Journal of Applied Sciences

ISSN 1812-5654

Journal of Applied Sciences 6 (1): 47-50, 2005
ISSN 1812-5654

Kinetics of Phenol-sorption by Raw Agro-wastes

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Abstract: Phenol is one of the most toxic industrial pollutants and even at low concentration it is reported to affect water quality and is harmful to human health. Although activated carbon has been one of the most commonly used adsorbents to treat organic compounds, yet its high cost and difficulty in recovery has directed extensive research on low cost adsorbents. As an alternative to activated carbon, a study has been carried out using various agro waste namely Rice Husk (RH), Cashew Nut Shell (CNS), Coffee Skins (CS), Corn Shell (CRS), Green Gram Husk (GGH) and Black Gram Husk (BGH). The kinetic study showed that the above agro wastes have shown better rate constants and diffusion coefficient as compared with activated carbon.

Key words: Phenol, sorption, kinetics, agro-wastes

INTRODUCTION

Phenol is an organic compound widely used in industries such as plastics, lubricants, paints, pharmaceuticals, herbicides and resins[1]. Chemically, phenol is a hazardous compound, if absorbed through the skin, inhaled or swallowed may lead to serious injuries or fatalities. One of the major threats due to phenol-toxicity lies in its ability to penetrate the skin rapidly. Various common phenolated-industrial-effluents have been reported to range between 35-8000 ppm[2]. As per the Environmental Protection Agency (EPA), the permissible limit of phenol for drinking water is 0.002 ppm.

The phenol removal has been achieved by various methods such as sorption[3], biological degradation[4], chemical oxidation[5] and solvent extraction[6]. Out of all these methods sorption technique is the most common method due to its simplicity and easy operation.

Many researchers have carried out studies on different types of wastes, which include industrial wastes (viz. fly ash, bottom ash, etc.), community or agricultural wastes (viz., sludge, roots/barks/stems /leaves/hulls/husks/pills/seeds of various plants)[7-10] as adsorbent in search of a cost-effective alternative to Activated Carbon (AC). However, most research were sporadic and were studied under different experimental conditions, with attempt to improve the adsorption capacity of the wastes (through various treatments: activation, oxidation, solvent extraction, etc.)[6,11,12]. However, the rate of adsorption (also called kinetics), which plays an important role in carrying out rapid-adsorption, a major requirement in handling high discharge rate of phenolated-effluents has not received due attention, even under varying adsorption conditions[13]. In pursuit of a systematic evaluation of kinetics of some common agro-wastes, the present research has been carried out, with a specific objective of evaluation the effectiveness of low cost adsorbents at uniform experimental conditions using agro waste as adsorbent with regard to rate constant and intra particular diffusion.

MATERIALS AND METHODS

Preparation of adsorbents: Rice husk, Cashew nut shell, Coffee skins, Corn shell, Green gram husk and Black gram husk, which are locally available, were used as adsorbent. These agricultural wastes were thoroughly rinsed with water to remove dust and soluble material and are allowed to dry at room temperature. The dried above wastes were crushed into powder and sieved through the sieves and particles retained on sieve No. 30 (600 μm) were collected for this study. In this study the results were compared with AR Grade activated carbon.

Preparation of adsorbate: Phenolated aqueous solution was prepared by dissolving AR grade phenol crystals in distilled water and is used as a stock solution to prepare the required concentration of the solution.

Adsorption studies: The experiments were conducted by using Rice husk, Cashew nut shell, Coffee skins, Corn shell, Green gram husk and Black gram husk as adsorbents at room temperature under batch mode, by adding known amount of adsorbent 0.1 g in 15 mL of synthetic phenol solution concentration of 100 ppm taken in a 600 mL beaker and adsorption was carried out for different durations of contact time (1, 2, 3, 4, 5, 6 and 7 h).

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After adsorption, the solutions were filtered through the Whatman 42 filter paper and Phenol optical density was analyzed by UV-Spectrophotometer at a wavelength of 270 nm.

Kinetics-rate constant: Rate constant is an extremely useful quantitative characteristic of a chemical or physical process. It gives the relationship between reaction rate and concentrations of reactants.

The rate constant equation is considered by assuming the adsorption reaction as a first order and reversible reaction. The rate constant can be calculated by the Lagergren Eq.[14]:

$$\text{Log}\,(C_{max} - C_t) = \text{Log}\,(C_{max}) - \frac{K_{ad}}{20303} \times t$$

C_{max} : Maximum Concentration of phenol, mg L^{-1}
C_t : Concentration of time at anytime
K_{ad} : First Order Rate constant of adsorption
t : Time

The graph plotted between log (C_{max}-C_t) and t the slope of the plot gives the rate constant for different adsorbents used for adsorption.

