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Enhanced adsorption performance of Reactive Red 120 azo dye from aqueous solution using quaternary amine modified orange peel powder



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ABSTRACT

Orange peel powder was chemically modified to enhance quaternary amine type content on the surface of adsorbent which was named as quaternary amine modified orange peel powder (QAMOPP). The effecting parameters on adsorption of Reactive Red (RR) 120 such as pH (2.0-9.0), contact time (0-300 min), adsorbent dosage (0.01–0.07 g/30 mL), initial RR120 concentration (100–1000 mg/L) and temperature (298–338 K) were studied. The QAMOPP was extensively characterized for its surface chemical bonding, morphological structure, and specific surface area, total pore volume and average pore diameter by employing FTIR, SEM and BET analysis. The experimental adsorption kinetic data followed the pseudo-second-order kinetic model equation with a regression coefficient of >0.9941 for all studied temperatures. The activation energy (E_a) is calculated to be 12.1 kJ/mol by using the Arrhenius equation. Adsorption isotherms of RR120 on QAMOPP were correlated with two- and three-parameter non-linearized isotherm equations viz. Langmuir, Freundlich, Dubinin-Radushkevich (D-R), Temkin, Sips, Toth, Khan and Redlich-Peterson (R-P). It was observed that the Langmuir ($R^2 = 0.9996$) and Khan ($R^2 = 0.9991$) were the best fit isotherm models to predict RR120 adsorption onto QAMOPP. pH study revealed that the adsorption capacity decreased with an increase in pH of the solution. Optimum adsorption of RR120 onto QAMOPP was observed at pH 2.0 (344.8 mg/g). The adsorption performance of QAMOPP increased with contact time until 110 min, when it became nearly constant. The negative values (-1.9114 to -5.9208 kJ/mol) of ΔG° , the positive values (0.102 kJ/mol K and 28.4 kJ/mol) of ΔS° and ΔH° parameters indicate that the adsorption of RR120 onto QAMOPP was spontaneous, feasible and endothermic, respectively. Desorption experimental studies showed optimum RR120 recovery (92%) when 0.1 M NaOH was used as an eluent. Hence to remove RR120 from aqueous media QAMOPP can be considered as a powerful alternative adsorbent material.

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1. Introduction

Among the several wastewaters from agricultural, domestic and industrial resources enters into the environment in different seasons throughout the year, comprising a huge concentration of pollutant chemicals such as heavy metals, dyes, insecticides, cyanide and hydrocarbon solvents. The effluents of many industries such

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as plastic carpet weaving, food processing, dyeing, leather tanning, pulp, paper, textile, cosmetics, pharmaceutical, etc. consist dyes as common pollutants [1]. Mainly dyes are divided into three main groups; anionic, non-ionic and cationic dyes. Reactive azo dyes are commonly used in textile industries. During the textile dyeing process, the estimated loss is about 10–60%, which was highest responsible for the large quantities of dye wastewater into the environment. Reactive azo dyes are, the most problematic than the other type of dyes hence their removal from wastewater is must and extremely important. The higher concentrations of them lead to skin irritation, dermatitis, carcinogenicity, mutagenicity and also toxic to aquatic life [2–4].

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Current treatment technologies like membrane filtration [5], electrochemical destruction [6], photochemical degradation [7], ion exchange [8], oxidation [9], coagulation [10,11] and adsorption [12] have been employed in treating effluents containing dyes. Among all these techniques, adsorption is generally the most feasible and adaptable technique due to its relatively low initial cost, lower waste production, simple operation design, reusability, easy operation, a broad range of adsorbents availability and excellent quality of the treated substances, particularly in well-designed adsorption processes. Materials locally available in large quantities such as industrial byproducts or agricultural wastes, natural materials can be utilized as low-cost adsorbent materials. Various lowcost adsorbents such as tea waste [13], cucumber peel [14], wood apple shell [15], rice bran [16], walnut and poplar woods [17], banana peel powder [18], dried prickly peal cactus (Opuntia ficus indica) cladodes [19], breadnut peel [20], barberry stem [21], bottle ground peel [22], jackfruit peel [23], mosambi (*Citrus limetta*) peel [24] sugarcane bagasse [25] and cashew nut shell [26,27] were successfully used in treatment of dyes as well as metal ions from aqueous media.

Orange peels, which are abundant, cheap and widely available biomaterials that are discarded in fresh fruit stalls/juice shops, could be used as an appropriated economic adsorbent for the removal of many different pollutants like dyes and heavy metal ions from aqueous solutions [28]. It in general consists of cellulose, lignin, pectin (galacturonic acid), hemicelluloses and chlorophyll pigments. These components have different functional groups for example amide, carboxyl and hydroxyl which can play an important role in the removal of dyes from wastewaters [29]. Recently, research has been focused on improving the adsorption capacity of adsorbents through chemical modifications [30-38]. These modifications used to adsorbents may introduce functional groups (amine, amide, carboxylate, hydroxyl, phosphate, etc.) in the structure of the adsorbents or increase their porosity, with an increase in their adsorption capacity. Many researchers developed chemical modified orange peel that has been fruitfully applied for the elimination of dyes and metal ions from aqueous solution, some of which are sodium hydroxidetreated orange peel [39], CTAB modified orange peel [39], activated carbon prepared by orange peel [40], HCl treated orange peel [41], activated carbon from orange peel [42], sulfuric acidtreated orange peel [43], aminated pumpkin seed powder [44], calcined magnetic orange peel [45], chemically modified orange peel [46] and grafted copolymerization-modified orange peel [47]. In this study, we have chosen QAMOPP as an adsorbent material for the removal of RR120 from aqueous media.

