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Removal of Bentazon and Metalaxyl pesticides from aqueous solutions by using chestnut shells: Process optimization by experimental design, adsorption kinetics and isotherm analysis

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Usability of agricultural waste chestnut shells as adsorbent for the removal of Bentazon and Metalaxyl pesticides from aqueous solutions was investigated. By using Box-Behnken experimental design, effects of pH (2.0, 3.5 and 5.0), adsorbent concentration (1, 2 and 3 g/50 ml), pesticide concentration (25, 50 and 75 mg/L) and processing time (40, 80 and 120 min) on adsorption were investigated and optimizations of the adsorption processes were performed. At the determined optimum conditions 85.1% Bentazon and 66.1% Metalaxyl removals were obtained. Also model equations that shows the effects of process parameters on adsorption were obtained. As a result of the analyzing the data obtained from the kinetics and equilibrium studies it was determined that the adsorption of Bentazon and Metalaxyl with chestnut shells could be represented with pseudo-second kinetic and Freundlich isotherm models. The results obtained from this study suggested that the agricultural waste chestnut shells could be used as cheap and easily accessible adsorbent for the removal of pesticides from waste waters.

Keywords: Bentazon, Metalaxyl, adsorption, experimental design, modelling.

Introduction

Pesticides are one of the most dangerous in organic toxic compounds that are being produced and used in parallel with the increasing food need in the world. The spread of pesticides to natural and drinking water sources poses a great threat to living beings. The pesticide contaminated water sources may be responsible for different water borne diseases with short and long term health effects ranging from allergic reactions to death. Pesticides infect the water bodies in many ways. The most important ones are the spread of the pesticides unconsciously applied to agricultural areas and the waste water of pesticide producing companies to surface and ground water[1–3].

Several treatment processes have been developed for pesticide removal. The most widely used methods include ozonization, photochemical reduction, aerobic and anaerobic biodegradation, membrane filtration and adsorption processes. Among these methods, adsorption is the most commonly used process for purification of water contaminated by pesticides and other toxic chemicals because of its high efficiency and ease of application. The activated carbon is the most commonly used adsorbent. However, despite the large surface area and very high adsorption capacity, the production cost of activated carbon is high. Therefore due to their low cost and ease of accessibility there is an increasing interest in the use of locally available adsorbents, charge minerals, waste materials and agricultural by-products[4–6].

Bentazone and Metalaxyl are two of widely used pesticides in Turkey. Bentazon (3-isopropyl-(1*H*)-2,1,3-benzothiadiazin-4(3*H*)-one-2,2-dioxide) is a broad spectrum post emergence herbicide that used for the selective control of broad leaf weeds, in alfalfa, rice, maize, beans, soybeans, pea, sorghum, onion, potatoes, peanut, flax, asparagus, fruit trees etc.[7]. Metalaxyl (methyl-N-(methoxyacetyl)-N-(2,6-xylyl)-DL-alanine) is a systematic fungiside used in control of plant diseases caused by air and soil-borne Peronosporales in several crops[8].

Turkey is one of the main countries in producing chestnut in the world with production of 62904 tons per year[9,10]. Hence, in the present study, the usability of chestnut shells as low cost adsorbent for the removal of Bentazon and Metalaxyl pesticides from aqueous solutions were investigated. Optimization and modelling of adsorption processes were accomplished by varying four independent parameters (pH, adsorbent concentration, pesticide concentration and processing time) using a Box-Behnken design with response surface methodology (RSM). Also at specified optimal conditions kinetic and equilibrium studies were performed and the most appropriate kinetic and isotherm models that represent the adsorption processes were determined.

Materials and methods:

Materials:

Pesticides Bentazon (at 99.99% purity) and Metalaxyl (at 99.99% purity) were obtained from Sigma Aldrich. Chestnut shells were obtained from a candied chestnut factory in Bursa-Turkey.

Before using in the experiments, the chestnut shells were thoroughly washed with distilled water to remove the dirt and dried in an oven at 50°C for 24 h. Then they were ground to powder in the range of 0.355–0.560 mm. Particle size was determined by sieve analysis. The ground shells were subjected to pre-treatments; first to heat treatment by boiling 15 min in distilled water then to chemical treatment in 0.6 *M* citric acid for 2 h. After pre-treatments the adsorbent was washed with distilled water, dried in an oven at 50°C and stored in a desiccator to be used in the experiments.

