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LETÍCIA FREDDO

MODELAGEM DO EQUILÍBRIO DE ADSORÇÃO BICOMPONENTES: APLICAÇÃO PARA ATRAZINA E SIMAZINA EM CARVÃO ATIVADO

CERRO LARGO

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Dissertação de Mestrado, apresentado ao Programa de Pós-Graduação em Ambiente e Tecnologias Sustentáveis da Universidade Federal da Fronteira Sul, como requisito parcial para obtenção do título de Mestre em Ambiente e Tecnologias Sustentáveis.
Linha de pesquisa: Desenvolvimento de Processos e Tecnologias.

Orientador: Prof. Dr. Bruno München Wenzel
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RESUMO

Este estudo desenvolve modelos matemáticos para explicar o equilíbrio de adsorção de atrazina e simazina por carvão ativado em condições experimentais mono e bicomponentes. Para os experimentos, diferentes concentrações foram testadas em quatro temperaturas diferentes (20, 25, 35 e 45 °C). Os testes foram desenvolvidos utilizando as seguintes condições fixas: 0,038 g de carvão ativado, tempo de adsorção de 12 horas e volume de solução de 200 mL. Os reatores foram levados ao banho termostático Dubnoff Bath SL-157 e os resultados das concentrações de atrazina, simazina foram monitorados usando o cromatógrafo líquido LC-ESI-MS (LC 2020, Shimadzu®). Um modelo geral que pudesse explicar o equilíbrio de adsorção multicomponente dos compostos foi desenvolvido, e a partir deste, várias hipóteses de modelos matemáticos foram pensados e testados para explicar o equilíbrio do processo. O modelo monocamada de dois sítios mostrou-se como o melhor modelo isotérmico para descrever o equilíbrio do sistema. Os resultados indicaram uma capacidade máxima de adsorção para 35°C (44,53 mg g $^{-1}$). Parâmetros termodinâmicos e constantes de equilíbrio mostraram que o processo é favorável e espontâneo para atrazina no sítio ativo S1 e para simazina no sítio ativo S2, revelando que, mesmo havendo competição pelos sítios, os dois compostos podem ser adsorvidos de modo eficiente na mesma solução aquosa. Os resultados termodinâmicos sugerem dois tipos de mecanismos de adsorção na superfície: físicos e químicos. Assim, o estudo traz um modelo matemático alternativo para explicar a adsorção bicomponente para atrazina e simazina e contribui para um melhor conhecimento do processo de adsorção multicomponente e equilíbrio do sistema que pode ser testado e aplicado a outros tipos de poluentes.

Palavras-chave: Equilíbrio de adsorção; carvão ativado; atrazina; simazina; adsorção multicomponente

ABSTRACT

This study develops mathematical models to explain the adsorption equilibrium of atrazine and simazine by activated carbon under single and bicomponent experimental conditions. For the experiments, different concentrations were tested at four different temperatures (20, 25, 35 and 45 °C).The tests were developed using the following fixed conditions: 0.038 g of activated carbon, adsorption time of 12 hours and solution volume of 200 mL. The reactors were placed in the Dubnoff Bath SL-157 thermostatic bath and the results of atrazine, simazine concentrations were monitored using the LC-ESI-MS liquid chromatograph (LC 2020, Shimadzu®).A general model that could explain the multicomponent adsorption equilibrium of the compounds was developed, and from this, several hypotheses of mathematical models were thought and tested to explain the equilibrium of the process. The two-site monolayer model proved to be the best isothermal model to describe the equilibrium of the system. The results indicated a maximum adsorption capacity at 35°C (44.53 mg g -1).Thermodynamic parameters and equilibrium constants showed that the process is favorable and spontaneous for atrazine in the S1 active site and for simazine in the S2 active site, revealing that, even with competition for the sites, the two compounds can be efficiently adsorbed in the same aqueous solution. The thermodynamic results suggested two types of surface adsorption mechanisms: physical and chemical. Thus, the study brings an alternative mathematical model to explain the bicomponent adsorption for atrazine and simazine and contributes to a better understanding of the multicomponent adsorption process and system equilibrium that can be tested and applied to other types of pollutants.

Keywords: bicomponent adsorption, atrazine, simazine, two-site equilibrium model

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LISTA DE SIGLAS E ABREVIATURAS

CA = Carvão ativado

ATZ = Atrazina

EDCs = Compostos desreguladores endócrinos

US EPA = Agência de Proteção Ambiental

q_e = Quantidade adsorvida no equilíbrio

C_o = Concentração inicial de adsorvato

C_e = Concentração de adsorvato após equilíbrio

V = Volume de líquido

SMZ = Simazina

LISTA DE SIGLAS E ABREVIATURAS (ARTIGO EM INGLÊS)

AC = activated carbon

S1 = active site 1

S2 = active site 2

$k_{j,i}$= equilibrium constant

n= adsorption order

$C_{i,e}$= concentration

i= compound

j= active surface site

$q_{i,e}$= amount of compound adsorbed in equilibrium

G = gibbs free energy

T = temperature

ΔG = gibbs free energy change

μ_k= chemical potential of generic K specie

v_k= stoichiometric coefficient

$\mu°_k$= standard state chemical potential

a_k= activity of specie K

$\gamma_{i,j}$ = activity coefficient

$C°$ = standard state concentration

MM_i = molar mass

H = enthalpy

ΔH = enthalpy change

S = entropy

ΔS = entropy change

C_o = initial concentration

C = equilibrium concentration

V = volume

m = mass of adsorbent

f_{obj}= objective function

R^2 = determination coefficient

AICc = akaike information criteria

n_p = number of parameters

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1. INTRODUÇÃO

O processo de adsorção vem se destacando nas pesquisas de tratamento de efluentes, especialmente pela remoção de poluentes que se encontram em baixas concentrações. Considerando a presença de poluentes em águas superficiais e subterrâneas, existe a probabilidade de encontrar diferentes poluentes em uma mesma amostra aquosa. Este é o caso dos agrotóxicos utilizados para complementar a produtividade de atividades agrícolas. No Brasil, este setor caracteriza a principal atividade econômica do país, fazendo com que o mesmo seja o maior consumidor de agrotóxicos desde 2009 (IBGE, 2019). Apesar do uso desses produtos aumentarem a produtividade agrícola, podem vir a causar algumas consequências negativas, como impactos na saúde humana (VANDENBERG; NAJMI; MOGUS, 2020) e também no meio (DUTRA; FERREIRA, 2017).

Entre os herbicidas que são utilizados no Brasil, estão atrazina e simazina, cuja ocorrência vem sendo identificada (tanto simultaneamente quanto de forma individual) em amostras de águas subterrâneas e superficiais em estudos realizados na região noroeste do Rio Grande do Sul (RS), Brasil (HOFFMANN, 2019; FRANK, 2019; KERKHOFF, 2020; CAYE, 2019).

