Evalution of Barley Straw and its Ash in Removal of Phenol from Aqueous System

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Abstract: The adsorption behavior of barley straw and its ash for phenolic compound from aqueous solutions has been investigated. Batch kinetics and isotherm studies were carried out under varying experimental conditions of contact time, phenol concentration, adsorbent dose and pH. Adsorption equilibrium of barley straw and barley straw ash were reached within 6 hours and 3 hours for phenol concentration 1000-5000 µg L^{-1}, respectively. Kinetics of adsorption obeyed a first-order rate equation. The adsorption of phenol increases with decreasing the solution pH value. The suitability of the Freundlich and Langmuir adsorption models to the equilibrium data were investigated for each phenol-sorbent system. The results showed that the equilibrium data for all the phenol-sorbent systems fitted the Freundlich model (R^2=0.98) best within the concentration range studied. A comparative study showed that barley straw ash is very effective than barley straw for phenol removal. The studies showed that the barley straw ash can be used as an efficient adsorbent material for removal of phenolic from water and wastewater.

Key words: Adsorption · Barley straw · Barley straw ash · Phenol · Agricultural waste

INTRODUCTION

It is difficult to separate industrial growth from environmental pollution. So, excessive release of toxic organic matter into the environment due to industrialization has created a great global concern during recent years. Phenols as a class of organics are similar in structure the more common herbicides and insecticides in that they are resistant to biodegration. Phenol is very soluble in water. Their presence in water supplies are noticed as had taste and odor [1]. In the presence of chlorine in drinking water, phenols form chlorophenol, which has a medicinal taste, which is quite pronounced and objectionable [2]. Phenols are considered as priority pollutants since they are harmful to organisms at low concentrations and many of them have been classified as hazardous pollutants because of their potential harm to human health. Stringent US Environmental Protection Agency (EPA) regulation call for lowering phenol content in the wastewater less than 1 mg L^{+} [1, 3].

There are many methods such as oxidation, precipitation, ion change, solvent extraction and adsorption for removing phenols and its derivatives from aqueous solution [2, 4-6]. Adsorption is a well-established and powerful technique for treating domestic and industrial effluents [7]. However, in water treatment the most widely used method is adsorption onto the surface of activated carbon [8]. Activated carbons remove many of the impurities occurring in water and wastewater [8, 9]. In spite of these characteristics, because of the high cost and variable performance of carbon regeneration, single use materials are desirable [2, 10]. This has led many workers to search for more economic, practical and efficient techniques. Bottom ash, brick-kilm ash, fly ash, peat, soil, rice husk, wood, saw dust, bagasse and carbonized bark are some new adsorbent used for organic pollutants, [2, 5, 7, 11]. In the search for new and low cost agricultural wastes as source material for widely uses, barley straw is an agricultural waste produced as by-product of the barley milling industry [7, 12]. The utilization of this source of biomass would solve both a disposal problem and also access to cheaper material for adsorption in water pollutants control system [13]. Chemical composition (w/w) of raw barley straw consists of cellulose (37.5%), hemicelluloses (36.1%), lignin (15.5%), ash (4.8%) and wax (2.5%) [14]. The availability of specific functional groups such as hydroxyl (-OH) existing in the cellulose, hemicelluloses as well as lignin structure suggests a potential of using barley straw as an adsorbent material [15]. The barley straw ash has more

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than 90 wt% of silica with high porosity and large surface area, because it retains the skeleton of cellular structure. These properties of the barley straw ash can are used to synthesize siliceous raw materials such as clay materials [5]. The aim of this study was to explore the possibility using barley straw and barley straw ash for removing phenol from aqueous solution. The influences of various factors, such as initial pH and initial pollutant concentrations on the sorption capacity were also studied. The Freundlich and Langmuir models were used to analyze the adsorption equilibrium.

MATERIAL AND METHODS

Preparation of Sorbent: The barley straw used was obtained from the west part of Iran. The barley straw were crushed and sieved with a 30-mesh siever. Then, the straws were thoroughly washed distilled water to remove all dirt and were dried at 100°C till constant weight. The dried straws were stored in desiccator until used. The barley straw ash obtained from burning of barley straw in electrical oven at 400°C for 3 hours. The barley straw ash was sieved with an 80-mesh siever and stored in a desiccator until used.

