# RESEARCH

**Open Access** 



# Synthesis of molecularly imprinted polymer for the removal of cyanazine from aqueous samples

Rachel Marcella Roland<sup>1</sup>, Showkat Ahmad Bhawani<sup>1\*</sup> and Mohamad Nasir Mohamad Ibrahim<sup>2</sup>

# Abstract

**Background** Cyanazine (CYZ) is one of the triazine herbicides to prevent broadleaf grass and weeds in crops. Despite its affordability and productivity in increasing crop yield, the extensive usage of CYZ contributes to environmental pollution and poses risks to living organisms. Most research has focused on detecting CYZ in the environment and its toxicity to humans and the ecosystem. For these reasons, molecular imprinting technology (MIT) can be applied to produce an effective adsorbent material of high binding affinity and selectivity towards its target compound which is known as molecularly imprinted polymers (MIPs). In this study, MIP was prepared by precipitation polymerization using CYZ as a template molecule, methacrylic acid (MAA), acrylamide (AAm) and 4-vinylpyridine (4VP) as functional monomers, and ethylene glycol dimethacrylate (EGDMA) as cross-linker in the ratio of 1:6:12, respectively. The effects of contact time, initial concentration, pH, and polymer dosages on the adsorption efficiencies of MIPs were also investigated in this study.

**Results** MIPs of CYZ were successfully synthesized by precipitation polymerization method with a non-covalent approach using different functional monomers such as methacrylic acid (MAA), acrylamide (AAm) and 4-vinylpyridine (4VP). For the comparison study, the non-imprinted polymer (NIP) was synthesized without the addition of CYZ, the template molecule. The FTIR analysis indicated the interactions among CYZ and functional monomers (MAA, AAm or 4VP) in the presence of EGDMA as a cross-linker. The FESEM analysis showed that only MIP (AAm) and NIP (AAm) had regular and spherical polymer particles while MIP (MAA), NIP (MAA), MIP (4VP) and NIP (4VP) were agglomerated and irregular in shape. The EDX analysis showed that the MIPs were mainly composed of carbon and oxygen. Meanwhile, the BET analysis of MIP (AAm) had higher surface area, total pore volume and average pore radius than that NIP (AAm). Based on the batch binding study, MIP (AAm) (83.30%) had the highest binding efficiency than the MIP (MAA) (76.96%) and MIP (2VP) (76.90%) at a contact time of 240 min. The optimum conditions for the highest binding efficiency of MIP (AAm) were obtained at an initial concentration of 6 ppm, pH 7 and polymer dosage of 0.1 g polymer beads. The adsorption efficiency of MIP (AAm) with CYZ at the optimum parameters resulted in 86.39%. The selectivity test showed that MIP (AAm) was more selective towards CYZ than AME, the competitive compound with relative selectivity coefficient of 2.36. The kinetic isotherm of MIP (AAm) was best explained according to the pseudo-secondorder kinetic model while the adsorption isotherm of MIP (AAm) was based on the Langmuir adsorption isotherm model. The MIP (AAm) was tested in the distilled water (DIW), tap water and river water spiked with CYZ and a substantial amount of CYZ was removed with a recovery of 86.67%, 84.75% and 84.69%, respectively.

**Conclusion** The MIPs of CYZ were successfully synthesized by the precipitation polymerization method using different functional monomers. Among those MIPs, MIP (AAm) showed the highest rebinding efficiency and therefore

# \*Correspondence:

Showkat Ahmad Bhawani sabhawani@gmail.com

Full list of author information is available at the end of the article



© The Author(s) 2023. **Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/ficenses/by/4.0/. The Creative Commons Public Domain Dedication waiver (http://creativecommons.org/publicdomain/zero/1.0/) applies to the data made available in this article, unless otherwise stated in a credit line to the data.

this MIP was selected for further studies. The best combination of CYZ, AAm was the main factor that contributed to the morphological and chemical properties, as well as the efficiency and selective binding performance of MIP (AAm). Since MIP (AAm) showed a substantial removal efficiency of CYZ in the environment specifically water sources, it has the capability to act as an adsorbent material for various purposes such as solid-phase extraction techniques and a stationary phase in various chromatographic techniques.

**Keywords** Molecularly imprinted polymer, Precipitation polymerization, Cyanazine, Tap water, River water, Initial concentration, pH, Polymer dosage, Selectivity, Contact time

## **Graphical Abstract**



### Introduction

Generally, molecular imprinting technology (MIT) is an assuring method that can produce molecularly imprinted polymers (MIPs), which are extensively cross-linked polymers with highly specific binding sites and highly selective towards their target compound [1]. The molecular imprinting process begins with the organization of the functional monomer and the template molecule, then functional monomer-template complexes co-polymerize in the presence of an appropriate amount of cross-linker, and finally the removal of the template from the polymer cavity [2]. The optimum ratio of the template molecule, functional monomer, cross-linker, initiator and porogenic solvent is essential

because they influenced the binding efficiency of the resultant MIP. Hence, MIPs are generated whereby the shape, size and position of the functional groups and the polymer cavities are complementary with the template molecule. There are various types of molecular imprinting methods to synthesize MIPs such as bulk polymerization [3], In situ polymerization [4], suspension polymerization [5], emulsion polymerization [1, 6, 7], grafting polymerization [8], seed polymerization [9] and precipitation polymerization [10–15]. Among these, the precipitation polymerization method is the most employed MIP technique because it can generate a high yield of polymers with uniform and spherical polymer particles [16]. MIPs involve easy and low-cost

preparation methods, have good storage stability, high mechanical strength and high resistance towards heat, and pressure as well as in harsh chemical media [17]. Therefore, MIPs have been widely used in various applications including separation materials [18], sensors [19], drug delivery [20] and catalysis [21].

Cyanazine (CYZ) or 2-[(4-chloro-6-(ethylamino)-1,3,5triazin-2-yl)amino]-2-methyl propanenitrile is a triazine herbicide. Generally, CYZ acts as weed control to kill unwanted plants by inhibiting photosynthesis in plants such as broadleaves weeds and annual grasses [22]. The usage of CYZ in agricultural fields is cost-effective and efficient in increasing the yield of crops. However, the uncontrollable and prolonged usage of CYZ in agriculture can be detrimental to mankind and the ecosystem as it is relatively persistent in the environment causing water and soil pollution. This is because CYZ has been reported by Environmental Protection Agency (EPA) as a hazardous substance and dangerous compound applied in the agriculture method [23]. For example, CYZ can cause contamination in the soil where it is applied and rainwater may transport CYZ to other areas or waterways such as nearby rivers that eventually kill the aquatic life. Besides that, CYZ has poor solubility in water and hence it is commonly dissolved in an organic solvent when used, which later causes environmental pollution [24]. Moreover, CYZ might travel into the groundwater supply and contaminate the water sources. CYZ, atrazine and simazine are herbicides that had been found in increasing amounts in both surface water and groundwater [25, 26]. Furthermore, CYZ is among seven 1,3, 5-triazine herbicides that cause growth inhibition, development retardation, thyroid gland histology and axial malformation in amphibian tadpoles [27]. CYZ also has adverse effects towards humans including chronic bronchitis [28], diabetes [29] and danger of birth defects [30].

Much research has been more focused on the determination of CYZ in the environment [31-37] and its toxicity towards mankind and the ecosystem [38, 39]. For these reasons, a selective and efficient approach to removing CYZ in aqueous samples including tap water and river water is essential for mankind and other living organisms and this can be successfully conducted by using MIPs. Few studies on the removal of CYZ in various samples such as natural water [40], tap water, onion, rice, and maize [41] proved that MIP had performed as an excellent adsorbent material. The drawbacks of the research were polymerization methods applied were time-consuming, employed advanced instruments such as potentiostat/galvanostat model PGSTAT302 and gas-chromatography and used large amounts of chemicals and solvents that were not environmentally friendly throughout the research.

Hence, in this research, the MIPs were prepared using precipitation polymerization for only 6 h. CYZ was selected as the template molecule or target compound and the functional monomers are methacrylic acid (MAA), acrylamide (AAm) and 4-vinyl pyridine (4VP), which are acidic, neutral, and basic, respectively. The binding interaction of CYZ, the template molecule with MAA, AAm and 4VP (functional monomers) was established by a self-assembly or non-covalent imprinting approach which involves non-covalent interactions. In the self-assembly approach, the functional monomer is used in excess compared to the number of moles of template molecule to aid the formation of templatefunctional monomer complexes [42]. Ethylene glycol dimethacrylate (EGDMA) was chosen as the cross-linker. The cross-linker is used to control the morphology of the polymer matrix, stabilize the imprinted binding sites, and provide mechanical stability to the polymer matrix [42]. Therefore, cross-linker was used at high ratios to generate MIP with porous structure and adequate mechanical stability [43] as well as to sustain the stability of the binding sites after template removal [7]. In MIP synthesis, a solvent is responsible for gathering and dissolving the template molecule, functional monomer, cross-linker, and initiator into a single phase called a pre-polymerization mixture [44]. Azo-bis-isobutyronitrile (AIBN) was used as the initiator, the starting material for the polymerization of MIPs and only a small amount of initiator is required to activate the polymerization process [42]. The most interesting part of this study is the usage of three different functional monomers of different natures (acidic, neutral, and basic) for the polymerization reaction that produces three different sets of MIPs. The MIP with the highest binding efficiency was selected for further studies including adsorption studies, selectivity test and MIP application for the removal of CYZ from environmental samples such as river water and tap water.

