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Ultra-sonication assisted removal of an anionic dye using solvent impregnated resin: Response surface methodology optimization

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Textile industries create a critical marine living situation as most unfixed dyes dumped as an effluent without further dye-fixing treatment. In this work, methyl orange dye was removed from the aqueous solution by ultrasonication process using Amberlite XAD-7HP resin impregnated with Aliquat-336. The experiments were designed by central composite design of response surface methodology. A regression model was proposed. Operating parameters were optimized, and at optimum conditions, the dye removal efficiencies were 98.57% (experimental) and 99.94% (predicted). Kinetic studies were performed at optimum conditions and intra-particle diffusion model fitted the kinetic data.

Keywords: Methyl orange, impregnated resin, response surface methodology, ultrasonication.

Introduction

Methyl Orange (MO) is a harmful anionic-azo dye(-N=N-) and non-biodegradable.The use of solvent impregnated resin (SIR) assisted with ultrasonication could be a better alternative. The ultrasonication enhances the adsorption efficiency of the adsorbent[1,2]. SIR shows many significant advantages: good stability, fast adsorption rate, and excellent reusability and non-polluted[3,4]. In the present study, Amberlite XAD-7HP resin was impregnated with Aliquat-336 (AX7) and used to remove MO dye. Operating parameters such as AX7 dosage (*A*), pH (*B*), MO concentration (*C*), and sonication time (*D*) were changed and experimental conditions were found out by CCD of RSM using MINITAB v. 17.1.0. Their effect was investigated ultrasonically on the percent removal. Total 31 designed experiments were performed.

Experimental

Impregnated resin (AX7) was prepared following three basic steps[5] (i) washing: Amberlite XAD-7HP resin (purity > 97.0 wt.%, Sigma Aldrich, USA) was washed with ethanol (99 vol.%, Merck, Germany) and double distilled water to remove impurities; (ii) impregnation: to impregnate 1 g of Aliquat-336 per g of resin, 11.17 mL of Aliquat-336 (purity >97 wt.%, Sigma Aldrich, USA) and 40 mL of hexane (99 vol.%, Merck, Germany) was mixed to prepare a solution in which 10 g of washed resin was added. Then, this mixture was kept in water bath shaker for 24 h at 298 K; and (iii) drying: the filtered resin was dried in an oven for 12 h at 313 K.

40 mL of MO dye (purity > 85.0 wt.%, Merck, Germany) was taken in a beaker and required amount of AX7 was added. The experiment was performed at 20 kHz frequency and at 30% amplitude in probe type ultrasonicator at different experimental conditions (Table 1).

Results and discussion

Adsorbent characterization:

Washed and prepared AX7 resins were characterized using FTIR and SEM-EDX published elsewhere[5]. The FTIR results of AX7 showed a new peak of a quaternary amine group at 1467 cm^{-1} and 1385 cm^{-1}, and in SEM-EDX, the appearance of 1.11 wt.% Cl^- confirmed the impregnation of Aliquat-336.

Experimental design: ANOVA

Statistical analysis of ANOVA was done to interpret the

Table 1. Experimental design and analysis of variance

Factor	Parameter	$-\alpha$	Low	High	$+\alpha$	
A	AX7 dosage (g)	0.05	0.06	0.08	0.09	
B	pH (–)	2	4	8	10	
C	MO concentration (mg/L)	20	25	35	40	
D	Sonication time (min)	1	1.5	2.5	3	
Source	DF	Adj SS	Adj MS	*F*-value	*P*-value	Remark
Model	14	3961.86	282.99	153.04	0.000	Significant
Linear	4	2272.37	568.09	307.23	0.000	Significant
A	1	118.33	118.33	63.99	0.000	Significant
B	1	576.10	576.10	311.56	0.000	Significant
C	1	23.80	23.80	12.87	0.002	Significant
D	1	1554.13	1554.13	840.49	0.000	Significant
Square	4	1191.38	297.85	161.08	0.000	Significant
A×*A*	1	0.17	0.17	0.09	0.769	–
B×*B*	1	717.63	717.63	388.10	0.000	Significant
C×*C*	1	0.12	0.12	0.07	0.799	–
D×*D*	1	550.86	550.86	297.91	0.000	Significant
2-way interaction	6	498.11	83.02	44.90	0.000	Significant
A×*B*	1	22.84	22.84	12.35	0.003	Significant
A×*C*	1	304.73	304.73	164.80	0.000	Significant
A×*D*	1	47.99	47.99	25.95	0.000	Significant
B×*C*	1	0.75	0.75	0.41	0.533	–
B×*D*	1	92.19	92.19	49.86	0.000	Significant
C×*D*	1	29.61	29.61	16.01	0.001	Significant
Error	16	29.59	1.85			–
Lack-of-fit	10	24.33	2.43	2.78	0.112	–
Pure error	6	5.25	0.88			–
Total	30	3991.44				
R^2 = 99.26%						

effect of input parameters (Table 1). The regression equation is obtained as:

$$\%\text{Removal} = 51.4 - 1956\,A + 18.75\,B - 7.027\,C + 108.64\,D - 761\,A\times A - 1.2524\,B\times B + 0.0026\,C\times C - 17.56\,D\times D + 59.7\,A\times B + 87.28\,A\times C - 346.4\,A\times D - 0.0216\,B\times C - 2.400\,B\times D + 0.544\,C\times D \quad (1)$$