Chemicals: The test solutions were prepared by diluting of stock solution of phenol to the desired concentrations. A stock solution was obtained by dissolving 1.0 g of phenol, (obtain from Merek), in cooled distilled water and dilute to 1000 ml. Intermediate phenol solution was obtained by dissolving 100 ml of stock solution of phenol in distilled water and dilute to 1000 ml and finally, standard phenol solution prepared by dissolving 100ml intermediate phenol solution in distilled water and dilute to 1000 ml. The concentration range of phenol prepared from stock solution varied between 1000 μg L^{-1} to 5000 μg L^{-1} for both adsorbents. Before mixing the adsorbent, the pH of each test solution was adjusted to the required value with diluted and concentrated H$_2$SO$_4$ and NaOH solution, respectively. All pH measurements were carried out with a pH meter model E520, Metrohm Herisan.

Absorption Studies: Sorption studies were conducted in a routine manner by the batch technique. Each phenol solution was placed in 250 ml beakers and a known amount of adsorbents (1 to 5 g L^{-1}) was added to each beaker. The beakers were agitated on a shaker at 120 rpm constant shaking rate for 6 hours to ensure equilibrium was reached. For the studies with the barley straw, before analysis, samples were distilled by distillation apparatus

according to standard methods [16]. Then, distilled samples analyzed for the remaining phenol. The studies were performed at a constant temperature of 25°C to be representative of environmentally relevant condition. For the studies with the barley straw ash, before analysis, samples were centrifuged at 5000 rpm for 5 min and the supernatant fluid analyzed for the remaining phenol. Kinetic experiments were conducted using a know weight of adsorbent dosage and employing phenol concentration. Finally the suitability of the Freundlich and Langmuir adsorption model to the equilibrium data were investigated for phenol - sorbent system. All the experiments were carried out in duplicates and the average value were used for further calculations.

Analysis of Phenol: The concentration of residual phenol in the sorption medium was determined with direct photometric method. At the end, after the preparation of samples according to the standard methods, the residual phenol concentrations were measured using spectrophotometer equipment (spectrophotometer DR-2000, HACH). The absorbance of the colored complex of phenol with 4-aminoantipyrine was read at 500nm [16].

RESULTS AND DISCUSSION

The adsorption of phenol in aqueous solution on barley straw and its ash were examined by optimizing various physicochemical parameters such as; pH, contact time, the amount of adsorbent and adsorbate.

Effect of Initial pH: The adsorption of phenol from aqueous solution is dependent on the pH of the solution, which affects the surface charge of the adsorbent, degree of ionization and speciation of the adsorbate species. The results are displayed in Fig.1. As was expected, the adsorbed amount decreases with increasing the pH value. This can be attributed to the depending of phenol ionization on the pH value. The ionic fraction of phenolate ion φ_{ions} can be calculated from from [3]:

$$\varphi_{ions} = \frac{1}{[1+10^{(pk_a - pH)}]}$$

Obviously, φ_{ions} increases as the pH value increased. Accordingly, phenol, which is a weak acid (pKa=10), will be adsorbed to a lesser extent at higher pH values due to the repulsive force prevailing at higher pH value [3, 17]. Also, in the higher pH range phenol forms salts, which readily ionize leaving negative charge on
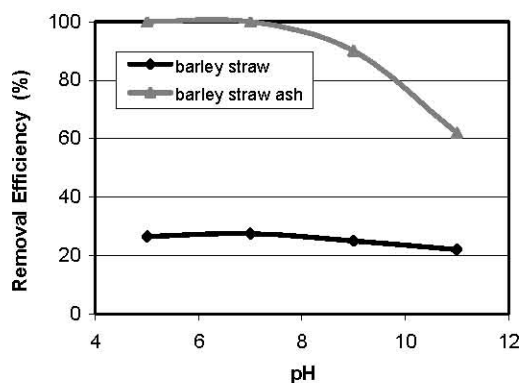
Fig. 1: Effect of pH on the removal of phenol by barley straw and its ash (Adsorbent dosage=2 g L^{-1} ml, phenol concentration= 1000 μg L^{-1})
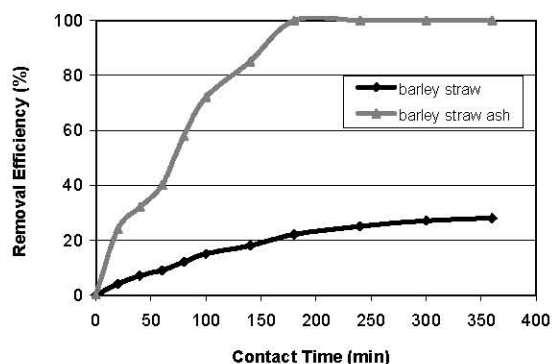