#### **Results and discussion**

#### **FTIR analysis**

The FTIR analysis was conducted to distinguish the functional groups present in the synthesized polymers, associated with the interaction among the template (CYZ), functional monomers (MAA, AAm and 4VP) and crosslinker (EGDMA). The general mechanism of MIP synthesis, showing the binding interactions between the CYZ as template monomer and AAm as a functional monomer to produce template molecule-functional monomer complexes in the presence of EGDMA as cross-linker, and later generate MIPs after the template removal, is displayed in Fig. 1.

Meanwhile, the IR spectra of the synthesized MIP (MAA), MIP (AAm) and MIP (4VP) before washing



Fig. 1 The general mechanisms of MIP synthesis

were shown in Fig. 2 which provides a better understanding of the bond interactions within the MIPs and NIP. Based on Fig. 2, only the IR spectrum of MIP (AAm) shows a weak and broad peak at 3355.60 cm<sup>-1</sup>, demonstrating the N–H stretching of the amide group from AAm (functional monomer). All IR spectra of MIP (MAA), MIP (AAm) and MIP (4VP) showed peaks at the band of 2884.42 cm<sup>-1</sup> to 2985.68 cm<sup>-1</sup>, indicating the C–H stretching of an alkyl group from CYZ (template) and EGDMA (cross-linker). The IR spectrum of CYZ proved the presence of the C-H alkyl group at around 2939.77 cm<sup>-1</sup> and 2983.14 cm<sup>-1</sup>, as shown in Fig. 3. These peaks may also indicate the C–H stretching of the alkyl group from MAA as shown in the IR



Fig. 2 The IR spectra of MIP (MAA), MIP (AAm) and MIP (2VP) of CYZ

spectrum of MIP (MAA). Besides that, a strong peak in IR spectra of MIP (MAA), MIP (AAm) and MIP (4VP) can be detected from the range of 1721.38  $cm^{-1}$ to1723.01 cm<sup>-1</sup>, which corresponded to the C=Ostretching of ester group from EGDMA (cross-linker). The peak at 1721.38 cm<sup>-1</sup> of MIP (MAA) may also correspond to the C=O stretching of the carboxylic acid group from MAA (functional monomer). The peaks of MIP (AAm) at 1671.56 cm<sup>-1</sup> and 1614.52 cm<sup>-1</sup> were attributed to the C=O stretching of the amide group from AAm (functional monomer). A medium peak of MIP (MAA) at 1636.72 cm<sup>-1</sup>, showing the C=Cstretching of the alkenyl group from MAA (functional monomer). Medium peaks present in the IR spectrum of MIP (4VP) at 1558.34 cm<sup>-1</sup> and 1597.98 cm<sup>-1</sup> was displaying the C=C bending of an aromatic group from 4VP. Moreover, MIP (MAA), MIP (AAm) and MIP (4VP) had medium peaks at 1452.00 cm<sup>-1</sup>, 1450.44  $\text{cm}^{-1}$  and 1449.50  $\text{cm}^{-1}$ , respectively. These peaks were attributed to CH<sub>2</sub> bond bending and CH<sub>3</sub> bending of CYZ (template), EGDMA (cross-linker) and either MAA or AAm or 4VP (functional monomers). The peaks present between 1140.41 cm<sup>-1</sup> and 1388.80 cm<sup>-1</sup> in IR spectra of MIP (MAA), MIP (AAm) and MIP (4VP) were showing a strong peak of C–O–C stretching and medium peak of CH<sub>3</sub> bending of EGDMA (cross-linker). In addition, the peaks present in IR spectra of MIP (MAA), MIP (AAm) and MIP (4VP) from the range of 756.76 cm<sup>-1</sup> to 757.92 cm<sup>-1</sup> showing the C–Cl stretching of CYZ (template). These peaks may also represent the C-H bending of the alkene group in EGDMA (cross-linker).

For comparison, the IR spectra of MIP (AAm) and NIP (AAm) were shown in Fig. 4. The IR spectra showed that the peaks of MIP (AAm) were similar but slightly shifted as compared to NIP (AAm). This is due to the interaction between AAm (functional monomer) with CYZ, the template molecule during the synthesis of MIP (AAm). The presence of N-H stretching of the amide group from AAm (functional monomer) was detected in the IR spectrum of NIP (AAm) with a slight band shifting at 3361.96 cm<sup>-1</sup> as compared to MIP (AAm) (3350.60 cm<sup>-1</sup>). The peaks of NIP (AAm) were at 2888.06  $\text{cm}^{-1}$  and 2984.03  $\text{cm}^{-1}$ , meanwhile, the peaks of MIP (AAm) were slightly shifted at 2887.19 cm<sup>-1</sup> and 2983.29 cm<sup>-1</sup>. These peaks were corresponding to the C-H stretching of EGDMA (cross-linker). For MIP (AAm), these peaks may also have been associated with the C-H stretching of CYZ (template), due to the addition of CYZ during the synthesis of imprinted polymer.



Fig. 3 The IR spectrum of CYZ

The presence of C=O stretching of the amide group from AAm (functional monomer) can be observed from the peaks of NIP (AAm) at 1670.17  $\,\mathrm{cm^{-1}}$  and 1619.21 cm<sup>-1</sup>. Similarly, MIP (AAm) had slight band shifting at 1614.52 cm<sup>-1</sup> and 1671.56 cm<sup>-1</sup>, showing the C=O stretching of the amide group from AAm (functional monomer). NIP (AAm) and MIP (AAm) had a medium peak at 1450.27  $\text{cm}^{-1}$  and 1450.44  $\text{cm}^{-1}$ , respectively. This showed the CH<sub>2</sub> bending and CH<sub>3</sub> bending of EGDMA (cross-linker) in both NIP (AAm) and MIP (AAm). This peak may also indicate the CH<sub>3</sub> bending of CYZ (template) in the MIP (AAm) that causes a slight band shifting than that of NIP (AAm). Another CH<sub>3</sub> bending from EGDMA (crosslinker) was detected in MIP (AAm) and NIP (AAm) at 1450.44 cm<sup>-1</sup> and 1388.73 cm<sup>-1</sup>, respectively. A strong peak at 1142.04 cm<sup>-1</sup> of NIP (AAm) was associated with the C–O–C stretching of the ester group from EGDMA (cross-linker). Similarly, a strong and slightly shifted peak at 1142.34 cm<sup>-1</sup> of MIP (AAm) was related to the C-O-C stretching of the ester group from EGDMA (cross-linker). Another medium peak was detected at 757.86 cm<sup>-1</sup> and 757.31 cm<sup>-1</sup> for MIP (AAm) and NIP (AAm), respectively. These peaks were associated with the C-H bending of the alkene group in EGDMA (cross-linker) and AAm (functional monomer). Slight band shifting at the peak of MIP (AAm) (757.86 cm<sup>-1</sup>) may also be due to the presence of the C–Cl stretching of CYZ (template).

#### **FESEM** analysis

In this study, the morphologies of MIPs and NIPs were analyzed using FESEM at a magnification of 10,000X as shown in Fig. 5 (a-f). It was observed that MIP (MAA) and MIP (4VP) were agglomerated and in irregular shape, meanwhile, MIP (AAm) and NIP (AAm) were spherical and nearly regular in shape (Fig. 5). The template-monomer interaction affects the polymer production of regular-size distribution with a dispersed polymer surface [45]. It was calculated that the average diameter size of MIP (MAA), MIP (AAm) and MIP (4VP) were 0.64 µm,  $0.86 \,\mu\text{m}$  and  $0.96 \,\mu\text{m}$ , respectively. This may be due to the usage of different functional monomers such as MAA, AAm and 4VP for the fabrication of the MIPs of CYZ. In comparison, the average diameter of NIP (MAA), NIP (AAm) and NIP (4VP) were 0.70 µm, 0.98 µm and 1.05 µm, respectively. This may be due to the absence of the CYZ template added for the synthesis of the NIPs.