Residuals plots (Fig. 1) show that the experimental points lie on the normality line, and the error lies between –2 and +2 which is an acceptable range.

Interaction effects: Contour plots

The surface contour plots of significant 2-way interactions; *A*×*B*, *A*×*C*, *A*×*D*, *B*×*D* and *C*×*D* (P-value <0.05)[4] shown in Fig. 2(a-e). At hold values of *C* = 30 mg/L and *D* = 2 min (Fig. 2a), by increasing *B* (2 to 10), the removal of MO dye increased. At hold values of *B* = 6 and *D* = 2 min (Fig. 2b), more removal of MO was observed at *C* = 20 mg/L, and removal was low at *C* = 40 mg/L, with *A* = 0.05 g. At lower dye concentration, sufficient active sites were available for adsorption, and at higher dye concentration, number of dye molecules increased which increased the competition between dye molecules for active vacant sites. At hold values of *B* = 6 and *C* = 30 mg/L (Fig. 2c), with increase in *D* (1 to 3 min), the removal was significant. It indicated that the effect of *D* was more as compared to *A*. In another significant interaction (Fig. 2d), at hold values of *A* = 0.07 g and *C* = 30 mg/

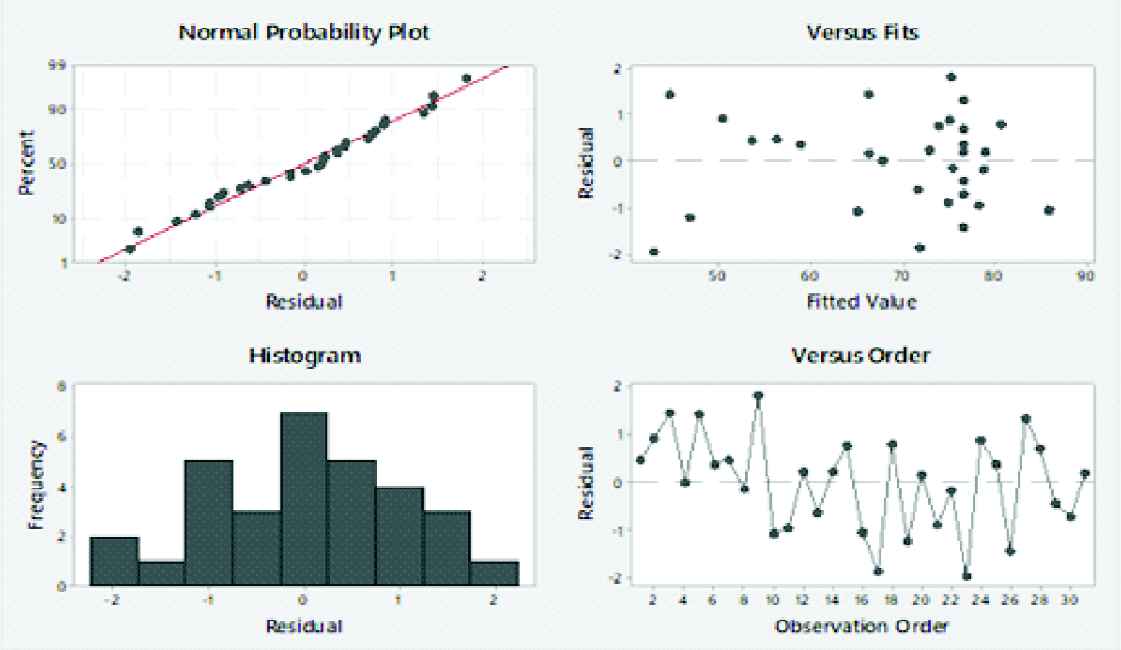


Fig. 1. Residual plots for methyl orange dye removal percentage.