This study aims to determine the adsorption behavior of RR120 using QAMOPP. The different controlling experimental conditions such as an effect of pH (2.0-9.0), contact time (0-300 min), adsorbent dosage (0.01-0.07 g/30 mL), initial RR120 concentration



Fig. 1. Molecular structure of RR120.

(100–1000 mg/L) and temperature (298–338 K) have been investigated and optimized. In addition to this, the adsorption equilibrium data were evaluated using the two- and three-parameter nonlinearized isotherm models. Kinetics and thermodynamics of the adsorption at different temperatures (298–338 K) were also studied. Desorption experiment studies were conducted to identify the recovery of RR120 and the QAMOPP for reuse.

2. Materials and methods

2.1. Chemicals and equipment

In the present study, all reagents used were of analytical reagent (AR) grade and were used as without further purification. The pH of the solutions was determined by using digital pH meter (Elico, LI-129). Standard buffer (4.0, 7.0 and 10.0) solutions are used to calibrate the pH meter. The RR120 concentrations were analyzed by UV–visible spectrophotometer (JASCO, V-750, Japan) at a maximum wavelength of 515 nm.

2.2. Adsorbate

Reactive Red (RR) 120 [Dye content \geq 50%; Molecular weight: 1469.98; Linear formula: C₄₄H₂₄Cl₂N₁₄O₂₀S₆Na₆; λ_{max} : 515 nm] was purchased from Sigma-Aldrich (India). The molecular structure of RR120 is presented in Fig. 1. To prepare RR120 stock solution (1000 mg/L) a desired amount of RR120 was dissolved in double deionized water (Milli-Q Millipore 18.2 Ω cm⁻¹-conductivity). A stock solution was further diluted to obtain the desired concentrations (100 to 1000 mg/L) were used in all the adsorption experiments.

2.3. Preparation of QAMOPP

Waste orange peel (OP) materials were collected from a Pullampeta (Kadapa district, Andhra Pradesh, India) town fruit and juice shops. The OP was washed with a tap as well as deionized water several times to remove dirt and other contaminants and air dried for 24 h. The dried OP was cut into small pieces and dried at 70 °C inside an oven for 24 h. The oven dried OP was grinding well to a fine powder. This obtained powder named as OPP.

Quaternary amine modified orange peel powder (QAMOPP) was prepared according to the method proposed by Gurung et al. [48]. In a typical run, the mixtures of 10.0 g dry OPP, 10.0 g formaldehyde (HCHO) and 40 mL of Conc. HCl was stirred for 24 h at 90 °C in a three-neck round bottom flask. The product of chloromethylation was diluted with double deionized water and the solid was filtered and washed with double deionized water a number of times to ensure the filtrate became neutral. The obtained chloromethylated product was dried in an oven at 50 °C for overnight. Then, 9.0 g of the product was mixed with 40 mL of 50% dimethylamine ((CH₃)₂NH) solution and 20 mL of 37% HCHO solution and heated at 90 °C with continuous string for 12 h to get dimethylamine modified OPP. The product was filtered and washed with 0.1 M HCl solution followed by several washings with water and dried for 24 h at 50 °C. The obtained dimethylamine ((CH₃)₂NH) modified OPP was further mixed together with 0.6 mL methyl iodide (CH₃I), 0.2 g sodium carbonate (Na₂CO₃) and 0.6 g sodium iodide (NaI) in 10 mL methanol (CH₃OH) to remove any unreacted methyl iodide and successively washed with double deionized water until a neutral pH was reached. The obtained residue was further washed with 0.1 M NaCl to get the chloride salt of quaternary amine modified OPP which as dried at 50 °C inside an oven for 24 h. Finally, the oven dried product was ground and sieved into smaller particles by a 50 mesh size. The modified OPP is called as QAMOPP. The reaction occurs as follows:



2.4. QAMOPP characterization

The FTIR spectra of the QAMOPP and RR120-loaded QAMOPP were done on FTIR spectrometer (Nicolet IS10, Thermo Scientific, USA). Pure KBr pellet and 1:10 (sample with KBr) pellets were used as blank and samples for FTIR measurement. The functional groups of the samples were recorded in the frequency range of 400–4000 cm⁻¹. The specific surface area, total pore volume and average pore diameter of QAMOPP were analyzed by adsorption-desorption of N₂ at 77 K using BET surface analyzer (BELSORP, BEL Japan). The sample was degassed at 323 K for 12 h to obtain a residual pressure < 10⁻⁶ mm Hg. The QAMOPP before and after RR120 adsorption was loaded onto the copper substrate after sputter-coated with a homogeneous gold layer for measuring surface morphologies using SEM (JEOL, JSM-7600F, Japan).