Experimental design:

Box-Behnken design using Design Expert 9.0 software was applied to optimize the four selected factor, pH (A), adsorbent concentration (B), pesticide concentration (C) and time (D), for enhancing the adsorptions of Bentazon and Metalaxyl by chestnut shells. The factors were investigated at three different levels (low, medium, high) as pH (2, 3.5, 5), adsorbent concentration (1 g/50 ml, 2 g/50 ml, 3 g/50 ml), pesticide concentration (25 mg/L, 50 mg/L, 75 mg/L), time (40 min, 80 min, 120 min). The complete design that consisted 27 runs was shown in Table 1.

Table 1. Experimental results of Bentazon and Metalaxyl adsorption by chestnut shells

#	A	B	C	D	Adsorption %	
					Bent.	Meta.
1	3.5	2	50	80	25.8	55.1
2	2	2	50	120	62.5	58.2
3	3.5	1	50	120	29.6	42.6
4	3.5	2	75	120	34.1	55.0
5	5	1	50	80	14.5	40.3
6	2	1	50	80	56.1	44.3
7	5	2	50	40	21.1	53.6
8	2	2	75	80	63.1	54.6
9	5	3	50	80	31.8	60.9
10	3.5	1	50	40	20.2	37.4
11	3.5	2	25	40	31.0	48.3
12	3.5	2	75	40	25.5	47.1
13	5	2	75	80	24.9	52.9
14	3.5	3	75	80	56.8	65.1
15	3.5	2	50	80	30.6	51.4
16	3.5	2	25	120	38.3	55.3
17	5	2	50	120	32.0	58.5
18	2	2	25	80	71.2	58.2
19	3.5	3	25	80	26.2	67.2
20	5	2	25	80	28.7	56.2
21	3.5	1	75	80	42.1	38.5
22	2	2	50	40	61.7	50.4
23	3.5	3	50	120	35.7	67.1
24	2	3	50	80	78.6	70.4
25	3.5	3	50	40	35.2	60.9
26	3.5	2	50	80	28.5	53.3
27	3.5	1	25	80	31.5	47.2

Design experiments:

Each of the 27 experiments included in the Box-Behnken design was carried out with 50 mL of pesticide solution. After the required solution pH was adjusted by using 0.1 *M* HCl and 0.1 *M* NaOH solutions the adsorption process was initiated by addition of the determined amount of adsorbent into the flask. The flask was kept in temperature controlled shaker at 150 rpm and 25°C. At the end of the determined adsorption time samples were taken from the solution and centrifuged at 14000 rpm for 3 min. The pesticide concentration analyses of supernatant solutions were performed by spectrophotometric method. The analyses were repeated for 3 samples and the mean values used.

Kinetic experiments:

In order to determine the kinetics of adsorption, each experiments in the Box-Behnken design were carried out for 120 min and pesticide concentration was examined with respect to time.

Equilibrium experiments:

In order to determine the adsorption isotherms the experiments were conducted at different adsorbent concentrations (0.5, 1.0, 2.0, 2.5 and 3.0 g/50 ml) at the optimum pH and pesticide concentration values obtained from the Box-Behnken design. During the experiments the pesticide concentration was examined with respect to time. The experiments were carried out for 300 min to determine the exact equilibrium values.

Analytic measurements:

Residual pesticide concentrations were determined by analysis of samples absorbance using a UV-Vis spectrophotometer (Shimadzu UV-150-02). The absorbance of samples were measured at λ_{max} of pesticides which are 230 nm and 215 nm for Bentazon and Metalaxyl respectively.

The percentage adsorption (Ads%) and adsorption capacity (q_t) values were calculated according to the following equations:

$$\text{Ads\%} = 100\times(C_0 - C_t)/C_0 \tag{1}$$

$$q_t = V(C_0 - C_t)/M \tag{2}$$

where C_0 and C_t are the pesticide concentrations (mg/g) at initial and at processing time t (min), V (L) is the solution volume and M (g) is weight of the adsorbent.