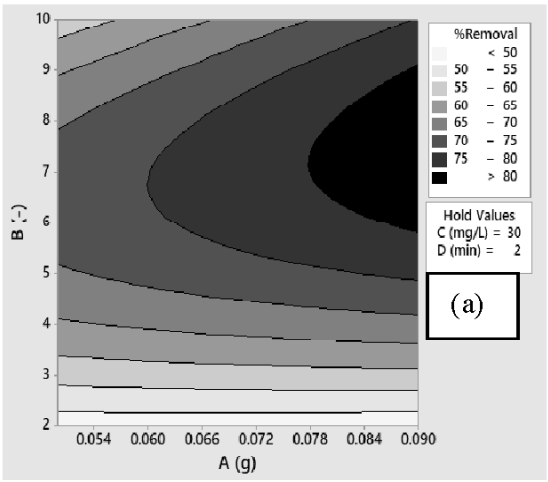
L, the increased *B* and *D* facilitated adsorption. The interaction effect of *D* and *C*, at hold values of *A* = 0.07 g and *B* = 6 (Fig. 2e) shows that dye adsorption was more at high value of *D* (= 3 min). It showed that the effect of *D* was higher than the effect of *C*.

Optimization and kinetic study:

The optimum parameters obtained by CCD were *A* = 0.09 g, *B* = 7.5, *C* = 40 mg/L and *D* = 2.8 min. At these optimum parameters, the maximum removal of MO dye was found to be 98.57% (experimental) and 99.94% (predicted). Kinetic study was performed at these optimum conditions. Among different kinetic models applied (Table 2), IPD model (Fig. 3) best-fitted the data (R^2 = 0.990).

Probable adsorption mechanism:

The main functional groups present in MO dye are sulfonate ions, azo group and benzene rings, and resin pores



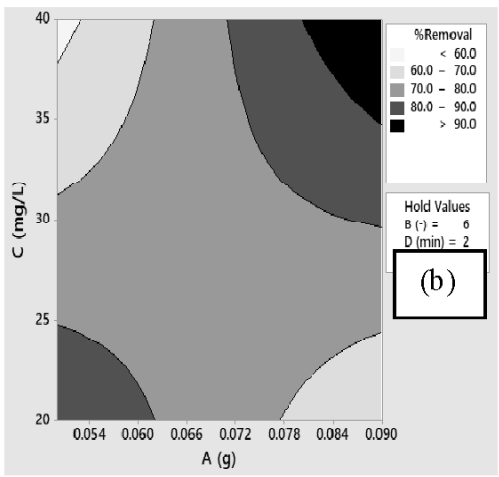


Fig. 2. (contd.)