2.5. Adsorption and desorption studies

Batch sorption experiments were carried out in falcon tubes (50 mL) by adding a fixed quantity of QAMOPP with 30 mL of RR120 solution. The pH value was adjusted (using 0.1 M HCl or NaOH) between 2.0 and 9.0. The adsorbent dosage on RR120 adsorption was performed by varying the amount of adsorbent from 0.01 to 0.07 g/30 mL. The kinetic experiment was conducted in 250 mL conical flask containing 0.2 g of QAMOPP and 120 mL RR120 solution with an initial concentration of 300 mg/L. The experiment was repeated at 308 and 318 K temperatures also. The contact time was varied from 0 to 300 min. The equilibrium isotherm of RR120 onto QAMOPP was carried out at 298 K. A 0.05 g of QAMOPP with 30 mL RR120 solution (of different initial concentrations 100 to 1000 mg/L) was agitated at 180 rpm for 4 h at 298 K. The adsorption studies were also carried out at five temperatures (298-338 K) in order to estimate the thermodynamic (ΔG° , ΔH° and ΔS°) parameters. The average value (done twice) of every experiment was taken for data analysis. The remaining concentration of RR120 within the solution was measured by means of an UV-visible spectrophotometer after proper dilution. Based on the initial and final concentrations of the RR120, the adsorption capacity and removal efficiency of the QAMOPP was measured using the following Eq. (1):

$$q_e = \frac{(C_o - C_e)V}{m} \tag{1}$$

For the desorption study, 0.1 g of QAMOPP was added to 30 mL (300 mg/L, pH = 2.0) of RR120 solution and the mixtures were agitated on a reciprocating shaker at a constant speed of 180 rpm and 298 K for 4 h. Afterwards, the RR120-loaded adsorbents were magnetically separated and the remaining RR120 concentration in the solutions was determined using UV-visible spectrophotometer. After then, RR120-loaded adsorbents were filtered and dried at 70 °C inside an oven for

24 h. For the desorption process, the RR120-loaded adsorbents were added into 30 mL of 0.1, 0.3, 0.5, 0.7 and 1.0 M NaOH eluents. The mixtures were agitated at 180 rpm for 4 h. Subsequently, the adsorbent was separated magnetically. The amount of RR120 desorbed into the solutions was analyzed by UV–visible spectrophotometer. The efficiency of RR120 desorbed from the QAMOPP was calculated using the following Eq. (2):

$$Desorption \ efficiency = \frac{Amount \ of \ RR120 \ desorbed}{Amount \ of \ RR120 \ adsorbed} \times 100$$
(2)

2.6. Chi-square (χ^2) analysis

The equivalent mathematical statement of χ^2 test can be represented as:

$$\chi^2 = \sum \left(\frac{\left(q_e - q_{e,m}\right)^2}{q_{e,m}} \right) \tag{3}$$

where $q_{e,m}$ and q_e are equilibrium adsorption capacities (mg/g) obtained from the experimental and calculated data by the isotherm model, respectively. The best fitting of the non-linear isotherm model to the experimental data was evaluated on the basis of the lower value of χ^2 .

3. Results and discussion

3.1. Characterization of the adsorbent

The FTIR spectrums of the QAMOPP and RR120 loaded on QAMOPP are shown in Fig. 2. The spectrum of QAMOPP before adsorption (Fig. 2(a)) showed the distinct major bands at 3469, 2971, 1589, 1490, 1247, 1153, 1015, 836 and 695 cm⁻¹. In particular, the strong broad peak at 3469 $\rm cm^{-1}$ is associated to the stretching vibration of hydroxyl (-OH) and amine (-NH) functional groups of the QAMOPP surface, while the band at 2971 cm^{-1} corresponds to the –C-H stretching vibration. The remaining major bands of QAMOPP could be attributed as below: 1589 cm⁻¹ (N—H bending vibrations of amine), 1490 cm⁻¹ (N—N stretching vibrations of azide), 1247 cm⁻¹ (stretching vibration of – S=O group), 1153 cm⁻¹ (stretching vibration of the –C-N), 1015 cm⁻¹ (stretching vibrations of C—O), 831 cm⁻¹ (aromatic C—H bending vibrations) and 695 cm⁻¹ (-S-O stretching). After the adsorption of RR120, the peaks at 3457, 2928, 1588, 1476, 1246, 1152, 1013, 836 and 689 cm^{-1} was found on the spectrum (Fig. 2(b)). Comparison of FTIR spectra of RR120 loaded QAMOPP with unloaded QAMOPP displayed considerable changes in some peaks. A small number of bands (1589, 1247, 1153 and 1015 cm^{-1}) on the QAMOPP were not shifted mean that they were not participated in the adsorption process.



Fig. 2. FTIR spectra of QAMOPP: (a) before adsorption and (b) after adsorption.

A number of bands showed shift like 3457, 2928, 1476, 836 and 689 cm^{-1} (Fig. 2(b)) indicates the bonds formation between QAMOPP and RR120 dye molecules. Therefore, it can be concluded that hydroxyl and amine functional groups may play a considerable role in the adsorption of RR120 on the QAMOPP surface.

The morphological pattern of QAMOPP before and after RR120 adsorption is studied using SEM. The SEM/EDAX images of the samples are shown in Fig. 3. Before the adsorption a smooth surface morphology as observed (Fig. 3(a)), while after the adsorption of RR120 on the QAMOPP, a layered structure on the surface of adsorbent and rough morphology was observed (Fig. 3(b)). In general rough surfaces provide high porosity and surface areas those are favorable for molecular diffusion and the adsorption of contaminants. The EDAX spectrum of the QAMOPP shown in Fig. 3(c) clearly indicates that the composite chiefly contains C (56.25 wt% 62.77 at.%), N (15.43 wt% 14.77 at.%), O (25.16 wt % 21.08 at.%), Mg (0.64 wt% 0.35 at.%), P (1.49 wt% 0.64 at.%), S (0.39 wt% 0.16 at.%) and K (0.64 wt% 0.22 at.%).

