

The increase in the initial pH of the solution, increased the percentage of removal of Cd(II) ions (Figure 6). The final pH slightly varies after adsorption and the change in pH are found to be of the order of 0.2-0.8 units. The optimum initial pH is fixed as 7.0. This is in harmony with the literature reports [8, 20-22].

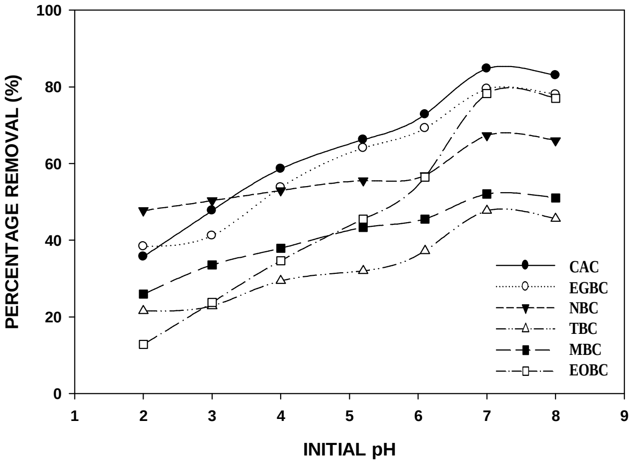

Figure 6 Effect of Initial pH for the removal of Cd(II) ions by adsorption onto CAC and IPACs

CONCLUSION

The potential use of various activated carbons including EGBC, NBC, TBC, MBC and EOBC as an adsorbent for cadmium was studied and the results were compared with CAC. These new adsorbents are able to remove the cadmium (II) ions from aqueous solutions, and the adsorption capacity was strongly dependent on the adsorbent nature, dosage, initial metal ions concentration and initial pH. The experimental data well fitted to the isotherm and kinetic equations, with good correlation coefficients. The relative order of adsorption capacity is CAC>>EGBC>NBC>TBC>MBC>EOBC. These results can be helpful in designing a wastewater system for the removal of metal ions.

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