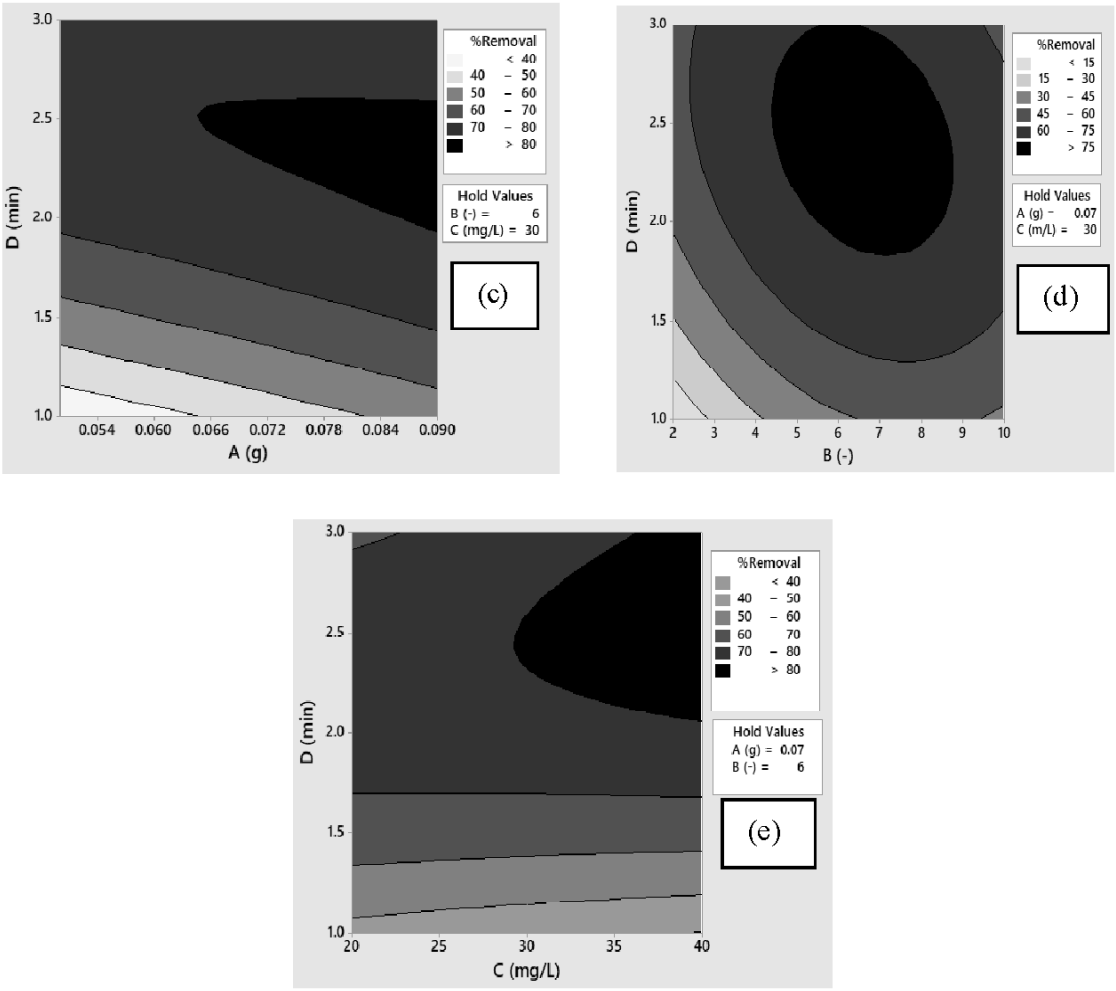


Fig. 2. Surface contour plots of (a) AX7 dosage vs pH, (b) AX7 dosage vs MO concentration, (c) AX7 dosage vs sonication time, (d) pH vs sonication time, (e) MO concentration vs sonication time.

Table 2. Parameters of kinetic models

Pseudo-first order	Pseudo-second order	Intra-particle diffusion (IPD)	Elovich
q_m (mg/g) = 17.52	q_m (mg/g) = 23.52	k_{in} = 10.24	α = 9.64
k_1 (1/min) = 3.56	k_2 (mg/g/min) = 0.04	c = 0.17	β = 0.20
R^2 = 0.769	R^2 = 0.972	R^2 = 0.990	R^2 = 0.959

contain Aliquat-336 which is having an amine group. There is a possibility that adsorption occurred due to the electrostatic interaction between the positively charged amine group of Aliquat-336 and negatively charged sulfonate ion ($-SO_3^-$).

Regeneration study:

The regeneration study was carried out in a water bath shaker using 2 *M* HCl. It was found that regenerated resin was reused successively up to two cycles without affecting

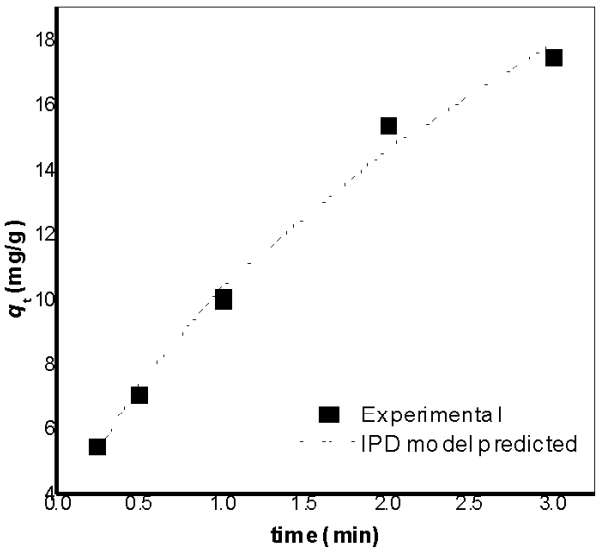


Fig. 3. Contact time effect on the adsorption capacity to remove methyl orange dye.

its adsorption capacity (~17.52 mg/g). Further, in the third cycle, the adsorption capacity was slightly decreased from 17.52 mg/g to 15.43 mg/g.

Conclusions

This investigation showed that ultrasonic-assisted adsorption process exhibits significant advancements, as it requires far less adsorbent, decreased adsorption time, and boosted adsorption effectiveness. At optimum conditions obtained by CCD (A = 0.09 g, B = 7.5, C = 40 mg/L and D = 2.8 min), the maximum removal of MO dye was 98.57% (experimental) and 99.94% (predicted). The experimental data best fitted to the predicted values (R^2 = 99.26%). In the kinetic study, IPD model best fitted to the experimental data (R^2 = 0.990) and AX7 successively reused up to two cycles.

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References

1. E. A. Dil, M. Ghaedi and A. Asfaram, *Ultrason. Sonochem.*, 2017, **34**, 792.
2. S. Dashamiri, M. Ghaedi, K. Dashtian, M. R. Rahimi, A. Goudarzi and R. Jannesar, *Ultrason. Sonochem.,* 2016, **31**, 546.
3. A. Anjali and D. Datta, *J. Environ. Chem. Eng.*, 2019, **7**, 103502.
4. M. Iqbal and D. Datta, *Chem. Eng. Res. Des.,* 2019, **152**, 402.
5. S. Batra, D. Datta, N. S. Beesabathuni, N. Kanjolia and S. Saha, *Process Saf. Environ. Prot.,* 2019, **122**, 232.