Alguns adsorventes podem ser utilizados para remover agrotóxicos pela tecnologia de adsorção, e dentre eles, se encontra o carvão ativado (CA), que pode ser obtido através da manipulação de materiais naturais, e tem a capacidade de remover atrazina e simazina (VIEIRA *et* al., 2021; WEI et al., 2018). Entretanto, foi observado que há na literatura uma escassez de estudos que tratem da remoção simultânea dos dois compostos em questão (atrazina e simazina), e a aplicação de modelos de equilíbrio podem fornecer diversas informações e ajudar a descrever o processo, explicitando a necessidade de mais estudos nessa linha. Outro aspecto importante que tem recebido menor atenção são os estudos de adsorção relativos à integração de conceitos termodinâmicos (efeito da temperatura) no ajuste de modelos de equilíbrio de adsorção, o que é desejável para permitir um número adequado de graus de liberdade ao aplicar modelos com maior número de parâmetros.

De acordo com Koopal *et* al. (2020), normalmente a abordagem do equilíbrio de adsroção multicomponente é baseada em suposições de que existe competição pelo mesmo sítio ativo. A sorção de um componente principal é frequentemente estudada em soluções com concentrações constantes dos outros componentes, transformando-o em um problema de pseudo-monocomponentes e aplicando equações de isotérmicas de monocomponentes.A aplicação para sítios heterogêneos normalmente está associada ao uso de funções de distribuição das afinidades (KOOPAL *et* al., 2020; GARCÉS; MAS, 2004) que podem trazer uma complexidade matemática adicional para resolver modelos de isotermas. Nesse contexto, o propósito deste estudo é avaliar o equilíbrio de adsorção para atrazina e simazina em meios aquosos por carvão ativado e desenvolver modelos de equilíbrio que sejam capazes de descrever o sistema. Os modelos desenvolvidos foram ajustados em uma etapa, usando princípios termodinâmicos, a um conjunto de resultados experimentais obtidos em diferentes situações (individualmente e mistura) e diferentes condições de temperatura (20, 25, 35 e 45ºC). A partir da seleção do melhor modelo, discutiu-se o desempenho e o significado físico dos parâmetros.

1.1.OBJETIVOS

1.1.1. Objetivo geral

Avaliar modelos de equilíbrio da adsorção de atrazina e simazina, tanto individualmente como em conjunto, utilizando carvão ativado comercial.

1.1.2. Objetivos específicos

- Desenvolver e ajustar modelos de equilíbrio para adsorção de atrazina e simazina;
- Determinar se há ou não competição por sítios ativos do adsorvente;
- Avaliar a influência da temperatura no processo;
- Obter as isotermas de adsorção mono e multicomponentes.

1.1.3. Estrutura do trabalho

O presente trabalho foi estruturado em 3 capítulos. O primeiro é destinado para a introdução, apresentando uma contextualização do tema, bem como a problemática envolvida e possíveis soluções a serem propostas. No segundo capítulo se encontra uma revisão bibliográfica do tema em questão, bem como informações relevantes sobre os agrotóxicos estudados e o processo de remoção aqui proposto. O terceiro capítulo é dedicado para o artigo “Modeling of bicomponent adsorption equilibrium: application to system atrazine-simazine in bioadsorbent” que foi produzido sobre o trabalho desenvolvido e que será submetido a publicação, no qual consta a apresentação da metodologia, dados experimentais e discussão dos resultados.

2. REVISÃO BIBLIOGRÁFICA

2.1.ATRAZINA

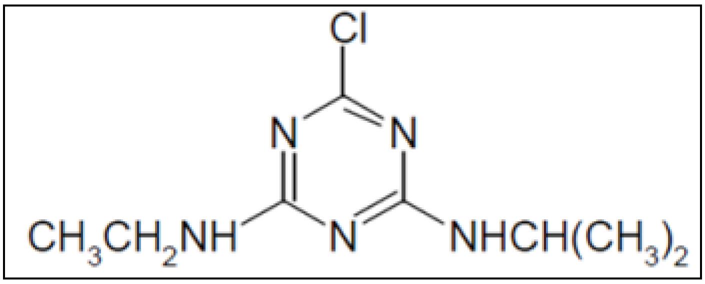
A atrazina (1-Chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine) é um dos principais herbicidas utilizados no controle de plantas daninhas de folhas largas, especialmente em culturas de milho, cana-de-açúcar e sorgo, que apresentam elevada relevância no cenário econômico brasileiro. Pertencente ao grupo das triazinas, este herbicida é especialmente empregado na cultura do milho, aplicado na pré e/ou pós-emergência (HANG *et al.*, 2007). A estrutura química desse composto pode ser vista na Figura 1.

A atrazina (ATZ) é um composto hidrofóbico com classe de toxicidade III (ligeiramente tóxica) e periculosidade ambiental classe II (perigosa). Estima-se que a dosagem desse herbicida normalmente encontra-se entre 3 a 5 L por hectare plantada (MORAES, 2019; ABNT NBR, 2019).

A atrazina é conhecida por possuir potencial de efeito cancerígeno e desregulador endócrino que em muitos organismos, causa alteração no equilíbrio hormonal e, portanto, interfere no crescimento, desenvolvimento e reprodução em humanos (VANDENBERG; NAJMI; MOGUS, 2020). O herbicida também pode produzir uma inibição reversível da fotossíntese, pois os substituintes no anel de triazina prejudicam o metabolismo microbiano, o que faz com que a degradação abiótica e biótica ocorram lentamente, e, portanto, se degradando mais lentamente no ambiente em comparação com a maioria dos herbicidas comerciais existentes (HANG *et al.*, 2007).

Em relação as propriedades físico-químicas, a solubilidade em água é um fator a se destacar, tendo em vista que herbicidas que apresentam baixa solubilidade tendem a sorver mais e dessorver menos à fração sólida do solo. Desta maneira há menor mobilidade, menor lixiviação e menor degradação, implicando em maior persistência e bioacumulação. Já herbicidas com alta solubilidade em água tendem a sorver menos e dessorver mais, apresentando, portanto, maior mobilidade e potencial de lixiviação, com maior degradação e menor persistência e bioacumulação (VIEIRA *et al.*, 2021). Neste contexto, a adsorção destaca-se devido a sua facilidade de implementação como tecnologia de remoção de atrazina do meio aquoso além da possibilidade de utilização de biocarvão oriundo de biomassa vegetal.

Figura 1- Estrutura química da atrazina.



Fonte: Lebaron*et al*., 2008.