Modelling of kinetic and equilibrium data:

Adsorption kinetics examines the time relationship between adsorbate and adsorbent and plays an important role in understanding of adsorption steps affecting the rate of adsorption[11]. The kinetic data obtained from the study was analyzed using pseudo-first order (eq. (3)), pseudo-second order (eq. (4)), intraparticle diffusion (eq. (5)) and Elovich (eq. (6)) kinetic models to determine the kinetics of removal of Bentazone and Metalaxyl pesticides from aqueous solutions by chestnut shells.

$$q_t = q_e\,[1 - \exp(-k_1 t)] \tag{3}$$

$$\frac{t}{q_1} = \frac{1}{k_2 q_c^2} + \frac{1}{q_c}\,t \tag{4}$$

$$q_t = k_p t^{1/2} + C \tag{5}$$

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \tag{6}$$

In eqs. (3)–(6), q_e (mg/g) and q_t (mg/g) are the amount of pesticide adsorbed per unit mass of adsorbent at equilibrium and at time t (min), k_1 (1/min), k_2 (g/mg min) and k_p (mg/g min$^{1/2}$) are pseudo-first order, pseudo-second order and intraparticle rate constants, C (mg/g) is a constant, α (mg/g min) is initial adsorption rate, β (g/mg) is desorption constant.

The adsorption isotherms that describe the relation between the equilibrium concentration of the adsorbate (C_e) and the quantity of adsorbate on the surface of the adsorbent (q_e) at constant temperature are employed to describe the adsorption[12]. Langmuir (eq. (7)), Freundlih (eq. (8)) and Temkin (eq. (9)) isotherm models were used to further analyse the adsorption of Bentazone and Metalaxyl pesticides by chestnut shells.

$$\frac{1}{q_e} = \frac{1}{q_m} + \left(\frac{1}{q_m K_L}\right)\frac{1}{C_e} \tag{7}$$

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{8}$$

$$q_e = \frac{RT}{b_t}\ln K_F + \frac{RT}{b_t}\ln C_e \tag{9}$$

In equations (7) – (9), q_m (mg/g) is the maximum adsorption capacity, C_e (mg/L) is the equilibrium concentration of the pesticide in solution, K_L (L/mg), K_F (mg$^{1-1/n}$ L$^{1/n}$ /g) and K_T (L/mg) are the Langmuir, Freundlich and Temkin constants respectively, 1/n is the Freundlich constant related to adsorption intensity, R is the universal gas constant (8.314 J/mol K), T (K) is the temperature and b_T (J g/mol mg) is the Temkin isotherm constant related to the heat of adsorption.

Results and discussion

Box-Behnken experimental design results:

Box-Behnken design was applied to optimize the four selected factor, pH, pesticide concentration, adsorbent concentration and time, for enhancing the adsorptions of Bentazon and Metalaxyl by chestnut shells. A total of 27 experiments (involve 3 replication of the central point) with different combination of factors were performed. The result of these experiments were presented in Table 1. The maximum adsorption was obtained as 78.60% for the Bentazon and as 70.40% for the Metalaxyl. It was observed that the absorption % increases as pH value decreased and the amount of adsorbent increased.

Based on the model analysis performed by using Design Expert 9.0 quadratic models were chosen to represent the relationship between the adsorption% and the selected process parameters. The models were shown in eqs. (10) and (11). The results of variance analysis of the models were summarized in Table 2.

Table 2. Analysis of variance results for quadratic models

Pesticide	R^2	*F*-value	*p*-value	Charac.
Bentazon	0.91	8.69	0.0003	Significant
Metalaxyl	0.96	21.88	< 0.0001	Significant

The quadratic model equation obtained for the adsorption of Bentazon by chestnut shell:

$$\% \text{ Ads} = + 188.784 - 61.345A - 10.448B - 1.3146C + 0.0728D - 0.8667AB + 0.02867AC + 0.04208AD + 0.1997BC - 0.05563BD + 0.00325CD + 6.419A^2 + 3.452B^2 + 0.0085C^2 - 0.002935D^2 \quad (10)$$