The specific surface area, total pore volume and average pore diameter play an essential role in the adsorption capacity and adsorption rate of the QAMOPP. The reason is that these properties can provide more active adsorption sites, which improve the adsorption rate of QAMOPP. The specific surface area, total pore volume and average pore diameter of the QAMOPP were found to be 38.6 m²/g, 0.291 cm³/g and 11.13 nm, respectively. These properties increased the possibility of the RR120 to be adsorbed onto QAMOPP.

3.2. Effect of pH

One of the vital factors that affect adsorption process is solution pH due to its control on surface charge and solubility of adsorbent. The effect of pH on the adsorption capacity of RR120 onto QAMOPP was studied in various pH conditions ranging from 2.0 to 9.0 at 298 K, constant initial RR120 concentration of 300 mg/L, adsorbent dosage of 0.05 g and contact time of 110 min. As can be seen from Fig. 4, the adsorption of RR120 onto QAMOPP is intimately dependent on the pH of the solution. The adsorption capacity of RR120 decreased from 143.9 to 3.87 mg/g with increasing pH solution from 2.0 to 9.0, and a maximum adsorption capacity was reached at an equilibrium pH of around 2.0 and this pH was chosen for the further sorption experiments. RR120 has six sulphonate (R-SO³⁻) groups, which are easily dissociated in aqueous solution, leaving the dye molecule with a net negative charge.

$RR120-SO_3Na \rightarrow RR120-SO_3^- + Na^+$



1 2 3 4 5 6 Full Scale 5553 cts Cursor: 0.000 keV

Fig. 3. SEM images of (a) QAMOPP (b) RR120 loaded QAMOPP and (c) EDAX spectrum of QAMOPP.



Fig. 4. Effect of pH on RR120 adsorption onto QAMOPP.

$$S - OH \xrightarrow{H^+} S - OH_2^+ + RR120 - SO_3^- \rightarrow S - OH_2^+ \rangle - - \langle RR120 - SO_3^- \rangle = SO_3^- \langle RR120 - SO_3^- \rangle = SO_3^- \rangle$$

$$S - OH \xrightarrow{OH} S - O^- + RR120 - SO_3^- + H_2O \rightarrow S - O^- \langle - - - \rangle RR120 - SO_3^-$$

where S denotes the surface of QAMOPP.

At lower pH, the positively charged surface (active sites) of the QAMOPP attracts the negatively charged RR120 that enhances the uptake. Whereas at higher pH the abundance of hydroxide ions competes with RR120 and the ionic repulsions between the negatively charged surface and RR120 molecule results lower adsorption of RR120. The outer surface of the QAMOPP does not have exchangeable anions at higher pH values. The lower pH of the solution is suitable for the adsorption of reactive dyes [49–51].

3.3. Effect of adsorbent dosage

Adsorbent dosage also plays an important role in the adsorption of RR120 from aqueous solution. Experiments were carried out at different adsorbent dosages (0.01, 0.02, 0.03, 0.04, 0.05, 0.06 and 0.07 g/30 mL) and fixed initial RR120 concentration (300 mg/L). The results of the dosage of QAMOPP for the adsorption of RR120 are shown in Fig. 5. This figure shows that the removal efficiency of RR120 increased (32.4 to 91%) when the adsorbent dose was increased (0.01 to 0.07 g/30 mL). This condition may be due to higher surface area and the quantity of adsorption exchangeable active sites that are available for adsorption. If the adsorption capacity was articulated as the quantity of dye adsorbed per unit mass of the adsorbent (mg/g), the adsorption capacity of QAMOPP for RR120 decreased (290.7 to 118.7 mg/g) with increasing adsorbent dosage (0.01 to 0.07 g/30 mL) (Fig. 5). This may be due to reduce in total available surface area of adsorbent as of overlapping or aggregation of adsorption sites resulting in an increase in diffusion path length for the RR120. In this study, the maximum removal efficiency 91% was found at 0.05 g/30 mL. This adsorbent dosage was considered for all the adsorption studies.

3.4. Effect of contact time on RR120 uptake

Contact time studies are vital in describing the adsorption rate and estimation of equilibrium time for dye adsorption. The impact of contact time (different time intervals ranging from 0 to 300 min) on the adsorption of RR120 using QAMOPP was studied under the optimal conditions: pH 2.0, initial RR120 concentration 300 mg/L, adsorbent dosage 0.3 g and different temperatures. As shown in Fig. 6, the adsorption capacity of RR120 was gradually increased with time and reached equilibrium condition after 110 min due to the presence of highly available surface area and active adsorption sites. However, after this time, an equilibrium was achieved when the adsorbent surface becomes saturated. Thus, the contact time of 110 min was considered as an equilibrium time and was used for further experiments.



Fig. 5. Effect of adsorbent dosage for RR120 adsorption onto QAMOPP.



Fig. 6. Effect of contact time on RR120 adsorption onto QAMOPP at different temperatures.