Fig. 2: Effect o f contact time on the removal of phenol by barley straw and its ash (Adsorbent dosage=1 gL^{-1}, phenol concentration=1000 μg L^{-1})

the phenolic group. At the same time the presence of hydroxyl ions on the adsorbent prevents the uptake of phenolate ions [2, 17]. Similar behavior has been reported by Halhouli *et al* (1997) for the adsorption of phenol by activated carbon and adsorption of phenol onto bentonite by Banat. [3]. pH also affects the surface properties of the sorbent, i.e., surface charge of the cells used as sorbent. At very low pH values, the surface of the sorbent would also be surrounded by the hydronium ions, which enhance the phenol interaction with binding site of the sorbent by greater attractive forces, hence its uptake on polar adsorbent is reduced [2, 5].

Effect of Contact Time: The adsorption data for the uptake of phenol versus contact time at 1000 μg L^{-1} initial concentration with 1 g L^{-1} of both were carried out in pH value of 7. The results show that equilibrium time required for the adsorption of phenol on barley straw and its ash are almost 6 hours and 3 hours respectively. These results also indicate that the sorption process can be considered
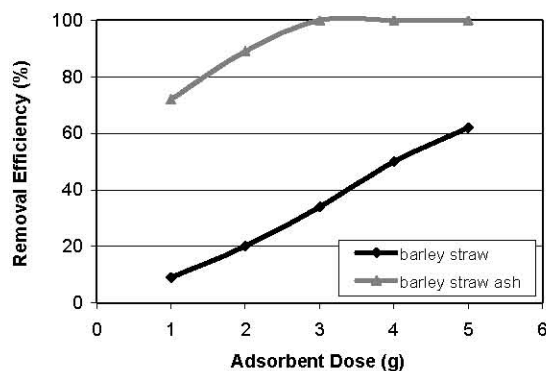

Fig. 3: Effect of adsorbents dose on the removal of phenol by barley straw and its ash (pH = 7, phenol concentration = 5000 μg L^{-1})

very fast because of the largest amount of phenol attached to the sorbent within the first 120 min of adsorption. This indicates that barley straw ash would require less residence time for the complete removal of phenol compared to barley straw. Fig. 2 shows the effect of contact time on the removal of phenol by barley straw and its ash. The kinetics of phenol adsorption on both barley straw and its ash follows the first-order rate expression.

Effects of Adsorbent Amount: The amount of adsorbent on the efficiency of adsorption was also studied. Fig. 3 shows the removal of phenol by barley straw and its ash at the solution pH of 7. Adsorbents dosages were varied from 1 to 5 for barley straw and its ash, respectively. The results show that for removal of 5000 μg L^{-1} of phenol in 100 ml of solution, a minimum dosage of 3 g L^{-1} of barley straw ash is required for 100% removal of phenol. But, with this condition by barley straw, the removal efficiency is 34%. It is evident that for the quantitative removal of different value of phenol in 100 ml a high dosage of barley straw is required. The data clearly shows that the barley straw ash is more effective than barley straw for removal of phenol. The results also clearly indicate that the removal efficiency increases up to the optimum dosage beyond which the removal efficiency is negligible (especially about ash).

Effect of Initial Phenol Concentration: The equilibrium sorption capacities of the sorbents obtained from experimental data at different initial phenol concentration are presented in Fig. 4. As seen from results, the sorption capacities of the sorbents increased with increasing phenol concentration while the adsorption yields of phenol showed the opposite trend. When the initial
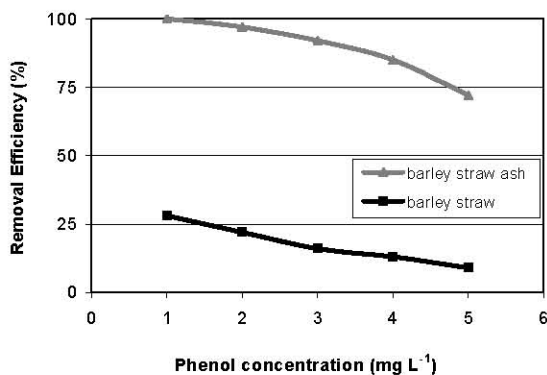
Fig. 4: Effect of phenol concentration on the removal efficiency (Adsorbent dosage = 1 g L^{-1}, pH = 7)