(d) NIP (MAA) (e) NIP (AAm) (f) NIP (4VP) **Fig. 5** The SEM micrographs of **a** MIP (MAA), **b** MIP (AAm), **c** MIP (4VP), **d** NIP (MAA), **e** NIP (AAm) and **f** NIP (4VP) of CYZ



Fig. 6 The EDX analysis of (a) MIP (MAA), b MIP (AAm) and (c) MIP (4VP) of CYZ

#### **EDX** analysis

The energy dispersive X-ray (EDX) analysis was carried out to determine the amount of main chemical elements in the synthesized MIP (MAA), MIP (AAm) and MIP

Properties	Magnitude MIP (AAm)	Magnitude NIP (AAm)	
Surface area (m <sup>2</sup> /g)	21.019	10.870	
Average pore radius (Å)	104.900	91.824	
Total pore volume (cm <sup>3</sup> /g)	1.868	0.025	

(4VP) of CYZ. Based on Fig. 6 (a), MIP (MAA) was composed of carbon, oxygen, and chlorine of 87.89%, 12.01% and 0.10%, respectively. Similarly, MIP (AAm) was also comprised of carbon (70.51%), oxygen (29.38%), and chlorine (0.12%) as depicted in Fig. 6 (b). Lastly, there was about 76.67% of carbon, 23.26% of oxygen and 0.06% of chlorine in MIP (4VP) as shown in Fig. 6 (c). This concluded that the MIP (MAA), MIP (AAm) and MIP (4VP) were mainly composed of carbon and oxygen, indicating the backbone of the polymer structure. A small percentage presence of chlorine in the MIPs was due to the chlorine functional group in the CYZ template molecule.

#### **BET analysis**

The Brunauer-Emmett-Teller (BET) analysis was performed to distinguish the surface area, average pore radius and total pore volume of selected MIP (AAm) and NIP (AAm). The surface area, average pore radius and total pore volume of MIP (AAm) were greater than that of NIP (AAm), as shown in Table 1. This is because the addition of the CYZ template molecule in the MIP preparation generated specific binding sites that influenced the surface area, average pore radius and total pore volume of MIP (AAm). The presence of template molecules during MIP synthesis, resulting in MIP with imprinting effects [46]. Based on Table 1, the average pore radius of MIP (AAm) was 104.900 Å, indicating a porous polymer. In this research, toluene was selected as the porogen for the MIP synthesis which also contributed to the morphological characteristics of the resulting polymers. It has been reported that the concentration, volume, and structure of the porogen can affect the morphology, pore volume and surface area of the synthesized MIP and NIP [19]. Based on the BET results, the corresponding N<sub>2</sub> adsorption isotherms of both MIP (AAm) and NIP (AAm) of CYZ were classified under Type I, according to IUPAC classification [47]. This is because Type I indicates the polymers were microporous solids and the adsorption process occurred at a very low relative pressure region with the ratio between pressure and saturation pressure  $(P/P^{\circ}0.3)$ due to the interactions between the pore walls and the adsorbate were multidirectional [48]. Moreover, the hysteresis loops of MIP (AAm) and NIP (AAm) were based



on Type H1 hysteresis in which the solids have regular sizes and shapes [48].

#### **TGA** analysis

The thermogravimetric analysis (TGA) was conducted on the synthesized MIP (AAm) as shown in Fig. 7. The initial stage of MIP (AAm) weight loss started from ~ 31 °C to~48 °C, with a weight loss of about 4.45%. No significant weight loss can be found from ~48 °C to ~254 °C. This is due to the loss of moisture content or water content in the MIP (AAm). Drastic weight loss can be observed starting from ~ 334 °C to ~ 420 °C with a weight loss of 81.36%. This may be due to the decomposition of the decomposition of MIP (AAm). The final weight loss was continued until ~ 900 °C in which the remaining MIP (AAm) was less than 20%, indicating its thermal resistance. According to this analysis, different endothermic curves were observed through the DTA curve. The first endothermic curve showed the removal of moisture in the MIP (AAm). The second endothermic curve was observed in the range of>334 °C, indicating the breakage of crosslinking and thermal degradation of the synthesized MIP (AAm). This indicated the good thermal stability of the synthesized polymer due to the usage of EGDMA cross-linker which provide stability and rigidity to the MIP (AAm) structure.



Fig. 8 The comparison of batch binding studies among MIP (MAA), MIP (AAm) and MIP (2VP) of CYZ

#### **Batch binding analysis**

The experiment on batch binding was conducted to study the rebinding efficiency of the synthesized MIP (MAA), MIP (AAm) and MIP (4VP) at various contact times.

Figure 8 presented the rebinding efficiency of the synthesized MIP (MAA), MIP (AAm) and MIP (4VP). The three imprinted polymers of CYZ showed a similar trend as the rebinding efficiencies of MIP (MAA), MIP (AAm) and MIP (4VP) were increasing with the increasing contact time until 240 min, and then the rebinding efficiencies were decreasing gradually until 300 min. This indicated that at a contact time of 240 min, the rebinding of MIPs with the CYZ template had been achieved and the adsorption phase had reached its equilibrium. This study was also used to determine the most suitable combination for the MIP synthesis of CYZ with the selected functional monomer, resulting in MIP with the highest binding efficiency. Prior to this analysis, the MIPs of CYZ were prepared by precipitation polymerization using three different natures of functional monomers (acidic, neutral, and basic) namely MAA, AAm and 4VP, respectively. At 240 min, MIP (MAA), MIP (AAm) and MIP (4VP) attained their highest rebinding efficiencies of 53.87%, 83.30% and 60.14%, respectively. MIP (AAm) had the highest rebinding efficiency than that MIP (MAA) and MIP (4VP), indicating that the mixture of CYZ (template), AAm (neutral functional monomer), EGDMA (cross-linker), AIBN (initiator) and toluene (porogen) are the best combination of a pre-polymerization mixture to produce imprinted polymers with higher binding efficiency. This is because a suitable choice of functional monomer in MIP synthesis provides stronger interactions with the template molecule to generate more stable template-monomer complexes, resulting MIPs with greater imprinting effect [49–51]. It was clear that MIP (AAm) had the highest rebinding efficiency with CYZ and therefore, the batch binding study on the NIP (AAm) was also conducted for comparison purposes.

Figure 9 indicated that the rebinding efficiency of NIP (AAm) also had a similar trend but is much lower than that of MIP (AAm). The highest rebinding efficiency of NIP (AAm) was recorded at 240 min, which was only 56.17%, much lower than the rebinding efficiency of MIP (AAm). This is because the non-imprinted polymer was

synthesized without the presence of a CYZ template and therefore having non-specific binding sites. NIP had lower binding efficiency because it lacked specific recognition sites complementary to the template molecule [45]. Therefore, MIP (AAm) and NIP (AAm) were selected for further studies such as adsorption studies, selectivity tests and the application of polymers in environmental samples.

#### Effect of initial concentration

In this study, a series of initial concentrations (1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 ppm) of CYZ solution were tested to determine the optimum initial concentration of CYZ with the highest adsorption efficiency. Meanwhile, other parameters such as the polymer dosage, pH of the solution and the contact time were kept unchanged. Figure 10 showed that as the initial concentration of CYZ solution was increased (1 to 6 ppm), the adsorption efficiencies of MIP (AAm) also increased, and then a further increase in initial concentrations of CYZ solution (7 to 10 ppm) lead to decrease in the adsorption efficiency of MIP (AAm). A similar trend was detected in NIP (AAm) but with much lower adsorption efficiency. Figure 10 indicated that the highest adsorption efficiency of MIP (AAm) was obtained at an initial concentration of 6 ppm CYZ solution (86.26%), meanwhile, the lowest adsorption efficiency of MIP (AAm) was observed at an initial concentration of 1 ppm CYZ solution (25.51%). This showed that different initial concentrations of CYZ influenced the adsorption efficiency of MIP (AAm) because an adequate number of CYZ complementary binding sites were required to sufficiently bind with the available recognition sites in the MIP (AAm). As expected, the highest adsorption efficiency of NIP (AAm) (53.54%) at 6 ppm CYZ solution was much lower than that of MIP (AAm). This revealed the successful incorporation of CYZ as a



**Fig. 9** The comparison of batch binding between MIP (AAm) and NIP (AAm) of CYZ



Fig. 10 The effect of initial concentration on MIP (AAm) and NIP (AAm) of CYZ

template molecule in MIP synthesis that produces specific binding that had high affinity and selectivity towards its target molecule. Thus, the optimum initial concentration for the highest adsorption efficiency of MIP (AAm) and NIP (AAm) was at 6 ppm of CYZ solution, because at this stage all the sites on the polymers have been occupied by the template molecule and had attained a saturation [52].