3.5. Adsorption kinetics

To evaluate the performance of an adsorbent and the mechanism of adsorption process adsorption kinetic studies are necessary. In the case of pollutant uptake, kinetics helps to select the optimum operating conditions for extending the process to large-scale adsorption systems [23]. To analyze the adsorption kinetics of RR120 onto QAMOPP two kinetic models, which are pseudo-first-order and pseudo-second-order models have been used for their validity with the experimental data. The nonlinear kinetic models are generally expressed as follows:

Pseudo-first-order [52]:

$$q_t = q_{e1}(1 - \exp(-k_1 t)) \tag{4}$$

Pseudo-second-order [53]:

Table 1

$$q_t = \frac{q_{e2}^2 k_2 t}{1 + q_{e2} k_2 t} \tag{5}$$

The kinetic parameters (q_{e1} , q_{e2} , k_1 , k_2 , and R^2) obtained by nonlinear regression method are presented in Table 1. As seen from this table, the low R^2 values (in the range of 0.9484–0.9740) and there is not a quite good agreement between the values of experimental $q_{e,exp}$ and calculated $q_{e1,cal}$ showed that the pseudo-first-order model is unsuitable for modeling the adsorption of RR120 onto QAMOPP for the studied temperature range. On the other hand, the high R^2 values (in the range 0.9967–0.9982) and excellent conformity between the $q_{e,exp}$ and $q_{e2,cal}$ values exposed that the adsorption mechanism of RR120 onto QAMOPP could be well modeled with the pseudo-second-order



Fig. 7. Kinetic parameters on RR120 adsorption onto QAMOPP at different temperatures.

model at all temperatures. The non-linear adsorption kinetic curves for RR120 are shown in Fig. 7.

3.6. Adsorption activation energy

The values of the pseudo-second-order rate constant k_2 at different temperatures are given in Table 1 were applied to approximate the activation energy of the adsorption process of RR120 onto QAMOPP by the Arrhenius equation can be expressed in Eq. (6):

$$\ln k_2 = \ln A_o - \frac{E_a}{RT} \tag{6}$$

 E_a can be obtained by plotting ln k_2 against the reciprocal of the absolute temperature (Fig. 8). Whether the adsorption process is physical or chemical can be known by the magnitude of E_a . The value of E_a obtained for the adsorption of RR120 onto QAMOPP is 12.1 kJ/mol. In general, 5 to 40 kJ/mol, is the range of activation energy for physical adsorption. From the results, the adsorption of RR120 onto QAMOPP is a physical adsorption process.

3.7. Adsorption isotherms

The information regarding the distribution of adsorbate molecules at the solid/liquid interface was obtained from numerous adsorption isotherm models. In this work, various two- and three-parameter nonlinearized isotherm models such as Langmuir, Freundlich, Dubinin-Radushkevich (D-R), Temkin, Sips, Toth, Khan and Redlich-Peterson (R-P) models were employed for testing the experimental equilibrium adsorption data.

Tuble 1			
Kinetic parameters obtained from	pseudo-first-order and ps	seudo-second-order at d	ifferent temperatures

Adsorbent	Temp. (K)	q _{e,exp}	Pseudo-first-	Pseudo-first-order model		Pseudo-second-order model		
		(mg/g)	q _{e1,cal} (mg/g)	k ₁ (1/min)	R ²	$q_{e2,cal} \ (mg/g)$	k ₂ (g/mg min)	R ²
QAMOPP	298 308 318	136.2 148.6 165.1	128.9 141.2 157.6	0.1065 0.1277 0.1600	0.9740 0.9621 0.9484	138.9 150.9 167.2	0.0013 0.0015 0.0017	0.9982 0.9967 0.9941



Fig. 8. Plot of ln k2 versus 1/T for the estimation of activation energy for RR120 adsorption onto QAMOPP.

3.7.1. Two-parameter isotherms

3.7.1.1. Langmuir isotherm. Langmuir isotherm [54] model predicts the monolayer coverage at the outer surface of adsorbent by assuming monolayer adsorption occurs at structurally and energetically homogeneous active sites. The non-linearized form of Langmuir isotherm is expressed by the following Eq. (7):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{7}$$

The maximum RR120 uptake by QAMOPP was 344.8 mg/g. The Eq. (8) describes the dimensionless constant separation factor or equilibrium parameter (R_L) that indicates the adsorption capacity.

$$R_L = \frac{1}{(1 + K_L C_o)} \tag{8}$$

If $0 < R_L < 1$, the isotherm will be favorable adsorption; for $R_L > 1$, the isotherm will be unfavorable adsorption; for $R_L = 1$, the isotherm will be linear adsorption and for $R_L = 0$, the isotherm will be irreversible adsorption. The values of R_L lay in the range of 0.03–0.22, indicating that adsorption of RR120 onto QAMOPP is favorable.

3.7.1.2. Freundlich isotherm. Freundlich isotherm [55] mainly considers that during the adsorption process the adsorption surface becomes heterogeneous. The non-linearized from of Freundlich isotherm is given by Eq. (9):

$$q_e = K_f C_e^{1/n} \tag{9}$$

The values of exponent *n* are in the range (1 < n < 10) of favorable adsorption. In this study, the *n* value was observed to be 3.832 (Table 2). The *n* value was between 1 and 10, indicates that the adsorption of RR120 onto QAMOPP is favorable.

3.7.1.3. Dubinin-Radushkevich (D-R) isotherm. The D-R isotherm [56] model gives the characteristic porosity and apparent energy of

Tabl	e	2

Isotherm parameters for RR120 adsorption onto QAMOPP.