The quadratic model equation obtained for the adsorption of Metalaxyl by chestnut shell:

$$\% \text{ Ads} = + 34.838 - 4.037A + 11.80B - 0.27033C + 0.20896D - 0.91667AB + 0.002AC - 0.01208AD + 0.066BC + 0.00625BD + 0.000225CD + 0.8537A^2 - 0.1542B^2 + 0.000493C^2 - 0.00068D^2 \quad (11)$$

The coefficient of determination (R^2) is a measure of the degree of fit. As seen from Table 2, the obtained high values of the determination coefficients R^2 (>0.90) indicate a high degree of correlation between the experimental and predicted values. Also the suggested models are very significant as evaluated by their very low p-values (< 0.05).

The optimization function of the Design Expert software allows to specify the different parameters that are desired to work according to the objectives of the designer. Hence based on the process economy for maximum pesticide removal in a short time, condition optimization and confirmation tests were performed by selecting the optimum pH value (pH 2), maximum pesticide (75 mg/L) and adsorbent amounts (3.0 g/50 mg) and minimum processing time (40 min). The obtained results were shown in Table 3. The good agreement between the experimental and predicted results indicate that response surface methodology is a very effective and powerful tool for optimizing the individual factors in a process.

Table 3. Condition optimization and confirmation results

	Pesticide	
	Bentazon	Metalaxyl
A: pH	2.018	2.009
B: Adsorbent cons. (g/50 ml)	3.000	3.000
C: Pesticide cons. (mg/L)	75.000	75.000
D: Time (min)	40.000	40.000
Predicted adsorption%	84.483	64.033
Exp. adsorption%	85.092	66.084

The most important parameter affecting the adsorption is pH as it influence the solubility of adsorbate and the surface ionizing functional groups of the adsorbent. The optimum pH value for the each of two adsorption processes was obtained as 2. The adsorption of pesticides were found to decrease with increasing pH. The higher adsorption at very acidic media could be attributed to the electrostatic interactions between the adsorbent surface and the pesticide solutions because at low pH values the adsorbent surfaces that includes carbohydrates, amines, hydroxyl, carboxylates and carbon fibers in their structures are coated with OH^- ions and the H^+ ion concentration of the Bentazone (pKa ~ 3.3) and Metalaxyl (pKa ~ 1.41) solutions which are weak acids are increased[6,13,14].

Three dimensional (3D) surface plots are very helpful to indicate the realationship between the independent variables and their effect on process. The relationships between the adsorption and the the selected factors were shown in Figs. 1–2. Each plot shows the effects of two variables within their studied ranges.

Adsorption kinetics:

The obtained kinetic data were analyzed using pseudo-first order, pseudo-second order, intraparticle diffusion and Elovich kinetic models and it was seen that the pseudo-second order kinetic model provided the best fits (based on R^2 values) among the four models at each condition. The constants and statistical data obtained for the pseudo-second order kinetic model were presented in Table 4.

Adsorption isotherm:

The results of the equilibrium experiments were presented in Fig. 3. The equilibrium data were modelled with the

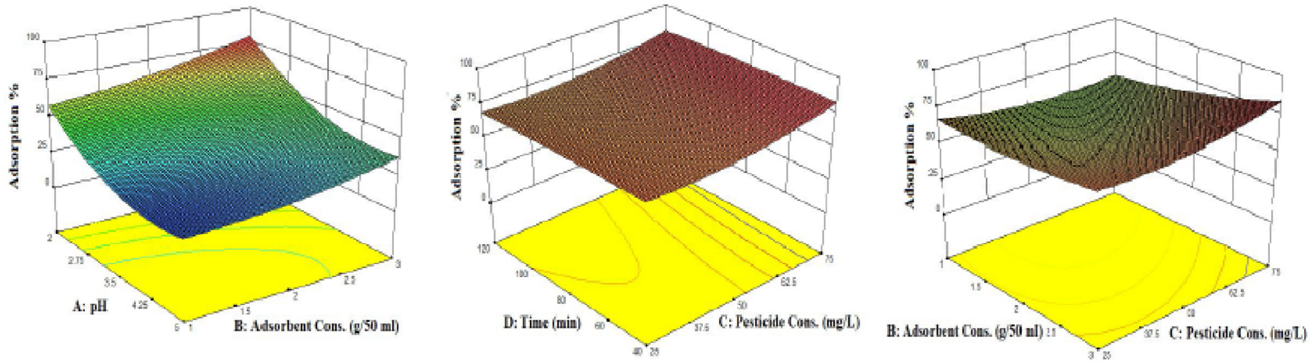

Fig. 1. 3D response surface plots of adsorption of Bentazon.