#### Effect of pH

For this study, the pH of CYZ solutions was adjusted to acidic, neutral, and basic such as pH 3 and pH 5, pH 7, pH 9 and pH 11, respectively. Meanwhile, other parameters such as the CYZ concentration, polymer dosage and contact time remained unchanged. Based on Fig. 11, the adsorption efficiency of MIP (AAm) towards CYZ was increased from an acidic condition (pH 3 and pH 5) to a neutral condition (pH 7), and then, decreased at the basic condition (pH 9 and pH 11). The highest adsorption efficiency of MIP (AAm) was attained at pH 7, neutral condition (86.39%) while the lowest adsorption efficiency of MIP (AAm) was obtained at pH 11, strong basic condition (14.41%). This revealed that pH condition had an influence on the MIP adsorption efficiency as too low or too high pH condition may disrupt the characteristics of the CYZ template molecule. This may be because of certain pH conditions may alter the functionality of the template molecule, hence not fitting suitably with the binding sites of the synthesized MIP [53]. Therefore, the rebinding of the synthesized MIP (AAm) is pH dependent. As expected, the adsorption efficiencies of NIP (AAm) were much lower than the adsorption efficiencies of MIP (AAm). This is because NIP does not have an imprinting effect in its polymer matrix, resulting in the formation of non-specific binding sites [54]. Since NIP (AAm) did not

100 90 80 70 Adsorption Efficiency, % MIP (AAm) 60 NIP (AAm) 50 40 30 20 10 0 5 11 pН

Fig. 11 The effect of various pH conditions on MIP (AAm) and NIP (AAm) of CYZ

have specific binding sites, the binding affinity and specificity between the NIP (AAm) and CYZ was weak, thus resulting in lower adsorption efficiency. NIP (AAm) also showed a similar trend as the MIP (AAm), whereby its adsorption efficiency towards CYZ was increased from acidic condition (pH 3 and pH 5) to neutral condition (pH 7), and then, decreased in basic conditions (pH 9 and pH 11).

#### Effect of polymer dosage

In this study, several polymer dosages (0.1 g, 0.2 g, 0.3 g, 0.4 g 0.5 g, 0.6 g and 0.7 g) were used to determine the effects of the amount of polymer used on the adsorption efficiencies of MIP (AAm). Meanwhile, other parameters such as the CYZ concentration, pH of the solution and the contact time have remained constant. Based on Fig. 12, the highest adsorption efficiency was obtained at the MIP (AAm) dosage of 0.1 g (86.39%), then the adsorption efficiencies were decreased gradually as the MIP (AAm) dosages increased (0.2 g, 0.3 g, 0.4 g 0.5 g, 0.6 g and 0.7 g), whereby the lowest adsorption efficiency was recorded at MIP dosage of 0.7 g (69.31%). Generally, an increasing amount of polymer contributed to an increasing number of recognition sites, resulting in higher adsorption efficiency of its template compound. However, a further increase in the amount of polymer does not necessarily increase its adsorption efficiency because the active recognition sites are hidden by the polymer particles that were clumping together. Hence, a further increase in the amount of MIP (AAm) led to a decrease in its adsorption efficiency because an abundance amount of polymer caused overcrowding of binding sites and eventually deterred the binding of CYZ template molecule to the recognition sites in the MIP cavity. Further increase in polymer dosage leads to a decrease in adsorption efficiency as the excess amount



Fig. 12 The effect of polymer dosage on MIP (AAm) and NIP (AAm) of CYZ  $\,$ 

of polymer leads to agglomeration of polymer particles and hence, hinders the binding process with the target molecule [1]. A similar trend of adsorption efficiencies can be seen on NIP (AAm) but with much lower adsorption efficiencies. Therefore, the optimum polymer dosage needed to obtain the highest binding efficiency was 0.1 g of polymer in which only a small amount of MIP (AAm) is required to efficiently remove the CYZ.

#### **Kinetic studies**

Three different kinetic models such as pseudo-firstorder, pseudo-second-order and intraparticle-diffusion were applied in kinetic studies to distinguish the adsorption process of CYZ on the surface of the MIP (AAm) as shown in Figs. 13, 14 and 15, respectively. Based on Table 2, the pseudo-second-order kinetic model has the highest correlation coefficient value which was closest to 1 ( $R^2 = 0.9819$ ) as compared to the two other kinetic models of the pseudo-first-order kinetic model ( $R^2 = 0.9733$ ) and intraparticle diffusion kinetic model ( $(R^2 = 0.8450)$ ). Therefore, the pseudo-second-order kinetic model was the best-fitted kinetic model for MIP (AAm) which the kinetic reaction was more inclined towards chemisorption, indicating that the CYZ molecule and the MIP (AAm) were involved in the rate-determining step of the adsorption process. The chemisorption process also involved a strong chemical bond formation between CYZ as the solute and MIP as the adsorbent. Moreover, this pseudo-second-order kinetic model also indicated that the adsorption rate of CYZ as the solute is proportional to the available binding sites on the MIP (AAm) as the adsorbent.

#### Adsorption isotherms

Two adsorption isotherms models namely Langmuir and Freundlich isotherms were examined to evaluate



Fig. 13 The pseudo-first-order kinetic model of MIP (AAm) of CYZ



Fig. 14 The pseudo-second-order kinetic model of MIP (AAm) of CYZ

the mechanism of adsorption and extent of the CYZ absorbed on the MIP (AAm) surface as shown in Fig. 16 and Fig. 17, respectively. Based on Fig. 16 and Fig. 17, the slopes and intercepts of the plots were applied for the calculations of isotherm factors such as  $q_{max}$ ,  $K_L$ ,  $R_L$ , n, 1/n and  $R^2$  values as displayed in Table 3.

Generally, the Langmuir adsorption isotherm is defined as mono-layer adsorption of adsorbate (CYZ) by MIP while the Freundlich adsorption isotherm is defined as multi-layer adsorption of adsorbate (CYZ) by MIP. In this case, the Langmuir isotherm appeared to be the best-fitted adsorption isotherm model of CYZ by MIP (AAm) due to a higher correlation coefficient value ( $R^2$ =0.9946) as shown in Table 3. The R<sub>L</sub> value is important to determine the type of adsorption isotherm, whether the adsorption is favourable ( $0 \le R_L \le 1$ ) or irreversible ( $R_L$ =1) [48, 52, 53]. Besides that, the R<sub>L</sub> value was 0.1455, suggesting favourable adsorption of



Fig. 15 The intraparticle-diffusion kinetic model of MIP (AAm) of CYZ

Kinetic models									
Pseudo-1st-order			Pseudo-2nd-order			Intraparticle-diffusion			
q <sub>e1</sub> (mg/g)	K <sub>1</sub> (1/h)	R <sup>2</sup>	q <sub>e2</sub> (mg/g)	K <sub>2</sub> (g/mgh)	R <sup>2</sup>	C <sub>o</sub> (mg/L)	K <sub>dif</sub> (mg/h <sup>1/2</sup> g)	C	R <sup>2</sup>
1.08616E+57	- 93.775	0.9733	0.0024	77.350	0.9819	1.3395	- 0.0023	0.0144	0.8450

 Table 2
 Three types of kinetic models tested on MIP (AAm) of CYZ







Fig. 17 The Freundlich isotherm model of MIP (AAm) of CYZ

CYZ by MIP (AAm) as depicted in Table 3. Hence, it can be deduced that the adsorption of CYZ on the surface of MIP (AAm) was mono layered.

#### Selectivity of the MIP

In this study, AME was selected as the competitive compound because it has an analogous chemical structure to CYZ, and is categorised as a 1,3,5-triazine herbicide which is one of the environmental pollutants. Based on the selectivity test, the distribution ratio, K<sub>D</sub> of MIP (AAm) was much higher for CYZ than Ametryn, meanwhile, the  $K_D$  of NIP (AAm) was slightly lower for CYZ than Ametryn, resulting in a higher selectivity coefficient, Ksel for CYZ than Ametryn (Table 4). Hence, the calculated relative selectivity coefficient, k' was 2.36, indicating that the synthesized MIP (AAm) was more selective towards its own template compound (CYZ) than the competitive compound (Ametryn). This is because the value of the relative selectivity coefficient (k') is greater than 1 indicating that the synthesized MIP showed a good performance as molecular recognition [55]. The factor affecting the selectivity of MIP (AAm) towards CYZ than AME was the specific recognition sites in the MIP (AAm) that fit suitably with CYZ in terms of position and size because CYZ was used as the template molecule for the MIP synthesis, resulting in the imprinting effect on MIP (AAm). The synthesized MIP had specific binding sites corresponding with its template molecule as compared to the competitive compound that did not have specific binding sites on the synthesized MIP [10]. Besides that, the polymer selectivity is also depending on the shape of the binding sites and the particle size of the material [56].