Isotherm	Parameters	Values
Two-parameter isotherm models		
Langmuir	$q_m (\mathrm{mg/g})$	344.8
	K_L (L/mg)	0.0352
	R^2	0.9996
	χ^2	3.8
Freundlich	$K_f(mg/g)$	69.9
	n	3.832
	R^2_{β}	0.9287
	χ^{2}	32.4
Temkin	b (J/mol)	0.039
	α (L/mg)	0.5472
	R ⁻	0.9676
Dubinin Paduchkovich	χ	19.5
Dubinin-Radusirkevicii	$q_m (\Pi g/g)$ $K (mol^2/I^2)$	287.9
	F(kI/mol)	495
	R^2	0.8463
	γ^2	53.6
	~	
Three-parameter isotherm models		
Sips	K_{S} (L/g)	12.11
	$a_{\rm S}$ (L/mg)	0.0352
	β_{S}	0.9999
	R	0.9925
Toth	χ	7.5
1001	q_{max} (IIIg/g) h_m (I/mg)	0.0347
	n _T	0.9849
	R^2	0.9896
	γ^2	11.2
Khan	a_{max} (mg/g)	344.2
	b_{K} (L/mg)	0.033
	a _K	0.986
	R^2	0.9991
	χ^2	6.5
Redlich-Peterson	K_{RP} (L/g)	11.723
	a_{RP} (L/mg)	0.0531
	β_{RP}	0.995
	R^2	0.9825
	χ^2	13.2

adsorption process. The non-linearized form of D-R isotherm is represented by the following Eqs. (10) and (11):

$$q_e = q_m \exp(-K\varepsilon^2) \tag{10}$$

where

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{11}$$

The mean free energy of adsorption process (E) is determined using following Eq. (12):

$$E = \frac{1}{\sqrt{2K}} \tag{12}$$

Depending on the values of *E*, the adsorption process may be physical or chemical. The magnitude of *E* determines the adsorption process. The range of *E* known for chemical adsorption is 8 to 16 kJ/mol, physical in nature is <8 kJ/mol and chemisorption is E > 16 kJ/mol. Based on the value of *E* (4.95 kJ/mol) we can justify the physical adsorption process plays a significant role in the adsorption of RR120 on QAMOPP surface.

3.7.1.4. Temkin isotherm. Temkin isotherm [57] model explains about the interactions between adsorbate and adsorbent. Assuming the linear (instead of logarithmic) decrease of heat of adsorption of all the molecules

in the layer and the binding energy distribution is uniform across the surface. The non-linearized form of Temkin isotherm has been used in the following Eqs. (13) and (14):

$$q_e = \beta \, \ln \alpha + \beta \, \ln C_e \tag{13}$$

$$\beta = \frac{RT}{b} \tag{14}$$

The value of *b* indicates whether it is physical (<8 kJ/mol) or chemical (between 8 and 16 kJ/mol) adsorption process. The value of *b* (0.039 kJ/mol) in the present study was lower than 8 kJ/mol, indicated that the adsorption of RR120 onto QAMOPP is physical adsorption process.

3.7.2. Three-parameter isotherms

3.7.2.1. Sips isotherm. Sips isotherm [58] is generally known as the combination of the Langmuir and Freundlich isotherm models that describes heterogeneous surface much better. Depending on the adsorbate concentrations low and high, the Sips isotherm approaches the Freundlich and Langmuir isotherms respectively. The nonlinearized form of Sips isotherm can be expressed as the following Eq. (15):

$$q = \frac{K_S C_e^{ls}}{1 + a_S C_e^{ls}} \tag{15}$$

When the value of β_s is 0 and 1 then the Sips isotherm become a Freundlich isotherm and Langmuir isotherm respectively which can be applied for ideal surfaces. The coefficient β_s for the present study was close to unity (Table 2), implying the RR120 adsorption was better represented by the Langmuir isotherm.

3.7.2.2. Toth isotherm. When the adsorbate concentration is low and high then the Toth isotherm [59] model is very useful in describing the adsorption process as this model gives a wide range of fit than Langmuir or Freundlich isotherm equation. The non-linearized form of Toth isotherm is determined from the following Eq. (16):

$$q = \frac{q_{\max} b_T C_e}{\left[1 + (b_T C_e)^{1/nT}\right]^{nT}}$$
(16)

If $n_T = 1$, Toth isotherm is reduced to the Langmuir isotherm equation. The estimated n_T value (Table 2) is close to unity, which suggest the RR120 adsorption fit the Langmuir isotherm model.

3.7.2.3. *Khan isotherm.* The Khan isotherm [60] model describes the experimental data with the minimum average percentage error by comparing several multicomponent adsorption isotherms. The non-linearized form of Khan isotherm is expressed as following Eq. (17):

$$q = \frac{q_{\max}b_K C_f}{\left(1 + b_K C_f\right)^{aK}} \tag{17}$$

If $a_{K} = 1$, Khan equation reduces to the Langmuir isotherm, whereas the term $b_{K}C_{f}$ is much greater than unity it can be simplified to a Freundlich type isotherm. In this study, the a_{K} value was close to unity (Table 2), which suggests that the adsorption of RR120 onto QAMOPP fit the Langmuir isotherm model.