phenol concentration was increase from 1000 µg L^{-1} to 5000 µg L^{-1} on barley straw and barley straw ash, the loading capacity increased from 0.028 mg/g to 0.053 mg/g of barley straw and from 0.1 mg/g to 0.36 mg/g of barley straw ash. Increasing the mass transfer driving force and therefore the rate at which phenol molecules pass from the bulk solution to the particle surface. This would results in higher phenol adsorption [18]. On a relative basis, however, the percentage adsorption of phenol decreases (Fig. 4) as the initial phenol concentration increases. The equilibrium uptake and adsorption yield were highest for the barley straw ash, which was expected, because of the greater specific surface area and the microporous structure of barley straw ash compared with barley straw.

Adsorption Isotherms: Several models have been published in the literature to describe experimental data is of adsorption isotherms. Analysis of the isotherm data is important in order to develop an equation that accurately represents the results and which could be used for design purposes. In this work, both models were used to describe the relationship between the amount of phenol adsorbed and its equilibrium concentration for both barley straw and its ash. The linear form of the Freundlich isotherm model is given by the following relation [2, 3, 5, 8, 17]:

$$\ln q_e = \ln K + \frac{1}{n}\ln C_e$$

Where: q_e is the amount adsorbed of equilibrium (mg/mg), C_e is the equilibrium concentration of the adsorbate (mg L^{-1}) and K and 1/n is the Freundlich constants related to adsorption capacity and adsorption intensity respectively, of the sorbent. The values of K and 1/n can be obtained from the intercept and slope, respectively, of the linear plot of experimental data of q_e

Table 1: Parameters of Freundlich and Langmuir isotherm models

	Freundlich constants			Langmuir constants		
	K	1/n	R^2	Q^0	b	R^2
Barley straw	0.032	0.389	0.99	0.067	1.017	0.98
Barley straw ash	0.368	0.245	0.98	0.314	46.411	0.97

versus C_e [2, 3, 5, 8, 17]. The linear form of the Langmuir isotherm model can be represented by the following relation [2, 3, 5, 8, 17]:

$$\frac{1}{q_e} = \frac{1}{Q^0} + \frac{1}{bQ^0}\frac{1}{c_e}$$

Where: Q^0 (mg/g) and b (L/mg) are the Langmuir constants related to the maximum adsorption capacity and the energy of adsorption, respectively. These constants can be evaluated from the intercept and slop of the linear plot experimental data of $1/q_e$ versus $1/C_e$ [2, 3, 5, 8, 17].

The Langmuir and Freundlich constants are display in Table 1. The results reveal that the adsorption of phenol on barley straw and its ash obeys the Freundlich adsorption isotherm. But, in general, R^2 Values, which are a measure of goodness-of-fit, show that both the Langmuir and Freundlich isotherm models can adequately describe the adsorption data. The higher value of k, the Freunlich constant, showed easy uptake of phenol from aqueous solution [2, 5]. The adsorption capacity k is the lowest for the phenol- barley straw system. The n value, which reflects the intensity of sorption, presents the opposite trend, but as seen from table 1 for all the sorbents and pollutants, n values were found high enough for separation. The higher fractional value of 1/n (0 < 1/n < 1) signifies that the surface of the sorbent is heterogeneous in nature [17]. The magnitude of Q^0 indicates that the amount of phenol per unit weight of sorbent to form a complete monolayer on the surface appears to be significantly higher for phenol– barley straw ash system in comparision to barley straw. A large value of b also implies that strong bonding of phenolnoccurred with sorbent [5]. Similar observation have been reported of the sorption of phenol on; bentonite, organobentonite and palm seed coat activated carbon and the sorption of antimony and cadmium on rice husk [2, 17-19].