#### Removal of CYZ from environmental samples

The synthesized MIP (AAm) of CYZ was used for the removal of CYZ from environmental samples. Good removal efficiencies of CYZ in DIW (21.64  $\mu$ g/mL), tap water (21.19  $\mu$ g/mL) and river water (21.17  $\mu$ g/mL) were attained by the synthesized MIP (AAm). Meanwhile,

Table 3 The adsorption isotherm models of MIP (AAm) of CYZ

Langmuir constants			Freundlich constants					
q <sub>max</sub> (mg/g)	K <sub>L</sub> (L/mg)	RL	R <sup>2</sup>	K <sub>F</sub> (mg/g)	n	1/n	R <sup>2</sup>	
0.2982	4.1902	0.1455	0.9946	0.3391	1.6033	0.6237	0.9839	

**Table 4** The distribution ratio, selectivity coefficients and relative selectivity coefficient of MIP (AAm) and NIP (AAm) of CYZ

K <sub>D</sub> MIP (AAm)	K <sub>D</sub> NIP (AAm)	K <sub>sel</sub>	k′
84.32	28.52	2.09	2.36
40.37	32.19	0.89	
	K <sub>D</sub> MIP (AAm) 84.32 40.37	K <sub>D</sub> MIP (AAm)         K <sub>D</sub> NIP (AAm)           84.32         28.52           40.37         32.19	K <sub>D</sub> MIP (AAm)         K <sub>D</sub> NIP (AAm)         K <sub>sel</sub> 84.32         28.52         2.09           40.37         32.19         0.89

much lower removal efficiencies of CYZ in DIW (13.43  $\mu$ g/mL), tap water (10.46  $\mu$ g/mL) and river water  $(10.00 \ \mu g/mL)$  were obtained by the NIP. This showed that the synthesized MIP (AAm) has specific binding sites complementary to CYZ as compared to the NIP (AAm) (Table 5). The addition of CYZ as a template molecule in the MIP (AAm) preparation led to the imprinting effect of CYZ that generated more specific binding sites in MIP (AAm) that were complementary to CYZ and therefore, MIP (AAm) was more selective towards CYZ than AME. Meanwhile, the preparation of NIP (AAm) did not involve the addition of CYZ, resulting in non-specific binding sites on its polymer structure and thus had much lower CYZ removal efficiencies in DIW, tap water and river water. The high affinity and specificity of MIPs were influenced by the presence of the template molecule during the molecular imprinting process [57]. Several other studies had been conducted for the removal of CYZ in environmental samples using adsorbents such as graphene [58], Fe<sub>3</sub>O<sub>4</sub> [59], granular activated charcoal [60], and magnetic adsorbent [61]. However, MIP is the best adsorbent to extract CYZ in the environment due to its better extraction efficiency and selectivity, as well as the MIP preparation method is straightforward and inexpensive. Moreover, the terbuthylazine stir bars coated with MIP had successfully extracted various triazine herbicides including CYZ from rice samples as this MIP-coated adsorbent had improved the selectivity and removal efficiency of CYZ [62].

#### Stability and reusability of MIP (AAm)

Due to their stability and reusability characteristics, MIP is denoted as versatile adsorbent material for molecular

recognition of target compounds that can be reused multiple times for MIP rebinding interactions with its target compound. MIP has the capability for rebinding with its template molecule or target compound numerous times without noticeably altering its molecular recognition efficiency. Table 6 illustrated the effect of the reusability of MIP (AAm) of CYZ on its removal efficiency for CYZ. It is apparent that a little decrease in the MIP (AAm) rebinding efficiency with CYZ from the first cycle to the sixth cycle, as mentioned in Table 6. This proved that the synthesized MIP had good stability and reusability as it can retain its high rebinding efficiency and selectivity even after multiple times of usage [61, 63]

#### Conclusion

Three functional monomers (MAA, AAm and 4VP) were applied to produce MIPs of CYZ via the precipitation polymerization method. The MIP (AAm) synthesized polymer was nearly of regular size and spherical shape, while both MIP (MAA) and MIP (4VP) were irregular in size and shape. Besides, MIP (AAm) also had the highest rebinding efficiency than that of MIP (MAA) and MIP (4VP). For comparison, NIP (AAm) was also synthesized in a similar way as the MIP but without the addition of a template and this resulted in a low rebinding efficiency because of the lack of any imprinting effect within its matrix. The ideal adsorption conditions for MIP (AAm) to attain its highest rebinding efficiency are an initial concentration of 6 ppm, CYZ template solution at pH 7 (neutral) and polymer dosage of 0.1 g polymer. The kinetic and adsorption isotherms of MIP (AAm) was best described by the pseudo-second-order kinetic isotherm model and the Langmuir adsorption isotherm model, respectively. The synthesized MIP (AAm) also has been successfully employed to remove CYZ herbicide from river water (84.69%), tap water (84.75%) and distilled water (86.57%). Thus, the synthesized MIP (AAm) could be a future promising extracting material for the removal of CYZ herbicide from the river and tap water.

Much of the previous research on the removal of CYZ herbicides by MIP were employing lengthy polymerization reactions and analyses were performed by HPLC which were time-consuming, expensive, and

Table 5 The removal of CYZ from river water, tap water and distilled water using MIP (AAm) and NIP (AAm)

Samples	Amount of CYZ added (µg/mL)	Amount of CYZ found (µg/mL)	MIP (AAm) Recovery (%)	RSD	Amount of CYZ found (μg/mL)	NIP (AAm) Recovery (%)	RSD
DIW	25	21.64	86.57	0.01	13.43	53.72	0.02
Tap Water	25	21.19	84.75	0.04	10.46	41.82	0.04
River Water	25	21.17	84.69	0.01	10.00	39.99	0.11

Table 6 The effect of reused times of MIP (AAm) for the removal of CYZ

Adsorption-desorption cycle	Removal percentage of CYZ by using MIP (AAm)
Cycle-1	86.50%
Cycle-2	86.14%
Cycle-3	85.69%
Cycle-4	85.30%
Cycle-5	85.01%
Cycle-6	84.30%

non-environmentally friendly due to the usage of large volumes of solvents. In this research, the methods used were more time-saving and inexpensive, than the reported methods because the MIP polymerization reaction only took a short period of time (6 h), and the utilization of UV-Vis spectrophotometer for binding analyses only required the usage of solvents in small amounts. This study is limited to removal of CYZ from the spiked water samples. However, the analytical characteristics showed that the methodology proposed in this research can be successfully applied to the analytical removal of CYZ herbicides in aqueous samples such as tap and river water. Therefore, the MIP (AAm) of CYZ can be applied without the need to couple it with other materials such as activated charcoal or magnetic materials to reduce the toxic waste residues produced during the analyses.

# Materials and methods

# Materials

Cyanazine (CYZ) ( $\geq$ 98% purity), ametryn (AME) ( $\geq$ 98% purity), methacrylic acid (MAA) (99% purity), ethylene glycol dimethacrylate (EGDMA) ( $\geq$ 97.5% purity) and 4-vinylpyridine (4VP) ( $\geq$ 94.5% purity) were purchased from Sidma-Aldrich. Acrylamide (AAm) ( $\geq$ 99% purity), azo-bis-isobutyronitrile (AIBN) (98% purity) and methanol (MeOH) (99.8% purity) were obtained from R & M Chemicals. Toluene (99.5% purity) was supplied by HmbG Chemicals. Acetic acid (AcOH) (95% purity) and acetone (Ace) (99.8% purity) were purchased from Bendosen Laboratory Chemical. Acetonitrile (HPLC grade) (99.9% purity) was bought from Fisher Scientific. Distilled water (DIW) was used throughout the study.

#### Synthesis of MIPs and NIP of CYZ

The polymers (MIPs and NIP) were synthesized by the precipitation polymerization method with three different functional monomers, using the procedure reported by Roland and coworkers [1, 12] with modification. In the process of polymerization, 100 mL of 1.0 mmol template solution (CYZ), 6.0 mmol of functional monomer (MAA), 12.0 mmol cross-linker (EGDMA) and 30 mg of initiator (AIBN) were poured into 250 mL conical flask. The mixture was sonicated (Brandson 2510) for 10 min and then degassed with nitrogen in an ice water bath for 15 min. After that, the conical flask was sealed tightly and immersed in a water bath (Biobase XMTD-204) at 80 °C for 6 h to complete the polymerization reaction. The synthesized polymer particles were collected by centrifugation (Gyrozen-406) at 4000 rpm for 15 min and dried at room temperature, 25 °C. A similar experimental procedure was followed for the MIP preparation using other two functional monomers as listed in Table 7. The non-imprinted polymer (NIP) was synthesized in a similar way but without the addition of the CYZ template molecule. The ratio of functional monomers was based on the number of possible hydrogen bonding within the chemical structure of CYZ, the template molecule while the ratio of cross-linker is double the ratio of functional monomers. Prior to this procedure, solubility tests were performed on each chemical constituent to ensure that each of them was soluble in the selected solvent specifically toluene (Table 7).

#### **Removal of CYZ from synthesized MIPs**

The synthesized MIPs were continuously washed with a mixture of MeOH and AcOH (6:4, v/v) until the CYZ template was not detected by a UV–Visible spectrophotometer (Agilent Cary 60) at 220 nm. Finally, the synthesized polymer particles were collected by centrifugation at 4000 rpm for 15 min and dried at room temperature, 25 °C.