Second order kinetics: the sorption data was also studied by second order mechanism described by Wu *et al.*[15].

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$$

Where, K_2 is the rate constant of second order adsorption in g mg^{-1} min^{-1} on further simplification of the above equation is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

it is of the form y = mx +c; where, $k_2 q_e^2$ = h, then equation can be re written as:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e}$$

the applicability of this equation can be studied by a plot of t/qt vs t, which gives a linear relationship from which the constants k_2, q_e and h can be determined.

Intraparticle diffusion: The structure of the solid and its interaction with the diffusing substance influence the rate of transport. Adsorbents may be in the form of a porous barrier here solute movement by diffusion from one fluid body to the other by virtue of concentration gradient[16]. Intra particle diffusion is a transport process species from the bulk of the solution to the solid phase. A plot between the amount of phenol adsorbed and square root of time gives the rate constant (slope of the plot) of intraparticle diffusion. Intraparticle diffusion can be calculated by using the intra particle diffusion model[17].

$$q_t = Kp\, t^{(1/2)} + C$$

q_t : Amount of phenol adsorbed at any time (mg g^{-1})
t : Time
C : Intercept
Kp : Intra particle diffusion rate constant (mg g^{-1} $h^{-1(1/2)}$)

RESULTS AND DISCUSSION

In the present study using different agro waste adsorption, rate constant Intra particular diffusion studies were carried out by using synthetic phenol solution. The studies were aimed at variation in phenol adsorption with different agro wastes as adsorbent.

Effect of agro waste: The optimum time of 6 h was found for the agro wastes as evident from plot between % of adsorption vs time. Figure 1 shows a high % of adsorption in Rice husk, Cashew nut shell, Coffee skins, Corn shell, Green gram husk and Black gram husk and activated carbon (up to 82.2, 79.3, 73.5, 70, 59.5, 54.5 and 95%, respectively). The result shows that the agro-wastes without any pretreatment are competent for activated carbon in adsorption process. It is found that rice husk has shown better adsorption than other agro wastes.

Determination of rate constant: To calculate the first order rate constant K_{ad}, experiments were performed with 100 ppm initial concentration of phenol. A graph plotted between log (C_{max}-C_t) and t for the different adsorbents yields a straight line (Fig. 2), the slope being the rate constant for different agro waste adsorbents used for adsorption (Table 1). In the present kinetic study, it was observed that the correlation of first order kinetics of activated carbon is highly favorable due to its high porosity and surface area. The raw agricultural wastes have shown varying correlations, however CRS and BGS have shown better correlation as compared with RH, CNS, CS and GGH. But the first order rate constant (k_{ad}) of CS, GGH and BGH have found high as compared with all other adsorbents including activated carbon. It indicates these agricultural wastes have a potential of adsorption, if treated properly. A graph was plotted between t/qt and t to evaluate the second order rate constants (K_2). It was observed that all these adsorbents obey the second order