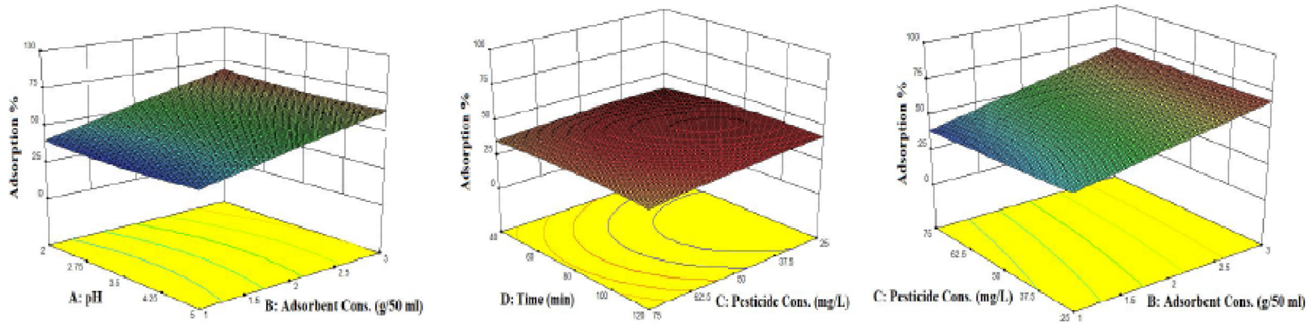

Fig. 2. 3D response surface plots of adsorption of Metalaxyl.

Table 4. Pseudo-second order kinetic model constants and statistical values

pH	Ads. cons. (g/50 ml)	Pest. cons. (mg/L)	Run	Bentazon				Metalaxyl			
				q_e (mg/g)	k_2 (g/mg min)	S	R^2	q_e (mg/g)	k_2 (g/mg min)	S	R^2
2.0	1	50	6	1.485	0.114	2.02	0.998	1.129	0.167	3.14	0.997
	2	25	18	0.431	3.397	3.98	0.999	0.374	0.605	4.72	0.999
		50	2	0.794	0.856	2.59	0.999	0.770	0.216	2.87	0.999
		75	8	1.202	0.379	4.39	0.993	1.086	0.177	1.89	0.999
	3	50	24	0.602	2.391	6.33	0.997	0.603	0.448	1.72	0.999
3.5	1	25	27	0.552	0.076	28.8	0.945	0.640	0.253	3.81	0.999
		50	10	0.938	0.041	6.69	0.991	1.111	0.151	0.95	0.999
		75	21	1.899	0.045	2.73	0.994	1.630	0.075	1.11	0.999
	2	25	11	0.276	0.331	24.5	0.989	0.356	0.580	8.32	0.998
		50	15	0.398	0.269	8.90	0.997	0.730	0.232	1.85	0.999
		75	4	0.617	0.208	13.4	0.984	1.075	0.151	1.64	0.999
	3	25	19	0.126	0.556	36.9	0.995	0.302	0.639	8.94	0.998
		50	23	0.366	0.481	12.5	0.995	0.581	0.381	1.38	0.999
		75	14	0.518	0.418	3.00	0.999	0.883	0.180	1.06	0.999
5.0	1	50	5	0.649	0.052	59.9	0.976	1.109	0.140	1.75	0.999
	2	25	20	0.234	0.266	51.1	0.968	0.233	0.266	51.1	0.968
		50	7	0.364	0.220	18.7	0.989	0.718	0.263	4.29	0.998
		75	13	0.533	0.199	8.29	0.995	1.069	0.167	0.97	0.999
	3	50	9	0.321	0.471	24.9	0.985	0.574	0.362	6.04	0.997