2.2.SIMAZINA

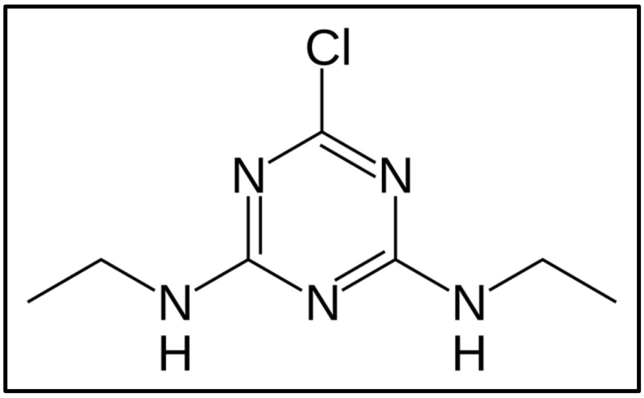
A simazina (SMZ), com um nome químico de 2-cloro-4,6-bis(etilamino) triazina, é o segundo herbicida de clorotriazina mais comumente usado para realizar o controle de ervas daninhas de folhas largas e gramíneas anuais em campos de cultivo, especialmente em milho, cana-de-açúcar e pomares em geral (SAI*et al*., 2015). Sua estrutura química pode ser observada na Figura 2.

É um composto que tem causado grande preocupação devido à sua persistência moderada, difícilbiodegradação e alta toxicidade ecológica. Estudos anteriores revelaram que a simazina pode ser considerada perigosa para o meio ambiente, podendo gerar a mutagenicidade, toxicidade no desenvolvimento reprodutivo e toxicidade imunológica em animais, especialmente anfíbios, peixes e macrófitas (STARA *et al*., 2012).Além disso, a SMZ demonstrou ser tóxica em sistemas neuroendócrinos e influenciar o metabolismo da dopamina, o que leva a distúrbios neurológicos do sistema dopaminérgico em seres vivos. (LI *et al*., 2017).

Por causa dos efeitos neuroendócrinos em uma variedade de espécies a SMZ foi inclusa nas listas prioritárias de compostos desreguladores endócrinos (EDCs) pela Agência de Proteção Ambiental dos EUA (US EPA), o União Européia e Japão.

Nesse contexto se faz necessário o estudo de uma alternativa de remoção de SMZ em águas. E para isso, é importante pensar em uma tecnologia que consiga remover mais de um composto ao mesmo tempo, visto que SMZ e ATZ podem ser encontradas simultaneamente no meio ambiente. Então, a adsorção se encontra dentre as tecnologias que vem sendo estudadas para remoção de simazina em corpos d’água (SANNINO*et al*., 2013).

Figura 2 - Estrutura química da simazina

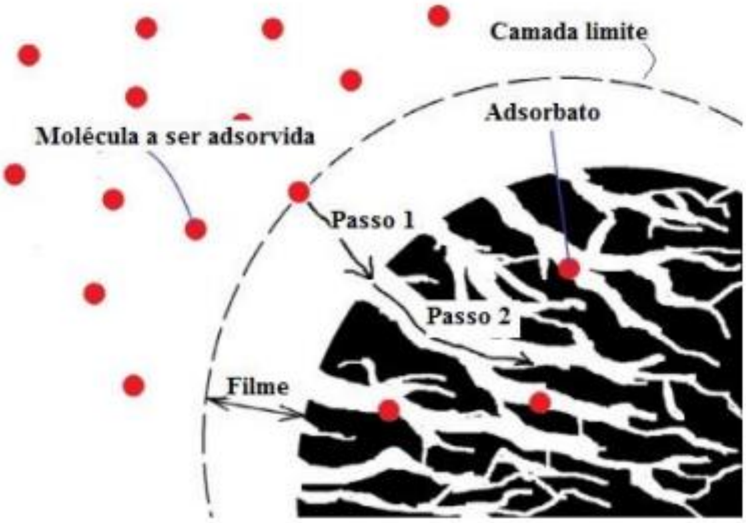


2.3.ADSORÇÃO

Adsorção é um fenômeno de superfície no qual a espécie que se acumula na interface do material é normalmente denominada de adsorbato, e a superfície sólida no qual o adsorbato se acumula é chamado de adsorvente. Efetivamente, a operação de adsorção pode ser realizada em modo contínuo ou descontínuo utilizando adsorventes porosos. Ainda, definida por METCALF; EDDY (2003) a adsorção consiste num fenômeno físico-químico onde uma substância que está em uma solução aquosa (adsorbato) é transferida para uma interface sólida (adsorvente). Ocorre no processo, a transferência de massa do adsorbato que esta solução para a superfície do adsorvente.

Na Figura 3, pode ser observada a ilustração do processo de adsorção. O passo 1 é quando a molécula a ser adsorvida passa da camada limite da superfície do material adsorvente e o passo 2, quando a molécula entra em contato com o material adsorvente e se aloca em seus poros.

Figura 3 - Processo de adsorção



Fonte: TAN; HAMEED, 2017.

Devido a adsorção ser resultado de uma combinação entre os tipos de forças químicas e físicas, são vários os fatores que podem influenciar neste processo, como área superficial, temperatura do sistema, pH do meio, natureza do solvente, propriedades do adsorvente e adsorbato(NASCIMENTO *et al*., 2014).

A quantidade a ser adsorvida em um sistema batelada, pode ser obtida a partir da Equação 1 (METCALF; EDDY, 2003):

$$qe = \frac{(C_o - C_e)V}{m} \qquad (1)$$

Onde:

qe = quantidade adsorvida no equilíbrio (mg g $^{-1}$);

CO = concentração inicial de adsorbato (mg L $^{-1}$);

Ce = concentração de adsorbato após equilíbrio (mg L $^{-1}$);

V = volume de líquido (L);

m = massa de adsorvente (g).

2.3.1. Adsorvente

Conhecendo-se o contaminante que se quer remover, é possível desenvolver adsorventes para diferentes aplicações. Desde os primeiros estudos realizados para remoção tanto de íons metálicos como agrotóxicos, o carvão ativado (CA) foi sem dúvida o mais popular e amplamente utilizado como adsorvente para aplicações em tratamento de água em todo o mundo (CANSADO; BELO; MOURÃO, 2018; WIŚNIEWSKA *et al*., 2017; ZHOU *et al.*, 2018). Essa abordagem possibilita um tratamento com baixo custo com aquisição do material adsorvente, grande disponibilidade do mesmo, além de resolver problemas relacionados ao descarte desses biomateriais.

A utilização de adsorventes de materiais naturais, disponíveis em grandes quantidades no meio ambiente, resíduos industriais, agrícolas e florestais tem sido estudada, e possuem alta capacidade de remoção de agrotóxicos. De acordo com Nabais *et al.* (2011), o uso de tais materiais corresponde à produção de mais de 300 mil toneladas por ano de carvão ativado sendo a madeira e a casca de coco os materiais mais relevantes.

Em trabalhos anteriores, alguns tipos de CA foram usados para remover a ATZe SMZpelo processo de adsorção (WANG *et al*., 2016; LLADÓ *et al*., 2015).