3.7.2.4. Redlich-Peterson (R-P) isotherm. The R-P [61] isotherm model is generally studied in large concentration intervals in the various systems (homogeneous and heterogeneous). This model uses hybrid elements

from both Langmuir and Freundlich isotherm models. The nonlinearized form of R-P isotherm can be expressed as the following Eq. (18):

$$q = \frac{K_{RP}C_f}{1 + a_{RP}C_f^{\beta_{RP}}} \tag{18}$$

When the value of $\beta_{RP} = 0$, the R-P model reduces to the Henry's law equation which is a linear isotherm, and to the Langmuir isotherms for $\beta_{RP} = 1$. For high adsorbate concentration, the R-P model reduces to the Freundlich isotherm. The β_{RP} value was close to 1 (Table 2), which indicates that the adsorption of RR120 onto QAMOPP equilibrium data can be approximated to fit the Langmuir isotherm.

The comparison results of the values of the Langmuir, Freundlich, Dubinin-Radushkevich (D-R), Temkin, Sips, Toth, Khan and Redlich-Peterson (R-P) model rate constants with correlation coefficients (R^2) and Chi-square (χ^2) are given in Table 2. As can be seen from Table 2, the correlation coefficient (R^2) and Chi-square (χ^2) values of all the isotherm models, it can be concluded that the Langmuir (two-parameter) and Khan (three-parameter) isotherm models are the best fitted models for the experimental data of RR120 adsorption on the QAMOPP because those displayed the higher R^2 and lower Chi-square (χ^2) values.

3.8. Comparison of the adsorption capacity with other adsorbents

The comparison of monolayer adsorption capacities of various adsorbents was reported in the literature [3,62–72] and the q_{max} (mg/g) values are listed in Table 3. From the results, it was observed that the maximum monolayer adsorption capacity of QAMOPP is superior to the literature, which shows perfect adsorption property and satisfactory performance for the removal of RR120 would be an effectively adsorbent.

3.9. Effect of temperature and thermodynamic study

The effect of temperature on the adsorption of RR120 onto QAMOPP was studied and presented in Fig. 9, for five different temperatures of 298, 308, 318, 328, and 338 K, at 300 mg/L initial RR120 concentration and pH 2.0. The equilibrium adsorption capacity of RR120 was increased (132.3 to 172.4 mg/g) with an increase in temperature (298 to 338 K) which is a sign of endothermic in nature of the adsorption. The increased adsorption capacity at higher temperatures may be due to the availability of the high surface area or exchangeable sites and high porosity. From these results, thermodynamic parameters (ΔG^o , ΔH^o and ΔS^o) were calculated using the following Eqs. (19)–(22):

$$\Delta G^o = -RT \ln K_c \tag{19}$$

Table 3

Comparison of adsorption capacity of QAMOPP with different adsorbents.

Adsorbent	Adsorption capacity (mg/g)	рН	References
Nanoparticles of Fe ₃ O ₄	166.67	2.5	[3]
Chitosan/zeolite	19.14	5.0	[62]
Chara contraria	92.35	1.0	[63]
Chitosan beads	114.9	4.0	[64]
Hydrilla verticillata	120.85	2.0	[65]
Jatropha curcas shells	42.5	2.0	[66]
Agave sisalana	110	2.0	[67]
Pumpkin husk	98.61	1.0	[68]
Cetylpyridinium-bentonite	81.97	2.0	[69]
Chitosan/modified montmorillonite	5.6	5.0	[70]
Activated carbon	267.2	2.0	[71]
Cumin herb wastes	47.88	2.0	[72]
QAMOPP	344.8	2.0	This study



Fig. 9. Effect of temperature on RR120 adsorption onto QAMOPP.

$$K_c = \frac{C_{Ae}}{C_e} \tag{20}$$

$$\Delta G^{o} = \Delta H^{o} - T \Delta S^{o} \tag{21}$$

$$\ln K_c = -\frac{\Delta G^o}{RT} = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R}$$
(22)

The values of ΔH^{o} and ΔS^{o} were determined from the slope and intercept of the linear plot of ln K_c versus 1/T (Fig. 10) using the Van't Hoff equation (Eq. (22)). The negative values of ΔG^{o} (-1.9114, -2.7935, -3.8229, -4.9472 and -5.9208 kJ/mol) at all temperatures (298, 308, 318, 328 and 338 K, respectively) indicated that the feasibility and spontaneity of the RR120 adsorption process onto QAMOPP. Moreover, the ΔG^{o} was inversely proportional to temperature and more favorable at higher temperatures and the reaction rate increases. The positive value of ΔH^{o} (28.4 kJ/mol) reveals that the RR120 adsorption onto the QAMOPP was endothermic, which means a portion of total energy is released when RR120 anions adsorbed on the active sites of



Fig. 10. Thermodynamic parameters on RR120 adsorption onto QAMOPP.



Fig. 11. Effect of NaOH concentration on desorption of RR120 from the QAMOPP.

QAMOPP. The magnitude of ΔG^o is between -20 and 0 kJ/mol means physisorption and between -400 and -80 kJ/mol. ΔH^o due to physisorption is lower than 84 kJ/mol, while ΔG^o due to chemisorption takes a value between 84 and 420 kJ/mol [73]. Therefore, the values of ΔG^o and ΔH^o suggest that adsorption of RR120 onto QAMOPP was driven by a physisorption. The positive value of ΔS^o (0.102 kJ/mol K) indicated an increased degree of disorderness at the solid-solution interface during the adsorption of RR120 on the active sites of QAMOPP.