Table 7	Template-monomer-crosslinker-initiator	or ratios for synthesis of MIPs and NIPs o	of CYZ

Polymer	Template	Functional Mono	omer	Crosslinker	Initiator	
	CYZ (mmol)	MAA (mmol)	AAm (mmol)	4VP (mmol)	EGDMA (mmol)	AIBN (mg)
MIP (MAA)	1	6	_	-	12	30
MIP (AAm)	1	-	6	-	12	30
NIP (AAm)	-	-	6	-	12	30
MIP (4VP)	1	_	_	6	12	30

#### **Characterization of MIPs and NIPs of CYZ**

FTIR analysis (Thermo Scientific Nicolet iS10 FTIR with Diamond ATR) was conducted on both MIPs and NIP of CYZ before wash and after wash to identify and compare the functional groups present in the IR spectral range of  $4000 \text{ cm}^{-1}$ – $500 \text{ cm}^{-1}$  [1, 10, 12].

FESEM and EDX analyses (JOEL JSM–IT500HR) were carried out to observe the morphology (size and shape) [1, 10, 12] and detect the elements present in the synthesized polymers at a magnification of 10 k [65], respectively.

BET analysis (Brunauer–Emmett–Teller Quantachrome Autosorb) was also performed on both MIP and NIP to measure the specific surface area, pore volume and average pore diameter of the synthesized polymers [1, 12].

Thermal analysis (Universal Analyzer 2000 with Universal V4.7A software) was employed at a temperature range of 30-900 °C at a heating rate of 10 °C/min to determine the stability temperature of the imprinted polymer [1, 12].

#### Batch binding of MIPs and NIP of CYZ

A batch binding study [1, 12] was carried out to determine the highest rebinding efficiency of CYZ with different MIPs and NIP. A series of 100 mL conical flasks containing 0.1 g of MIPs and NIP were added with 10 mL of 5 ppm CYZ solution. The conical flasks containing the mixture were agitated on an orbital shaker (Heathrow Scientific) at the speed of 150 rpm and the samples were collected at different time intervals (0, 5, 10, 15, 20, 25, 20, 60, 90, 120, 150, 180, 210, 240, 270 and 300 min). The concentrations of CYZ after the rebinding were observed by using a UV–Visible spectrophotometer.

The rebinding efficiencies of MIPs and NIP of CYZ were evaluated by using the following Eq. (1) [65]

Binding efficiency = 
$$[(C_i - C_f)/C_i] \times 100\%$$
 (1)

where  $C_i$  = the initial CYZ concentration in the solution before binding and  $C_f$  = the final CYZ concentration in the solution after binding.

#### Adsorption studies MIP and NIP of CYZ

In adsorption studies [1, 12], only MIP (AAm) and its NIP (AAm) were selected because they had the highest rebinding efficiency among the imprinted polymers.

#### **Effect of Initial Concentration**

A 0.1 g of MIP and NIP beads were added into a series of 100 mL conical flasks containing 10 mL of different CYZ concentrations (1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 ppm). The conical flasks containing the mixture were agitated on an orbital shaker at the speed of 150 rpm for 240 min. The

#### Effect of pH

A 0.1 g of MIP and NIP beads were added into a series of 100 mL conical flasks containing 10 mL of 6 ppm of CYZ solution at different pH (3, 5, 7, 9 and 11). The conical flasks containing the mixture were agitated on an orbital shaker at the speed of 150 rpm for 240 min. The concentrations of CYZ after the rebinding were observed by using a UV–Visible spectrophotometer. The rebinding efficiencies of MIPs and NIPs of CYZ were evaluated by using the following Eq. (1).

#### Effect of polymer dosage

Different amounts of MIP and NIP beads (0.1 g, 0.2 g, 0.3 g, 0.4 g, 0.5 g, 0.6 g and 0.7 g) were added into a series of 100 mL conical flasks containing 10 mL of 6 ppm of CYZ solution at pH 7. The conical flasks containing the mixture were agitated on an orbital shaker at the speed of 150 rpm for 240 min. The concentrations of CYZ after the rebinding were observed by using a UV–Visible spectrophotometer. The rebinding efficiencies of MIPs and NIPs of CYZ were evaluated by using the following Eq. (1).

#### **Kinetic studies of MIP of CYZ**

Three different kinetic models such as pseudo-first-order, pseudo-second-order and intraparticle-diffusion were applied in this study to investigate the rate and kinetic mechanism of MIP (AAm) adsorption. The experimental data of the batch binding study of MIP (AAm) was examined using these kinetic models. Equations (2, 3, 4) represented the linear equations of pseudo-first-order [66], pseudo-second-order [66] and intraparticle-diffusion [66], respectively. Among these kinetic models, only one kinetic model with a higher correlation coefficient ( $\mathbb{R}^2$ ) was selected as the best-fitted kinetic model which describes the adsorption of MIP (AAm).

**Pseudo** - first - order : 
$$\log (q_e - q_t) = \log (q_e) - K_1(t/2.303)$$
(2)

where,  $q_e$  = the amount of CYZ adsorbed at equilibrium time,  $q_t$  = the amount of CYZ adsorbed at any given time *t*,  $K_1$  = the pseudo-first-order equilibrium rate constant and *t* = the time interval of CYZ adsorption.

**Pseudo** - second - order : 
$$t/q_t = 1/K_2(q_e)^2 + t/q_e$$
(3)

where,  $q_e$  = the amount of CYZ adsorbed at equilibrium time,  $q_t$  = the amount of CYZ adsorbed at any given time

*t*,  $K_2$  = the pseudo-second-order equilibrium rate constant and *t* = the time interval of CYZ adsorption.

**Intraparticle – diffusion** : 
$$q_t = K_{dif}\sqrt{t} + C$$
 (4)

where,  $q_t$  = the amount of CYZ adsorbed at any given time *t*,  $K_{dif}$  = the intraparticle equilibrium rate constant, *t* = the time interval of CYZ adsorption and *C* = another kinetic constant.

#### Isotherm studies of MIP of CYZ

Two isotherm models including Langmuir and Freundlich isotherm models were employed in this study to describe the adsorption capability and surface of the MIP (AAm). The experimental data of the adsorption study (initial concentration) of MIP (AAm) was examined using both isotherm models. Equations (5, 7) represented the linear equations of Langmuir [66] and Freundlich isotherm [66] models, respectively. Between these two isotherm models, only one model with a higher correlation coefficient ( $\mathbb{R}^2$ ) was selected as the best-fitted isotherm model.

**Langmuir Isotherm** :  $C_e/q_e = (1/q_{max}K_L) + (C_e/q_{max})$ (5)

where,  $C_e$ =the CYZ concentration at equilibrium,  $q_e$ =the amount of CYZ adsorbed at equilibrium time,  $q_{max}$ =the maximum adsorption capacity of MIP (AAm) and  $K_L$ =the Langmuir constant.

Moreover, the  $R_L$  value (parameter of equilibrium) related to the fundamental characteristics of the Langmuir isotherm model was calculated by using Eq. (6) [66]:

$$R_{\rm L} = 1/(1 + K_{\rm L}C_{\rm e}) \tag{6}$$

where,  $K_L$  = the Langmuir constant and  $C_e$  = the CYZ concentration at equilibrium.

# Freundlich isotherm : $\ln(\mathbf{q}_e) = \ln(\mathbf{K}_F) + (1/n)(\ln \mathbf{C}_e)$ (7)

where,  $C_e$ =the CYZ concentration at equilibrium,  $q_e$ =the amount of CYZ adsorbed at equilibrium time,  $K_F$ =the Freundlich constant and n=constants associated with the intensity of adsorption.

#### Selectivity test of MIP of CYZ

In this selectivity study [1, 12], the two conical flasks one containing 0.1 g of MIP (AAm) and another with 0.1 g of NIP were added with 10 mL of a mixture of solution (6 ppm CYZ solution and 6 ppm AME). After that, the conical flasks were agitated on an orbital shaker at 150 rpm for 240 min. The concentrations of CYZ after the rebinding were observed by using reversed-phase high-performance liquid chromatography (RP-HPLC). The selectivity of MIP and NIP towards CYZ was expressed in terms of the distribution ratio ( $K_D$ ), using the following Eq. (8) [67].

$$K_{\rm D} = [(C_{\rm i} - C_{\rm f})/C_{\rm f}] (V/m)$$
 (8)

where  $C_i$  = the initial CYZ concentration in the solution before adsorption,  $C_f$  = the final CYZ concentration in the solution after adsorption, V = the volume of solvent used and m = the mass of MIP/NIP used.

The selectivity coefficients for CYZ, the template molecule relative to AME, the binding competitor for MIP and NIP were determined according to Eq. (9) [67]. and

Selectivity coefficient, 
$$K_{sel} = K_D^{CYZ}/K_D^{AME}$$
 (9)

where  $K_D^{CYZ}$  = the batch binding assay of MIP/NIP for CYZ and  $K_D^{AME}$  = the batch binding assay of MIP/NIP for AME.