A diferença na natureza dos adsorventes, como conteúdo elementar, porosidade e grupos funcionais, pode influenciar seu desempenho de adsorção em relação aos poluentes. Um único adsorvente com mais de um adsorbato pode ter diferentes mecanismos de adsorção devido às suas características variáveis. Considerando-se que os ambientes aquáticos reais podem ser contaminados por atrazina e simazina, fazem-se necessários os estudos de adsorçãobicomponentes para remoção simultânea de ATZ e SMZ.

Para esta presente pesquisa, foi utilizado um carvão ativado comercialmente disponível para realização dos experimentos.

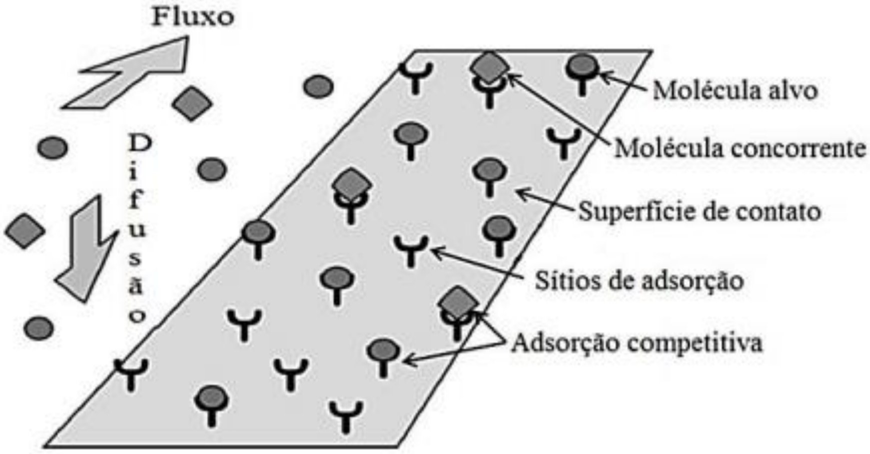
2.4.ADSORÇÃO COMPETITIVA DE MULTICOMPONENTES

O estudo da adsorção competitiva de compostos multicomponentes tornou-se fundamental, uma vez que a eliminação de impurezas da água ocorre por meio do mecanismo de adsorção competitiva, visto que a água no meio ambiente possui as mais diversas moléculas integradas ao sistema (GUN’KO, 2007).

Ainda de acordo com Gun’ko (2007), a adsorção competitiva conduz a uma taxa reduzida de energia para alcançar o equilíbrio e o tempo para que ocorra a adsorção é menor quando considerado a presença de multicomponentes.

A adsorção multicomponente provoca a redução da energia livre do sistema e neste caso, a contribuição da entropia é sempre desestabilizadora. Considera-se ainda, que os fatores de entalpia e entropia de adsorção dependem do tamanho molecular do adsorbato, das características da superfície e forma do adsorvente, da estrutura química das moléculas e da constituição de complexos de adsorção (ZHOU *et al.*, 2018). Na Figura 4 pode ser observada uma ilustração de como funciona a adsorção competitiva e como que a molécula alvo e a molécula concorrente competem pelos sítios ativos de adsorção.

Figura 4 - Adsorção competitiva



Fonte: Frantlovic*et al.*, 2013.

2.5.ISOTERMAS DE ADSORÇÃO

2.5.1. Isoterma de Langmuir

A isoterma de adsorção de Langmuir baseia-se na suposição de que o processo de adsorção ocorre na monocamada do adsorvente, corresponde a uma monocamada saturada de moléculas do adsorvato sem interações entre si, ou seja, apenas um sítio ativo adsorvente que permite a adsorção de uma molécula do soluto. Ainda, neste modelo, a energia de adsorção é considerada constante e é explicada em casos de adsorção em monocamada em superfícies perfeitamente lisas e homogêneas (LANGMUIR, 1918). O modelo é descrito pela Equação 2:

$$Q_e = \frac{Q_m K_L C_e}{1+ Q_m C_e} (2)$$

2.5.2. Isoterma de Freundlich

A adsorção heterogênea é expressa através do modelo isotérmico empírico de Freundlich. Este modelo é utilizado principalmente para superfícies de adsorção com distribuição de energia não uniforme, em sólidos heterogêneos, onde ocorre adsorção em multicamadas com interação entre as moléculas de adsorvato. Ainda, destaca-se que a equação de Freundlich não é capaz de prever dados de equilíbrio quando são utilizadas faixas de concentrações muito elevadas (MAURER, 2019; DO NASCIMENTO *et al.*, 2014). Essa isoterma considera para base de cálculo a superfície heterogênea e o calor de adsorção. Na Equação 3 é apresentado o modelo proposto pela isoterma de Freundlich:

$$Q_e = K_F \; {C_e}^{1/n} \quad (3)$$

2.5.3. Isoterma de BET

A forma da equação BET para adsorção em fase líquida, apresentada por Wang *et al.*, 1998, é dado pela Equação 4, onde C é a concentração da espécie adsorvente, *q1* é o calor de adsorção da primeira camada, *qL* é o calor de liquefação do gás adsorvente. Conforme apresentado na Equação 4, a quantidade *q* adsorvida na equação BET é dada pelo produto de dois termos. A equação BET usa três parâmetros de ajuste (*qm, b1* e *b2*) para correlacionar a relação entre *q* e *c*.

$$C = e^{\frac{q_1 - q_L}{R_L}} \quad (4)$$

2.6.ISOTERMAS DE ADSORÇÃO APLICÁVEIS A MULTICOMPONENTES

As isotermas podem descrever o equilíbrio da adsorção de compostos puros (monocomponentes) ou combinados (multicomponentes) e este conhecimento do melhor ajuste em relação aos modelos teóricos ou empíricos propiciam a compreensão do processo de adsorção. A adsorção multicomponente é considerada mais complexa do que a adsorção de compostos puros, devido principalmente aos fatores de heterogeneidade da mistura, características específicas da superfície do adsorvente, existência de adsorção competitiva e complicações advindas de interações laterais (ZHOU *et al*., 2018).

As isotermas aplicáveis a multicomponentes consideram que a disponibilidade da superfície do adsorvente para acomodar um determinado adsorvato é limitada pelos demais, pois o número total de moléculas que podem ser acomodadas na superfície é finito. Desta forma, com o aumento da concentração, as moléculas tendem a competir pelo acesso aos sítios de adsorção e aqueles componentes mais fortemente adsorvidos tendem a excluir os demais (GUIOCHON *et al.,* 2006). Desta forma, para o conhecimento mais detalhado do desempenho de uma tecnologia fundamentada em mecanismos de adsorção, deve-se considerar o equilíbrio de adsorção multicomponente (ZHOU *et al*., 2018).