3.10. Desorption studies

Desorption experiments reveal the recovery of RR120 from QAMOPP. NaOH solution was selected as a desorbing agent to desorb RR120 from the RR120-loaded QAMOPP. Various concentrations of NaOH (0.1, 0.3, 0.5, 0.7 and 1.0 M) were used as desorbing media for the regeneration of RR120-loaded QAMOPP and the results are offered in Fig. 11. The Efficiency of desorption was decreased, with increasing NaOH concentration (Fig. 11). The maximum desorption (92%) of RR120 from QAMOPP was achieved with 0.1 M NaOH, indicating that a lower concentration of NaOH was more efficient in releasing RR120. From the desorption studies, it is concluded that QAMOPP has shown better restorative potential and effectual for the elimination of RR120 from aqueous solution.

3.11. Adsorption mechanism

The adsorption of RR120 on QAMOPP depends on dye (RR120) structure and adsorbent surface properties. The main mechanism involved is an electrostatic attraction (major contribution) along with physisorption (minor contribution). The high anionic nature of dye varies depends on pH. In low pH solutions to high pH solutions the anionic nature decreases, correspondingly the adsorption capacity also follows the same trend (high at low pH and low at high pH). Because of the easily protonated nature of the hydroxyl groups (-OH) present on the surface of QAMOPP, they behave as positive groups ($-OH_2^+$) in acidic medium (pH = 2.0) where high adsorption capacity was observed in the present study. This is the common trend observed when electrostatic interactions play a significant role in the adsorption mechanism.

4. Conclusions

The QAMOPP used in the present study is an alternative adsorbent for RR120 removal from aqueous solution. The results showed that pH

(2.0–9.0), contact time (0–300 min), adsorbent dosage (0.01–0.07 g/30 mL), initial RR120 concentration (100–1000 mg/L) and temperature (298–338 K) highly affected the overall dye adsorption capacity of the adsorbent. The experimental kinetic data revealed that the adsorption process followed the pseudo-second-order model. Adsorption equilibrium data excellent fits within the following non-linearized isotherm equations order: Langmuir > Khan > Sips > Toth > Redlich-Peterson (R-P) > Temkin > Freundlich > Dubinin-Radushkevich (D-R), based on its high R^2 and low χ^2 values. Optimum adsorption of RR120 onto QAMOPP was observed at pH 2.0 (344.8 mg/g). The % adsorption of RR120 improved with an increase in dosage of the adsorbent. Desorption studies showed 92% recovery of RR120 with 0.1 M NaOH solution. Thermodynamic studies showed endothermic, feasible and spontaneous nature of the adsorption process. Finally, one can say that the QAMOPP is a competent material to remove RR120 from aqueous solution.

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Nomenclature

*A*_o: frequency factor, g/mg min

- *a_{Rp}*: Redlich-Peterson constant, L/mg
- *a_s*: Sips isotherm constants, L/mg
- *a_K*: Khan isotherm exponent
- *b:* Temkin isotherm constant, J/mol *BET:* Brunauer-Emmett-Teller
- b_{K} : Khan isotherm constant. L/mg

DK. KIIAII ISOLIIEIIII COIISLAIIL, L/IIIg

- b_T : Toth isotherm constant, L/mg
- C_{Ae} : amount of RR120 adsorbed on the solid phase at equilibrium, mg/L C_{Ae} : initial concentration of RR120, mg/L
- C_e : equilibrium (final) concentration of RR120, mg/L
- *E*: mean free energy, kJ/mol

 E_a : activation energy, kJ/mol

- FTIR: Fourier Transform Infrared Spectroscopy
- k_1 : rate constant of pseudo-first-order. 1/min
- k_2 : rate constant of pseudo-second-order, g/mg min
- *K*: Dubinin-Radushkevich isotherm constant, mol^2/l^2
- K_c : equilibrium adsorption distribution coefficient
- K_{f} : measure of adsorption capacity, mg/g
- K_L : coefficient related to affinity between adsorbate and adsorbent, L/mg
- K_{RP}: Redlich-Peterson constant, L/g
- *K_S*: Sips isotherm constant, L/g
- *m*: weight of the QAMOPP used for RR120 adsorption, g
- n: indicator for favorable or unfavorable adsorption process
- n_T : Toth isotherm exponent
- qe: amount of adsorbed RR120 by QAMOPP, mg/g
- q_{e1} , q_{e2} : amount of RR120 adsorbed at equilibrium, mg/g
- q_t : amount of RR120 adsorbed at time t, mg/g
- q_m : Langmuir isotherm maximum adsorbate uptake at equilibrium, mg/g
- q_m : Dubinin-Radushkevich monolayer capacity, mg/g
- q_{max} : Toth isotherm maximum adsorption capacity, mg/g
- R: gas constant, 8.314 J/mol K
- SEM: Scanning Electron Microscopy

T: temperature, K

- V: volume of dye solution, L
- ΔG° : Gibbs free energy change, kJ/mol
- ΔH° : enthalpy change, kJ/mol
- ΔS^{o} : entropy change, kJ/mol K

Greek letters

- α : equilibrium binding constant, L/mg
- β : Temkin constant related to the heat of adsorption, J/mol
- β_{RP} : exponent
- $\beta_{\rm S}$: heterogeneity coefficient

ɛ: Polanyi potential