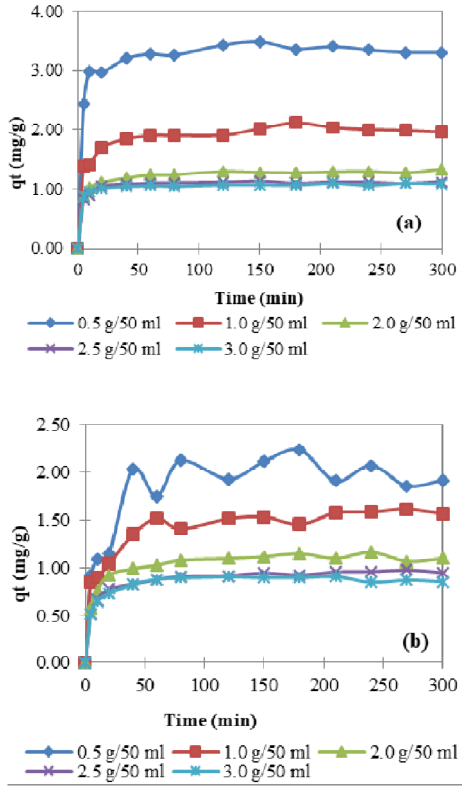

Fig. 3. Adsorption capacities with respect to time at different adsorbent concentrations for adsorption of (a) Bentazon and (b) Metalaxyl.

Langmuir, Freundlih and Temkin isotherms. The determined parameters of the models and R^2 values were given in Table 5. The results suggested that the adsorption of Bentazon and Metalaxyl on chestnut shell can be expressed with Freundlich isotherm model. Reasonably good fit of the data to Freundlih model implies that the adsorption points on the surface of the adsorbent are distributed heterogeneously and the adsorption processes are multilayer. The comparison of the data obtained from this study with the data from similar studies show that the Freundlich adsorption isotherm constant (K_F) obtained for the adsorption of Bentazone and/or Metalaxyl on chestnut shells are higher than the constants obtained for the adsorptions on willow chopping, garden waste compost, sandy loam soil, cow manure, straw, coconut chips[15], kaolinite[8] and clay[16] suggest that the chestnut shells is a more effective natural adsorbent than the other mentioned adsorbents.

Table 5. Isotherm model constants and statistical values for adsorption of Bentazon and Metalaxyl

Pecticide	Bentazon	Metalaxyl
Freundlich isotherm:		
K_F (mg$^{1-1/n}$ L$^{1/n}$ g^{-1})	0.172	0.059
n	1.407	1.157
S	0.285	0.052
R^2	0.854	0.991
Langmuir isotherm:		
q_{max} (mg/g)	2.900	7.247
K_L (L/mg)	0.051	6.10×10^{-3}
S	0.112	0.057
R^2	0.777	0.989
Temkin isotherm:		
K_T (L/mg)	0.164	0.091
b_T (J g/mol mg)	5.33×10^{-4}	4.62×10^{-4}
S	0.647	0.097
R^2	0.801	0.982

Conclusions

The performance of chestnut shells as adsorbent on removal of Bentazon and Metalaxyl pesticides were investigated by using Box-Behnken experimental design. The pesticide adsorption increased with increasing the adsorbent amount and decreased with increasing pH. Based on process economy for maximum pesticide removal in a short time, condition optimization was performed by selecting the optimum pH value (pH 2), maximum pesticide (75 mg/L) and adsorbent amounts (3 g/50 mg) and minimum processing time (40 min) and 84.48% and 64.03% Bentazone and Metalaxyl removals were achieved. The good agreement between the experimental and predicted results indicated that RSM is a very effective and powerful tool for optimizing the individual factors in a process. Equilibrium and kinetics studies showed that the adsorption of Bentazon and Metalaxyl by chestnut shells could be represented with pseudo-second order kinetic and Freundlich isotherm models. In view of the practical application of adsorbents, chestnut shells could serve as a low cost, versatile and eco-friendly alternative to the natural and commercial adsorbents for the removal of pesticides.

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