A maioria das isotermas de adsorção multicomponentes aplicáveis para a compreensão do processo adsortivo derivam ou da forma original ou de complementações do modelo proposto por Langmuir (1918).

Assim como a isoterma de Langmuir aplicada a multicomponetes, a isoterma de Freundlich para multicomponentes pode ser determinada com base no pressuposto de que a distribuição exponencial de energias de adsorção existe para cada componente. Consequentemente os coeficientes e expoentes determinados experimentalmente para as isotermas monocomponentes são parâmetros da isoterma multicomponente (SHEINDORF, REBHUN e SHEINTUCH, 1981).

Nota: Os resultados deste estudo estão apresentados na forma de um artigo científico na seção 3.

3. MODELING OF BICOMPONENT ADSORPTION EQUILIBRIUM: APPLICATION TO SYSTEM ATRAZINE-SIMAZINE IN BIOADSORBENT

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Highlights

- Several equilibrium models were tested to describe the atrazine and simazine adsorption process;
- Isotherm models considering bicomponent and monocomponent adsorption were developed;
- The competitive two-site monolayer model describes the multicomponent adsorption;
- The two compounds can be adsorbed simultaneously showing satisfactory adsorption capacities

Abstract

This study develops mathematical models to explain the adsorption equilibrium of atrazine and simazine by activated carbon under single and bicomponent experimental conditions. For the experiments, different concentrations were tested at four different temperatures (20, 25, 35 and 45 °C).The tests were developed using the following fixed conditions: 0.038 g of activated carbon, adsorption time of 12 hours and solution volume of 200 mL. The reactors were placed in the Dubnoff Bath SL-157 thermostatic bath and the results of atrazine, simazine concentrations were monitored using the LC-ESI-MS liquid chromatograph (LC 2020, Shimadzu®).A general model that could explain the multicomponent adsorption equilibrium of the compounds was developed, and from this, several hypotheses of mathematical models were thought and tested to explain the equilibrium of the process. The two-site monolayer model proved to be the best isothermal model to describe the equilibrium of the system. The results indicated a maximum adsorption capacity at 35°C (44.53 mg g $^{-1}$).Thermodynamic parameters and equilibrium constants showed that the process is favorable and spontaneous for atrazine in the S1 active site and for simazine in the S2 active site, revealing that, even with competition for the sites, the two compounds can be efficiently adsorbed in the same aqueous solution. The thermodynamic results suggested two types of surface adsorption mechanisms: physical and chemical. Thus, the study brings an alternative mathematical model to explain the bicomponent adsorption for atrazine and simazine and contributes to a better understanding of the multicomponent adsorption process and system equilibrium that can be tested and applied to other types of pollutants.

Keywords: bicomponent adsorption, atrazine, simazine, two-site equilibrium model

3.1.INTRODUCTION

The adsorption process has gained attention in researching works for wastewater treatment, especially for the removal of pollutants in low concentrations. Considering the presence of pollutants from effluents, ground and surface water, it is likely to find more than just one species in the same solution. It is the case coming from the use of pesticides in agricultural activities. In Brazil, this sector is the main economic activity, making the country the biggest pesticides consumer since 2009 (IBGE, 2019). Although the use of these products increases productivity, when mishandled it can cause negative consequences, such as impacts on the human's health (VANDENBERG; NAJMI; MOGUS, 2020) and environment (DUTRA; FERREIRA, 2017). Among the pesticides that are used in Brazil, there are atrazine and simazine, whose occurrence has been identified (simultaneously and individually conditions) in groundwater and surface water in the northwest region of the state of Rio Grande do Sul (RS), Brazil (HOFFMANN, 2019; FRANK, 2019; KERKHOFF, 2020; CAYE, 2019).

Among the possible adsorbents to be used for pesticides adsorption is powdered or granular activated carbon (AC), that can be obtained from different raw materials and be able to remove atrazine and simazine (VIEIRA *et* al., 2021; WEI et al., 2018). However, it was observed a lack of information in the literature about the simultaneous removal of both pesticides (atrazine and simazine). On the other hand, the application of equilibrium models that could be used to describe the multicomponent adsorption process is scarce. Another important aspect that has received minor attention is the adsorption studies regarding the integration of thermodynamic concepts (effect of temperature) in the adjustment of adsorption equilibrium models, which is desirable to allow an adequate number of degrees of freedom when applying models with a greater number of parameters.

According to Koopal *et* al. (2020), normally the approaches for multi-component adsorption equilibrium are based in the supposition of competition by same reactive sites. The sorption of a prime component is often studied at constant solution concentrations of the other components, turning it in a pseudo monocomponent problem and applying monocomponent isotherm equations. The application for heterogeneous sites normally is associated with the use of distributions functions of the affinities 27 (KOOPAL et al., 2020; GARCÉS; MAS, 2004) that can bring an additional mathematical complexity to solve the isotherm models. In this context, the purpose of this study is to evaluate the adsorption equilibrium for atrazine and simazine in aqueous media by an AC and develop bicomponent equilibrium models that can be able to describe the system. The models developed were adjusted in one step, using thermodynamic principles, to a set of experimental results obtained in different situations (individually and mixture) and different temperature conditions (20, 25, 35 and 45ºC). From the selection of the best model, the performance and physical meaning of the parameters were discussed.

3.2.DEVELOPMENT OF AN EQUILIBRIUM MODEL FOR BICOMPONENT ADSORPTION

3.2.1. Prologue

When removing pesticides or other compounds from ground and surface water using adsorption, it is likely to find more than just one species in the same solution. Considering these situations, it is desirable to conduct studieslead to the simultaneous removal of the aimed compounds.

In this context,among other aspects, will be needed mathematical models to explain the equilibrium of the process.The use of isotherm models to describe the equilibrium is necessary for the knowledge base of the nature of adsorption. These models present the fundamentals to determine the tendency of mobility and the maximum amount of an adsorbate compound in a porous adsorbent, which important data for implementation and improvements on the processes.

Not a lot of theories of what can happen in simultaneousremoval exist, so the main purpose of this paper is to develop models that can describe the equilibrium in the bicomponent adsorption process, based in some hypothesis. Also, test and find an appropriate model for a specific situation: the adsorption of simazine and atrazine in a bioadsorbent – which corresponds to the experimental data presented in this work.

The models developed and presented in this work start from the premise that the adsorption of the compounds occurs only in the monolayer above de adsorbent surface. For the system investigated here (adsorption of simazine and atrazine in bioadsorbent) this assumption is possible since in a preliminary step (not presented in this work) we adjusted several mono-component isotherm models where the best models obtained were the Freundlich and Langmuir - both reported as monolayers adsorption.