CONCLUSION

In this study, the abilit of barley straw and barley straw ash to adsorb phenol was investigated as a function of pH and initial phenol concentration. Barley straw and

barley straw ash adsorption capacity were strongly dependent on the pH of the solution. The sorption capacity was decreased with an increase in the pH and an increase in the initial phenol concentration. Although barley straw ash had a higher adsorption capacity (0.314 mg/g) for phenol, the experimental results indicate that barley straw ability to adsorb phenol and, consequently, its possible utilization in the treatment of phenol-contaminated solution, its adsorptive capacity was limited. Freundlich and Langmuir adsorption models expressed the sorption phenomena of phenol to the barley straw and its ash. Consequently, linear regression of the experimental data showed that the Freundlich equation best represented phenol adsorption data. The adsorption of phenol onto both the sorbents follows first-order kinetics. The model parameters would be useful for fabrication and designing of wastewater treatment plants. On the bases of this study, it may be concluded that barley straw and its ash especially, may be used as low-cost, natural and abundant sources for the removal of phenol. They may also be effective in removing other harmful species such as heavy metal ions present in effluents.

REFERENCES

1. Maleki, A., A.H. Mahvi, A. Mesdaghinia and K. Naddafi, 2007. Degradation and toxicity reduction of phenol by ultrasound waves. Bulletin of the Chemical Society of Ethiopia, 21(1): 33-38.

2. Rengaraj, S., S.H. Moon and R. Sivabalan, 2002. Agricultural solid waste for the removal of organics: adsorption of phenol from water and wastewater by Palm seed coat activated carbon. Waste Management, 22: 543-548.

3. Banat, F.A., B. Al-Bashir, S. Al-Asheh and O. Hayajneh, 2000. Adsorption of phenol by bentonit. Environmental Pollution, 107: 391-398.

4. Mahvi, A.H., A. Maleki, M. Alimohamadi and A. Ghasri, 2007. Photo-oxidation of phenol in aqueous solution: Toxicity of intermediates. Korean Journal of Chemical Engineering, 24(1): 79-82.

5. Aksu, Z. and J. Yener, 2001. A comparative adsorption/boisorption study of Mono-chlorinated Phenols onto various sorbent. Waste Management, 21: 695-702.

6. Maleki, A., M.B. Khadem Erfan, A. Seied Mohammadi and R. Ebrahimi, 2007. Application of commercial powdered activated carbon for adsorption of carbolic acid in aqueous solution. Pakistan Journal of Biological Sciences, 10: 2348-2352.

7. Oei, B.C., Sh. Ibrahim, Sh. Wang and H.M. Ang, 2009. Surfactant modified barley straw for removal of acid and reactive dyes from aqueous solution. Bioresource Technology, 100: 4292-4295.

8. Reynolds, T.D. and P.A. Richards, 1982. Unit operations and processes in environmental engineering. PWS publishers, California.

9. Sawyer, C.N. and P.L. Mc Carty, 1994. Chemistry for environmental engineering. Tata Mc Graw-Hill, New Delhi.

10. Wang, S.B., Y. Boyjoo, A. Choueib and Z.H. Zhu, 2005. Removal of dyes from aqueous solution using fly ash and red mud. Water Research, 39: 129-138.

11. Crini, G., 2006. Non-conventional low-cost adsorbents for dye removal: A review. Bioresource Technology, 97: 1061-1085.

12. Ibrahim, Sh., H.M. Ang and Sh. Wang, 2009. Removal of emulsified food and mineral oils from wastewater using surfactant modified barley straw. Bioresource Technology, 100: 5744-5749.

13. Williams, P.T. and N. Nugranad, 2000. Comparison of products from the pyrolysis and catalytic of rice husks. Energy, 25: 493-513.

14. Sun, R.C., X.F. Sun, P. Fowler and J. Tomkinson, 2002. Structural and physico-chemical characterization of lignins solubilized during alkaline peroxide treatment of barley straw. European Polymer Journal, 38: 1399-1407.

15. Wisniewska, S.K., J. Nalaskowski, E. Witka-Jezewska, J. Hupka and J.D. Miller, 2003. Surface properties of barley straw. Colloids and Surfaces B: Biointerfaces, 29: 131-142.

16. APHA, AWWA, WEF, 2005. Standard methods for the examination of water and wastewater, 21[Ed], Washington DC, USA.

17. Khalid, N., S. Ahmad, A. Toheed and J. Ahmad, 2000. Potential of rice husks for antimony removal. Applied Radiation and Isotopes, 52: 30-38.

18. Imagawa, A., R. Seto and Y. Nagaosa, 2000. Adsorption of chlorinated hydrocarbons from air and aqueous solutions by carbonized rice husk. Carbon, 38: 623-641.

19. Lin, S.H. and M.J. Chery, 2002. Adsorption of phenol & m-chlorphenol on organobentonites and repeated thermal regeneration. Waste Management, 22: 595-603.