Hence, the relative selectivity coefficient (k') was defined by Eq. (10) [67], as below.

$$k' = K_{MIP} / K_{NIP} \tag{10}$$

#### Removal of CYZ from tap water and river water

The collected tap water (Environmental Lab 1, FRST) and river water (Samarahan River) were filtered by using vacuum filtration to eliminate any suspended particles. Any presence of CYZ in the collected tap water and river water was monitored using a UV–Visible spectrophotometer.

Firstly, the filtered river water, tap water and DIW were spiked with 25  $\mu$ g/mL of CYZ, respectively. Secondly, 0.1 g of MIP (AAm) and NIP (AAm) were added to respective conical flasks containing 10 mL of spiked CYZ solution. The conical flasks containing the mixture were agitated on a shaker at 150 rpm for 240 min. Finally, the CYZ concentrations after adsorption were observed via a UV–Visible spectrophotometer. The CYZ removal efficiency in river water, tap water and DIW by using MIP (AAm) and NIP (AAm) were calculated using Eq. (1).

#### Abbreviations

сору
<i>licroscopy</i>

- EDX
   Energy Dispersive X-ray

   TGA
   Thermogravimetric analysis

   BET
   Brunauer-Emmett-Teller

   UV-Vis
   Ultra Violet-Visible spectrophotometry
- RP-HPLC Reversed-Phase High Performance Liquid Chromatography

#### Acknowledgements

The authors acknowledged the financial support from the Ministry of Higher Education Malaysia through Fundamental Research Grant Scheme (FRGS) FRGS/1/2021/STG04/UNIMAS/02/2.

#### Author contributions

RMR performed the experiments and interpretation of results, SAB supervised and designed the experiments and MNMI performed the TGA and BET and the interpretations of data. All authors read and approved the final manuscript.

#### Funding

Open Access funding provided by Universiti Malaysia Sarawak.

#### Availability of data and materials

All data generated or analysed during this study are included in this article.

#### Declarations

**Ethics approval and consent to participate** Not applicable.

#### .....

#### **Consent for publication**

Not applicable.

#### **Competing interests**

The authors declare that they have no competing interests.

#### Author details

<sup>1</sup>Faculty of Resource Science and Technology, Universiti Malaysia Sarawak (UNIMAS), 94300 Kota Samarahan, Sarawak, Malaysia. <sup>2</sup>School of Chemical Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia.

Received: 30 June 2023 Accepted: 25 August 2023 Published online: 12 September 2023

#### References

- 1. Roland RM, Bhawani SA. Synthesis of molecularly imprinted polymer for the removal of melamine. Asian J Chem. 2019;31:2770–6.
- Schirhagl R. Bioapplications for molecularly imprinted polymers. Anal Chem. 2013;86:250–61.
- Jin YF, Zhang YJ, Zhang YP, Chen J, Zhou XM, Bai LY. Synthesis and evaluation of molecularly imprinted polymer for the determination of the phthalate esters in the bottled beverages by HPLC. J Chem. 2013. https:// doi.org/10.1155/2013/903210.
- Ye L. Molecularly imprinted polymers with multi-functionality. Anal Bioanal Chem. 2016;408:1727–33.
- Nabavi SA, Vladisavljevic GT, Wicaksono A, Georgiadou S, Manovic V. Production of molecularly imprinted polymer particles with amide– decorated cavities for CO<sub>2</sub> capture using membrane emulsification/ suspension polymerisation. Colloids Surf A Physicochem Eng Asp. 2017;531:231–8.
- Sun Y, Ren T, Deng Z, Yang Y, Zhong S. Molecularly imprinted polymers fabricated using Janus particle-stabilized pickering emulsion and charged monomer polymerization. New J Chem. 2018;9:7355–63.
- Bhawani SA, Juarah NI, Bakhtiar S, Roland RM, Ibrahim MNM, Alotaibi KM, Moheman A. Synthesis of molecularly imprinted polymer nanoparticles for the removal of Sudan III. Asian J Chem. 2022;34:3269–74.
- Yu H, Shao P, Fang L, Pei J, Ding L, Pavlostathis SG, Luo X. Palladium ion-imprinted polymers with PHEMA polymer brushes—role of grafting polymerization degree in anti-interference. J Chem Eng. 2018;359:176–85.
- 9. Tian Y, Wang Y, Wu S, Sun W, Gong B. Preparation of ampicillin surface molecularly imprinted polymers for its selective recognition of ampicillin

- 10. Roland RM, Bhawani SA. Synthesis and characterization of molecular imprinting polymer microspheres of piperine: extraction of piperine from spiked urine. J Anal Methods Chem. 2016;2016:1–6.
- Lim KF, Holdsworth CI. Effect of formulation on the binding efficiency and selectivity of precipitation molecularly imprinted polymers. Molecules. 2018;23:2996–3014.
- Roland RM, Bhawani SA, Wahi R, Ibrahim MNM. Synthesis, characterization, and application of molecular imprinted polymer for extraction of melamine from spiked milk, water, and blood serum. J Liq Chromatogr Relat Technol. 2019;43:94–105.
- Bhawani SA, Bakhtiar S, Roland RM, Shafqat SR, Ibrahim MNM. Synthesis of molecularly imprinted polymers of vanillic acid and extraction of vanillic acid from spiked blood serum. J Appl Pharm Sci. 2020;10:56–62.
- Bhawani SA, Daud NAB, Bakhtiar S, Roland RM, Ibrahim MNM. Synthesis of molecularly imprinting polymers for the removal of Xylenol Orange from water. Nat Environ Pollut. 2020;19:825–30.
- Bhawani SA, Suhaili N, Roland RM, Bakhtiar S, Alotaibi KM, Ibrahim MNM. Template assisted synthesis of molecularly imprinted polymer for the extraction of p-Coumaric acid. Asian J Chem. 2020;34:2342–6.
- Lok CM, Son R. Application of molecularly imprinted polymers in food sample analysis—a perspective. Int Food Res J. 2009;16:127–40.
- Khajeh M, Heidari ZS, Sanchooli E. Synthesis, characterization and removal of lead from water samples using lead-ion imprinted polymer. J Chem Eng. 2011;166:1158–63.
- Balamurugan K, Gokulakrishnan K, Prakasam T. Preparation and evaluation of molecularly imprinted polymer liquid chromatography column for the separation of ephedrine enantiomers. Arab J Chem. 2011;9:528–36.
- 19. Reimhult K, Yoshimatsu K, Risveden K, Chen S, Ye L, Krozer A. Characterization of QCM sensor surfaces coated with molecularly imprinted nanoparticles. Biosens Bioelectron. 2008;23:1908–14.
- 20. Zaidi SA. Molecularly imprinted polymers as drug delivery vehicles. Drug Deliv. 2016;23:2262–71.
- Strikovsky A, Hradil J, Wulff G. Catalytically active, molecularly imprinted polymers in bead form. React Funct. 2003;54:49–61.
- 22. Schottler S, Eisenreich SJ, Capel P. Atrazine, alachlor, and cyanazine in a large agricultural river system. Environ Sci Technol. 1994;28:1079–89.
- Karimi-Maleh H, Karimi F, Fu L, Sanati AL, Alizadeh M, Karaman C, Orooji Y. Cyanazine herbicide monitoring as hazardous substance by DNA nanostructure biosensor. J Hazard Mater. 2022;423:127058.
- Gao S, Bie C, Ji Q, Ling H, Li C, Fu Y, Zhao L, Ye F. Preparation and characterization of cyanazine-hydroxypropyl-beta-cyclodextrin inclusion complex. RSC Adv. 2019;9:26109.
- Blahová J, Plhalová L, Hostovský M, Divišová L, Dobšíková R, Mikulíková I, Stěpánová S, Svobodová Z. Oxidative stress responses in zebrafish Danio rerio after subchronic exposure to atrazine. Food Chem Toxicol. 2013;61:82–5.
- Jin Y, Zhang X, Shu L, Chen L, Sun L, Qian H, Liu W, Fu Z. Oxidative stress response and gene expression with atrazine exposure in adult female zebrafish (Danio rerio). Chemosphere. 2010;78:846–52.
- Saka M, Tada N, Kamata Y. Chronic toxicity of 1,3,5-triazine herbicides in the postembryonic development of the western clawed frog *Silurana tropicalis*. Ecotoxicol Environ Saf. 2018;147:373–81.
- Valcin M, Henneberger PK, Kullman GJ, Umbach DM, London SJ, Alavanja MC, Sandler DP, Hoppin JA. Chronic bronchitis among nonsmoking farm women in the agricultural health study. J Occup Environ Med. 2007;49:574–83.
- Montgomery MP, Kamel F, Saldana TM, Alavanja MC, Sandler DP. Incident diabetes and pesticide exposure among licensed pesticide applicators. Agricultural health study, 1993–2003. Am J Epidemiol. 2008;167:1235–46.
- Weselak M, Arbuckle TE, Wigle DT, Walker MC, Krewski D. Pre- and postconception pesticide exposure and the risk of birth defects in an Ontario farm population. Reprod Toxicol. 2008;25:472–80.
- Dong L, Hou C, Yang M, Fa H, Wu H, Shen C, Huo D. Highly sensitive colorimetric and fluorescent sensor for cyanazine based on the inner filter effect of gold nanoparticles. J Nanopart Res. 2016;18:1–2.
- Lerch RN, Baffaut C, Sadler EJ, Kremer RJ. Long- term agroecosystem research in the central Mississippi River basin: goodwater creek experimental watershed and regional herbicide water quality data. J Environ Qual. 2015;44:28–36.