3.2.2. A general equilibrium model for bicomponent (A and B) adsorption in monolayer with two types of active sites (S1 and S2)

To develop an isotherm model for bicomponent adsorption, initially it is considered that there are two types of active sites (S1 and S2) supposing that the adsorbent maintains the adsorbate in only one layer above the surface. In this manner, the equilibrium relationships illustrated in Table 1 are possible. The compounds A and B compete for both active surface sites (S1 and S2). To establishthe equilibrium constants (Eqs.(1.a), (1.b), (2.a) and (2.b)) we forethought an adsorption order, even as employed in the Sips isotherm/Langmuir-Freundlich isotherm (SAADI *et al.*, 2015). In the equations of Table 1: $K_{j,i}$ is the equilibrium constant ($mg^{-\eta}L^{\eta}$) related to the adsorption of a "i" compound (*A* or *B*) adsorbed in an "j" active surface site (*S₁* or *S₂*) with an "η" adsorption order;[ ]denotes the molar concentration; $C_{i,e}$ is the concentration of a "i" compound (*A* or *B*) in the equilibrium ($mg\ L^{-1}$); α_1, α_2, β_1 and β_2 are the orders of adsorption.

Table 1 - Equilibrium relationship for bicomponent (A and B) adsorption in layer above adsorbent surface considering existence of two types of active sites (S1 and S2).

Compound	Equilibrium and equilibrium constant		Equation
	Active surface site type 1 (S_1)	Active surface site type 2 (S_2)	
A (atrazine)	$A + S_1 \rightleftarrows S_1 \cdot A$ $K_{S1,A} = \frac{[S_1 \cdot A]}{[S_1]C_{A,e}{}^{\alpha_1}}$	$A + S_2 \rightleftarrows S_2 \cdot A$ $K_{S2,A} = \frac{[S_2 \cdot A]}{[S_2]C_{A,e}{}^{\alpha_2}}$	(1.a), (1.b)
B (simazine)	$B + S_1 \rightleftarrows S_1 \cdot B$ $K_{S1,B} = \frac{[S_1 \cdot B]}{[S_1]C_{B,e}{}^{\beta_1}}$	$B + S_2 \rightleftarrows S_2 \cdot B$ $K_{S2,B} = \frac{[S_2 \cdot B]}{[S_2]C_{B,e}{}^{\beta_2}}$	(2.a), (2.b)

Considering the closed system presented in Table 1, we can express the ratio between the amount of compounds A and B adsorbed in the equilibrium ($q_{A,e}$and $q_{B,e}$, $mg\ g^{-1}$) and the maximum capacity of the first layer (q_m, $mg\ g^{-1}$) as the expressions of Equations (3) and (4).

$$\frac{q_{A,e}}{q_m} = \frac{[S_1 \cdot A] + [S_2 \cdot A]}{[S_1] + [S_2] + [S_1 \cdot A] + [S_1 \cdot B] + [S_2 \cdot A] + [S_2 \cdot B]} \tag{3}$$

$$\frac{q_{B,e}}{q_m} = \frac{[S_1 \cdot B] + [S_2 \cdot B]}{[S_1] + [S_2] + [S_1 \cdot A] + [S_1 \cdot B] + [S_2 \cdot A] + [S_2 \cdot B]} \tag{4}$$

By the supposition of existence of two types of active surface sites (S1 and S2), we can define the parameter r_{S1} (dimensionless), that represents the fraction of the active site S1 in the entire material, according to Eq. (5).

$$r_{S1} \equiv \frac{[S_1] + [S_1 \cdot A] + [S_1 \cdot B]}{[S_1] + [S_2] + [S_1 \cdot A] + [S_1 \cdot B] + [S_2 \cdot A] + [S_2 \cdot B]} \tag{5}$$

As a result of the combination of the Eqs (1)-(5), there are the Equations (6) and (7), that can be interpreted as a general monolayer model for bicomponent adsorption in two types of active sites.

$$q_{A,e} = \frac{q_m r_{S1} K_{S1A} {C_{A,e}}^{\alpha_1}}{1 + K_{S1A} {C_{A,e}}^{\alpha_1} + K_{S1B} {C_{B,e}}^{\beta_1}} + \frac{q_m (1 - r_{S1}) K_{S2A} {C_{A,e}}^{\alpha_2}}{1 + K_{S2A} {C_{A,e}}^{\alpha_2} + K_{S2B} {C_{B,e}}^{\beta_2}} \tag{6}$$

$$q_{B,e} = \frac{q_m r_{S1} K_{S1B} {C_{B,e}}^{\beta_1}}{1 + K_{S1A} {C_{A,e}}^{\alpha_1} + K_{S1B} {C_{B,e}}^{\beta_1}} + \frac{q_m (1 - r_{S1}) K_{S2B} {C_{B,e}}^{\beta_2}}{1 + K_{S2A} {C_{A,e}}^{\alpha_2} + K_{S2B} {C_{B,e}}^{\beta_2}} \tag{7}$$

3.2.3. Simplifying hypotheses

From the general model of Eqs (6) and (7), can be established a series of hypothesis, based on the following aspects:

(i) Concerning the number of active surface sites, can be distinguished two situations: only one type of active surface site or two active sites.

(ii) About the order of adsorption, also two possibilities: first order, as the traditional models, or a η-order, an adjustable parameter, as the Langmuir-Freundlich/Sips model.

(iii) Concerning the nature of adsorption, it could be a non-competitive, competitive or partially competitive. In the non-competitivenesssituation, compound A is adsorbed just in S1 and compound B is adsorbed just in S2, meaning that they don't have to compete with each other for the active sites.On other hand, in the competitive adsorption, compounds A and B can be adsorbed in both active sites (S1 and S2), therefore, they have to compete with each other to occupy them. The partially competitiveness hypothesiscan be unfolded in other two situations: (iii.1) compound A can be adsorbed by the two active sites, however, B can be adsorbed just by one active site, creating a competition only for the common site; (iii.2) compound B can be adsorbed by the two active sites and A just by one.

From the combination of these aspectswere developed ten hypotheses (H1 to H10) to explain the possible behavior of the two compounds in the adsorption process. The hypotheses, proper isotherm and model parameters are summarized inTable 2.

Table2 - Simplifying hypothesis, respective isothermand model parameters for bicomponent adsorption in monolayer.