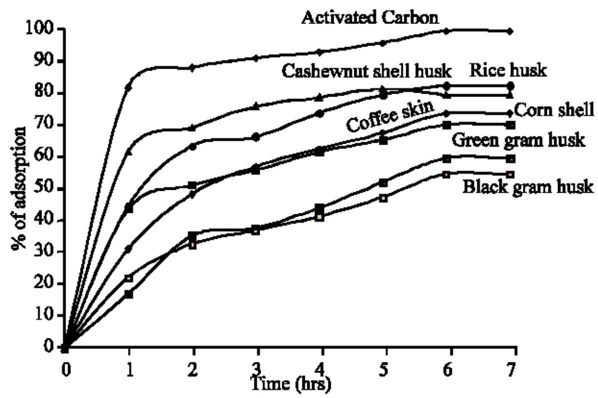

Fig. 1: Adsorption capacity of various agro wastes

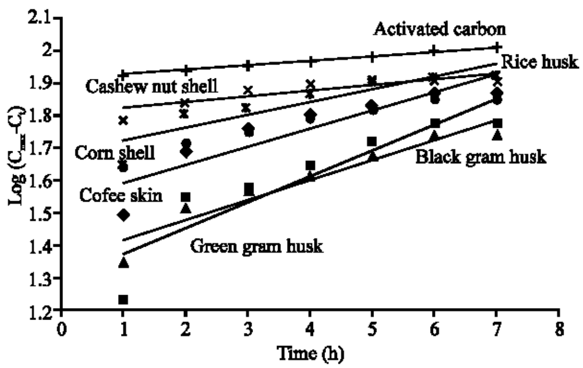

Fig. 2: First -order kinetics for different adsorbents

Table 1: First order rate constant for various adsorbents

Adsorbents	Rate constant K_{ad} (1 h^{-1})	Correlation compressed(R^2)
Activated Carbon (AC)	0.02	0.99
Rice Husk (RH)	0.09	0.80
Cashew Nut Shell (CNS)	0.04	0.73
Coffee Skin (CS)	0.12	0.82
Corn Shell (CRS)	0.07	0.91
Green Gram Husk (GGH)	0.18	0.82
Black Gram Husk (BGH)	0.14	0.91

Table 2: Second order rate constants for various adsorbents

Adsorbents	Rate constant K_2 (mg L^{-1} min^{-1})	Correlation compressed(R^2)
Activated Carbon (AC)	0.17	0.99
Rice Husk (RH)	0.05	0.99
Cashew Nut Shell (CNS)	0.21	0.99
Coffee Skin (CS)	0.03	0.99
Corn Shell (CRS)	0.07	0.99
Green Gram Husk (GGH)	0.05	0.78
Black Gram Husk (BGH)	0.03	0.97

kinetics (Fig. 3). The second order rate constant of CNS was found to be very high, compared to other adsorbents. The correlation coefficient for second order kinetics of all agro-wastes was found to be greater than 0.96 (Table 2). A comparison of first order kinetics the second order kinetic model provides the better correlation coefficients.

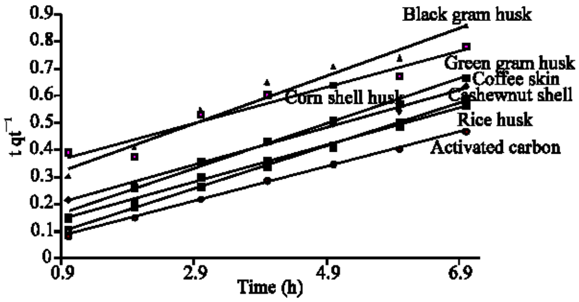

Fig. 3: Pseudo second-order kinetics for different adsorbents

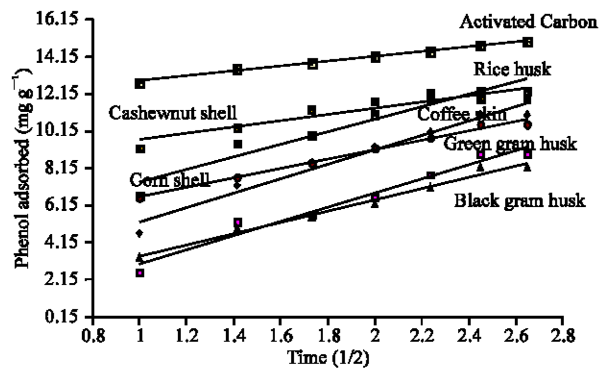

Fig. 4: Rate constant intra-particle diffusion

Table 3: Intra particle diffusion constant for different adsorbents

Adsorbents	Rate constant intra particle diffusion K_p (mg g^{-1} $min^{-1(1/2)}$)
Activated Carbon (AC)	0.16
Rice Husk (RH)	0.43
Cashew Nut Shell (CNS)	0.21
Coffee Skin (CS)	0.49
Corn Shell (CRS)	0.32
Green Gram Husk (GGH)	0.49
Black Gram Husk (BGH)	0.39

Determination of intraparticle diffusion: A graph was plotted between the amount of phenol adsorbed and square root of time. From the slope of the plots (Fig. 4), the rate constants of intraparticle diffusion for different agro waste adsorbents were calculated. It was observed that the intraparticle diffusion coefficient of three agro wastes (CS, GGH and RH) are found to be high as compared with other adsorbents (Table 3).

CONCLUSIONS

The raw agro wastes such as Rice husk, Cashew nut shell, Coffee skins, Corn shell, Green gram husk and Black gram husk have shown a considerable adsorption capacity without any treatment. The kinetic studies revealed that agro wastes are following second order kinetics better than to first order kinetic and the intraparticle diffusion studies revealed that CS, GGH and RH have better diffusion coefficient as compared with other wastes.

ACKNOWLEDGMENTS

The authors are very much thankful to Department of Science and Technology, New Delhi for sponsoring the project.

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