- Zhou Q, Ding Y, Xiao J. Simultaneous determination of cyanazine, chlortoluron and chlorbenzuron in environmental water samples with SPE multiwalled carbon nanotubes and LC. Chromatographia. 2007;65:25–30.
- Barbash JE, Thelin GP, Kolpin DW, Gilliom RJ. Major herbicides in ground water: results from the national water-quality assessment. J Envrion Qual. 2001;30:831–45.
- Ferrer I, Thurman EM, Barceló D. First LC/Ms determination of cyanazine amide, cyanazine acid and cyanazine in groundwater samples. Environ Sci Technol. 2000;34:714–8.
- Bruun L, Koch C, Jakobsen MH, Aamand J. A new monoclonal antibody for the sensitive detection of cyanazine and other s-triazine in water ELISA. Food Agric Immunol. 2000;12:252–62.
- Senseman SA, Lavy TL, Daniel TC. Monitoring groundwater for pesticides at selected mixing / loading sites in Arkansas. Environ Sci Technol. 1997;31:283–8.
- Abass K, Pelonen O, Rautio A. Chloro-s-triazines-toxicokinetic, toxicodynamic, human exposure and regulatory considerations. Curr Drug Metab. 2021;22:645–56.
- Chidya R, Derbalah A, Abdel-Dayem S, Kaonga C, Sakugawa H. Ecotoxicological and human health risk assessment of selected pesticides in Kurose River, Higashi-Hiroshima city (Japan). Water Environ Res. 2021;94:1676.
- Breton F, Fuzet P, Piletsky SA, Giardi MT, Rouillon R. Integration of photosynthesis biosensor with molecularly imprinted polymer-based solid phase extraction cartridge. Anal Chim Acta. 2006;569:50–7.
- 41. Djozan D, Ebrahimi B, Mahkam M, Farajzadeh MA. Evaluation of a new method for chemical coating of aluminium wire with molecularly imprinted polymer layer. Application for the fabrication of triazines selective solid-phase microextraction fiber. Anal Chim Acta. 2010;674:40–8.
- 42. Yan H, Row KH. Characteristics and synthetic approach of molecularly imprinted polymer. Int J Mol Sci. 2006;7:156–78.
- Vasapollo G, Sole RD, Mergola L, Lazzoi MR, Scardino A, Scorrano S, Mele G. Molecularly imprinted polymers: present and future prospective. Int J Mol Sci. 2011;12:5908–45.
- 44. Li G, Row KH. Recent applications of molecularly imprinted polymers (MIPs) on microextraction techniques. Sep Purif Rev. 2017;47:1–18.
- Arabzadeh N, Abdouss M. Synthesis and characterization of molecularly imprinted polymers for selective solid-phase extraction of *Pseudoepherine*. Colloid J. 2010;72:446–55.
- Sanagi MM, Salleh S, Ibrahim WAW, Naim AA. Molecularly imprinted polymers for solid phase extraction of orghanophosphorus pesticides. J Fundam Sci. 2010;6:27–30.
- Sing KSW, Everett DH, Haul RAW, Moscou L, Pierotti RA, Rouquerol J, Siemienewska T. Reporting physisorption data for gas-solid systems. Pure Appl Chem. 1985;57:603–19.
- Chang S, Clair B, Ruelle J, Beauchêne J, Renzo FD, Quignard F, Zhao G, Yamamoto H, Gril J. Mesoporosity as a new parameter for understanding tension stress generation in trees. J Exp Bot. 2009. https://doi.org/10. 1093/jxb/erp133.
- Zhong M, Wang YH, Wang L, Long RQ, Chen CL. Preparation and application of magnetic molecularly imprinted polymers for the isolation of chelerythrine from Macleaya cordata. J of Sep Sci. 2018;41:3318–27.
- Sánchez-González J, Peña-Gallego Á, Sanmartín J, Bermejo-Barrera P, Moreda-Piñeiro A. NMR spectroscopy for assessing cocainefunctional monomer interactions when preparing molecularly imprinted polymers. Microchem J. 2019;147:813–7.
- Wu H, Tian Q, Zheng W, Jiang Y, Xu J, Li X, Zhang W, Qiu F. Non-enzymatic glucose sensor based on molecularly imprinted polymer: A theoretical, strategy fabrication and application. J Solid State Electrochem. 2019;23:1379–88.
- Madikizela LM, Zunngu SS, Mlunguza NY, Tavengwa NT, Mdluli PS, Chimuka L. Application of molecularly imprinted polymer designed for the selective extraction of ketoprofen from wastewater. Water SA. 2018;44:406–18.
- Yusof NA, Rahman SKA, Hussien MZ, Ibrahim NA. Preparation and characterization of molecularly imprinted polymer as SPE Sorbent for melamine isolation. Polymers. 2013;5:1215–28.
- Zhang L, Zhang H, Li L, Zuo P, Zhao F, Liu M, Ye BC, Li Y. Pneumocandin B0-imprinted polymer using surface-imprinting technique for efficient purification of crude product. Ana Sci. 2016;32:923–30.

- Yang HH, Zhou WH, Guo XC, Chen HQ, Zhao HQ. Molecularly imprinted polymer as SPE sorbent for selective extraction of melamine in dairy products. Talanta. 2009;80:821–5.
- Zeng H, Wang Y, Liu X, Kong J, Nie C. Preparation of molecular imprinted polymers using bi-functional monomer and bi-crosslinker for solid-phase extraction of rutin. Talanta. 2012;93:172–81.
- Samarth NB, Kamble V, Mahanwar PA, Rane AV, Abitha VK. A historical perspective and the development of molecular imprinting polymer-A review. Chem Int. 2015;1:202–10.
- Wu XL, Meng L, Wu Y, Luk YY, Ma Y, Du Y. Evaluation of graphene for dispersive solid-phase extraction of triazine and neonicotine pesticides from environmental water. J Bras Chem Soc. 2015;26:131–9.
- Safari M, Yamini Y, Tahmasebi E, Ebrahimpour B. Magnetic nanoparticles assisted supramolecular solvent extraction of triazine herbicides prior to their determination by HPLC with UV detection. Micro Chim Acta. 2016;183:203–10.
- Ilavaský J, Barloková D, Marton M. Triazine herbicides removal from water with granular activated carbon. IOP Conf Ser Earth Environ Sci. 2020;609:012088.
- Liu Z, Wang J, Yang X, Wu Q, Wang Z, Yan H. Green construction of hydroxyl-functionalized magnetic porous organic framework for effective extraction of triazine herbicides from environmental water and watermelon juice samples. Anal Chim Acta. 2023;1260:341222.
- Zhong Q, Hu Y, Hu Y, Li G. Online desorption of molecularly imprinted stir bar sorptive extraction coupled to high performance liquid chromatography for the trace analysis of triazines in rice. J Sep Sci. 2012;35:3396–402.
- Zhang Z, Li L. Efficient synthesis of molecularly imprinted polymers with bio-recognition sites for the selective separation of bovine hemoglobin. J Sep Sci. 2018;41(11):2479–87.
- 64. Bhawani SA, Bakhtiar S, Shafqat SR. Synthesis of molecularly imprinted polymers for the selective extraction/removal of 2,4,6-trichlorophenol. The Open Eng J. 2019;13:122–33.
- Yusof NA, Beyan A, Ibrahim NA. Synthesis characterization of a molecularly imprinted polymer for Pb2+ uptake using 2-vinylpyridine as the complexing monomer. Sains Malaysiana. 2010;39(5):829–35.
- Alamrani NA, AL-Aoh HA. Elimination of congo red dye from industrial wastewater using *Teucrium polium L*. as low-cost local adsorbent. Adsorpt Sci Technol. 2021;2021:5728696.
- 67. Arabzadeh N, Abdouss M. Synthesis and characterization of molecularly imprinted polymers for selective solid-phase extraction of Pseudoepherine. Colloid J. 2010;72(4):446–55.

## **Publisher's Note**

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

# Submit your manuscript to a SpringerOpen<sup>®</sup> journal and benefit from:

- Convenient online submission
- ► Rigorous peer review
- Open access: articles freely available online
- ► High visibility within the field
- Retaining the copyright to your article

#### Submit your next manuscript at > springeropen.com