Hypothesis				Isotherm model	Parameters	Eq.
Nº	Number of active sites	Adsorption order	Nature of adsorption			
H1	One (S1)	First order	Competitive	$q_{A,e} = \frac{q_m K_{S1A} C_{A,e}}{1 + K_{S1A} C_{A,e} + K_{S1B} C_{B,e}}$ $q_{B,e} = \frac{q_m K_{S1B} C_{B,e}}{1 + K_{S1A} C_{A,e} + K_{S1B} C_{B,e}}$	q_m K_{S1A} K_{S1B}	(8.a) (8.b)

Hypothesis				Isotherm model	Parameters	Eq.
Nº	Number of active sites	Adsorption order	Nature of adsorption			
H2	One (S1)	η-order	Competitive	$q_{A,e} = \frac{q_m K_{S1A} {C_{A,e}}^{\alpha_1}}{1 + K_{S1A} {C_{A,e}}^{\alpha_1} + K_{S1B} {C_{B,e}}^{\beta_1}}$ $q_{B,e} = \frac{q_m K_{S1B} {C_{B,e}}^{\beta_1}}{1 + K_{S1A} {C_{A,e}}^{\alpha_1} + K_{S1B} {C_{B,e}}^{\beta_1}}$	q_m K_{S1A} K_{S1B} α_1 β_1	(9.a) (9.b)
H3	Two (S1 and S2)	First order	Non-competitive	$q_{A,e} = \frac{q_m r_{S1} K_{S1A} C_{A,e}}{1 + K_{S1A} C_{A,e}}$ $q_{B,e} = \frac{q_m (1 - r_{S1}) K_{S2B} C_{B,e}}{1 + K_{S2B} C_{B,e}}$	q_m r_{S1} K_{S1A} K_{S2B}	(10.a) (10.b)
H4	Two (S1 and S2)	η-order	Non-competitive	$q_{A,e} = \frac{q_m r_{S1} K_{S1A} {C_{A,e}}^{\alpha_1}}{1 + K_{S1A} {C_{A,e}}^{\alpha_1}}$ $q_{B,e} = \frac{q_m (1 - r_{S1}) K_{S2B} {C_{B,e}}^{\beta_2}}{1 + K_{S2B} {C_{B,e}}^{\beta_2}}$	q_m r_{S1} K_{S1A} K_{S2B} α_1 β_2	(11.a) (11.b)
H5	Two (S1 and S2)	First order	Partially competitive A (A -> S1 and S2; B -> S2)	$q_{A,e} = \frac{q_m r_{S1} K_{S1A} C_{A,e}}{1 + K_{S1A} C_{A,e}} + \frac{q_m (1 - r_{S1}) K_{S2A} C_{A,e}}{1 + K_{S2A} C_{A,e} + K_{S2B} C_{B,e}}$ $q_{B,e} = \frac{q_m (1 - r_{S1}) K_{S2B} C_{B,e}}{1 + K_{S2A} C_{A,e} + K_{S2B} C_{B,e}}$	q_m r_{S1} K_{S1A} K_{S2A} K_{S2B}	(12.a) (12.b)

Hypothesis				Isotherm model	Parameters	Eq.
Nº	Number of active sites	Adsorption order	Nature of adsorption			
H6	Two (S1 and S2)	η-order	Partially competitive (A -> S1 and S2; B -> S2)	$q_{A,e} = \frac{q_m r_{S1} K_{S1A} {C_{A,e}}^{\alpha_1}}{1 + K_{S1A} {C_{A,e}}^{\alpha_1}} + \frac{q_m (1 - r_{S1}) K_{S2A} {C_{A,e}}^{\alpha_2}}{1 + K_{S2A} {C_{A,e}}^{\alpha_2} + K_{S2B} {C_{B,e}}^{\beta_2}}$ $q_{B,e} = \frac{q_m (1 - r_{S1}) K_{S2B} {C_{B,e}}^{\beta_2}}{1 + K_{S2A} {C_{A,e}}^{\alpha_2} + K_{S2B} {C_{B,e}}^{\beta_2}}$	q_m r_{S1} K_{S1A} K_{S2A} K_{S2B} α_1 α_2 β_2	(13.a) (13.b)
H7	Two (S1 and S2)	First order	Partially competitive (A -> S1; B -> S1 and S2)	$q_{A,e} = \frac{q_m r_{S1} K_{S1A} C_{A,e}}{1 + K_{S1A} C_{A,e} + K_{S1B} C_{B,e}}$ $q_{B,e} = \frac{q_m r_{S1} K_{S1B} C_{B,e}}{1 + K_{S1A} C_{A,e} + K_{S1B} C_{B,e}} + \frac{q_m (1 - r_{S1}) K_{S2B} C_{B,e}}{1 + K_{S2B} C_{B,e}}$	q_m r_{S1} K_{S1A} K_{S1B} K_{S2B}	(14.a) (14.b)
H8	Two (S1 and S2)	η-order	Partially competitive (A -> S1; B -> S1 and S2)	$q_{A,e} = \frac{q_m r_{S1} K_{S1A} {C_{A,e}}^{\alpha_1}}{1 + K_{S1A} {C_{A,e}}^{\alpha_1} + K_{S1B} {C_{B,e}}^{\beta_1}}$ $q_{B,e} = \frac{q_m r_{S1} K_{S1B} {C_{B,e}}^{\beta_1}}{1 + K_{S1A} {C_{A,e}}^{\alpha_1} + K_{S1B} {C_{B,e}}^{\beta_1}} + \frac{q_m (1 - r_{S1}) K_{S2B} {C_{B,e}}^{\beta_2}}{1 + K_{S2B} {C_{B,e}}^{\beta_2}}$	q_m r_{S1} K_{S1A} K_{S1B} K_{S2B} α_1 β_1 β_2	(15.a) (15.b)

Hypothesis				Isotherm model	Parameters	Eq.
N°	Number of active sites	Adsorption order	Nature of adsorption			
H9	Two (S1 and S2)	First order	Competitive	$q_{A,e} = \frac{q_m r_{S1} K_{S1A} C_{A,e}}{1 + K_{S1A} C_{A,e} + K_{S1B} C_{B,e}} + \frac{q_m (1 - r_{S1}) K_{S2A} C_{A,e}}{1 + K_{S2A} C_{A,e} + K_{S2B} C_{B,e}}$ $q_{B,e} = \frac{q_m r_{S1} K_{S1B} C_{B,e}}{1 + K_{S1A} C_{A,e} + K_{S1B} C_{B,e}} + \frac{q_m (1 - r_{S1}) K_{S2B} C_{B,e}}{1 + K_{S2A} C_{A,e} + K_{S2B} C_{B,e}}$	q_m r_{S1} K_{S1A} K_{S1B} K_{S2A} K_{S2B}	(16.a) (16.b)
H10	Two (S1 and S2)	n-order	Competitive	$q_{A,e} = \frac{q_m r_{S1} K_{S1A} {C_{A,e}}^{\alpha_1}}{1 + K_{S1A} {C_{A,e}}^{\alpha_1} + K_{S1B} {C_{B,e}}^{\beta_1}} + \frac{q_m (1 - r_{S1}) K_{S2A} {C_{A,e}}^{\alpha_2}}{1 + K_{S2A} {C_{A,e}}^{\alpha_2} + K_{S2B} {C_{B,e}}^{\beta_2}}$ $q_{B,e} = \frac{q_m r_{S1} K_{S1B} {C_{B,e}}^{\beta_1}}{1 + K_{S1A} {C_{A,e}}^{\alpha_1} + K_{S1B} {C_{B,e}}^{\beta_1}} + \frac{q_m (1 - r_{S1}) K_{S2B} {C_{B,e}}^{\beta_2}}{1 + K_{S2A} {C_{A,e}}^{\alpha_2} + K_{S2B} {C_{B,e}}^{\beta_2}}$	q_m r_{S1} K_{S1A} K_{S1B} K_{S2A} K_{S2B} α_1 α_2 β_1 β_2	(17.a) (17.b)

3.2.4. Thermodynamics

For any process that involves chemical and/or phase equilibrium, the measure of the favorability is determined by the Gibbs free energy (*G*) at a fixed temperature (*T*) and pressure (*press*). The criteria for thermodynamic equilibrium was developed using the first and second laws of thermodynamics and can be stated as: any process at fixed T and $press$ occurs with $dG < 0$ and, at equilibrium, $dG = 0$ (Gibbs free energy is minimum).

Thus, for the equilibrium of adsorption (according with chemical formulas of Table 1), the change of Gibbs free energy can be expressed as: $\Delta G = \sum_k \nu_k \mu_k = 0$. Where: μ_k is the chemical potential of generic k specie ($kJ\ mol^{-1} K^{-1}$); ν_k is the stoichiometric coefficient (positive for products and negative for reagents) (*adm*). The chemical potential, in turn, is defined by: $\mu_k = \mu°_k + R\ T \ln(a_k)$; where $\mu°_k$ is the standard state chemical potential of “k”; and a_k is the activity of specie “k”; $R = 8.314 \times 10^{-3}\ J\ mol^{-1} K^{-1}$ is the ideal gas constant.

Combining these relationships, we can express the standard state Gibbs free energy change ($\Delta G° = \sum_{k=products} |\nu_k| \mu°_k - \sum_{k=reactants} |\nu_k| \mu°_k$) as presented in the Eq. (18), that is an expression of the Van't Hoff equation.

$$\Delta G°_{i,j} = -R\ T \ln\left(K^*_{j,i}\right) \tag{18}$$

Where: $\Delta G°_{i,j}$denotes the standard state Gibbs free energy change($kJ\ mol^{-1}$) related to the adsorption of a “i” compound (*A* or *B*) adsorbed in an “j” active surface site (*S₁* or *S₂*); $K^*_{j,i}$ is the thermodynamic equilibrium constant (adm), a ratio between the activities of the products and reactants.

Considering the adsorption of a “i” compound (*A* or *B*)adsorbed in an “j” active surface site (*S₁* or *S₂*) as the chemical formulas of the Table 1, the thermodynamic equilibrium constant can be expressed as:

$$K^*_{j,i} = \frac{a_{j \cdot i}}{a_j a_i} = \frac{1}{\gamma_{i,j}} \frac{([j \cdot i]/C°)}{([j]/C°)([i]/C°)^{\eta}} = \frac{1}{\gamma_{i,j}} \frac{[j \cdot i]}{[j]\left(\frac{C_{i,e}}{MM_i C°}\right)^{\eta}} \tag{19}$$

Where: $\gamma_{i,j} = 1$ is the activity coefficient; [ ]denotes the molar concentration; $C° = 1\ mol\ L^{-1}$ is the standard state concentration; η represents the order of adsorption; and MM_i is the molar mass of the specie “i” (for atrazine, $MM_A = 215.685 \times 10^3\ mg\ mol^{-1}$; and for simazine,$MM_B = 201.657 \times 10^3\ mg\ mol^{-1}$).

On the other hand, the standard state Gibbs free energy change ($\Delta G°$) varies with temperature according to thestandard state enthalpy change ($\Delta H°$, $kJ\ mol^{-1}$) and standard state entropy change ($\Delta S°$, $kJ\ mol^{-1} K^{-1}$)

$$\Delta G^{\circ}{}_{i,j} = \Delta H^{\circ}{}_{i,j} - \Delta S^{\circ}{}_{i,j}\, T \qquad (20)$$

Combining these expressions, and assuming the dimensionless equilibrium constant used in the model development (see Table 1) as $K_{i,j} = \frac{[j-i]}{[j] {C_{A,e}}^{\eta}}$, we can write:

$$K_{j,i} = \frac{\gamma_{i,j}}{(MM_i\; C^{\circ})^{\eta}} \exp\left(\frac{\Delta H^{\circ}{}_{i,j}}{R\,T} + \frac{\Delta S^{\circ}{}_{i,j}}{R}\right) \qquad (21)$$

In this way, this expression can be used to increase the degrees of freedom of the adjustment of the equilibrium model for experimental data obtained in different temperatures, taking as parametersΔH° and ΔS° instead of one equilibrium constant for each temperature.

3.3.MATERIAL AND METHODS

3.3.1. Materials

For these experiments, commercial activated carbon produced from rice husk was used to remove atrazine and simazine from aqueous solution made for each component and one solution that was made with the mix between the two of them.

3.3.2. Adsorption experiments

The laboratorial experiments were done in several batches. From a 1000 mgL^{-1} main solution of atrazine and simazinethe experimental runs were carried out as follow: different concentrations (0,5; 1,0; 1,5; 2,0; 2,5; 3,0; 4,0; 5,0; 6,0 and 7,0 mg/L) were tested in four different temperatures (20, 25, 35 and 45 °C).The same sequence of experiments were done to atrazine (A) and simazine (B) individually and finally, for a mixture of atrazine and simazine (equimolate condition). All the tests were developed with the same activated carbon weight: 0.0380 g, weight that was tested and fixed due to previous experiments. The Table 3 summarize the equilibrium experiments performed.

Table 3 - Summary of experimental runs.

Experimental run	Compound(s)	Temperature (ºC)	Initial concentration $(mg\ L^{-1})$	Final measurement
1	Atrazine (A), only	20	0,5; 1,0; 1,5; 2,0; 2,5; 3,0; 4,0; 5,0; 6,0; 7,0	Concentration of Atrazine
2		25		
3		35		
4		45		
5	Simazine (B), only	20		Concentration of Simazine
6		25		
7		35		
8		45		
9	Mixture of Atrazine (A) and Simazine (B)	20		Concentration of Atrazine and Simazine
10		25		
11		35		
12		45		

The reactors were taken to the Dubnoff Bath SL-157, with temperature control and agitation of 80 rpm. All experiments were made in triplicate and the mean was used for the determinations of the amount of atrazine (q_A, mg g^{-1}) and simazine adsorbed (q_B, mg g^{-1}) at equilibrium. From the measured final concentration of the compounds, the relationship $q = (C_0 - C)\,V/m$ was employed to determine de adsorbent capacity. Where:C_0 and $C$are the initial and equilibrium concentrations (mg L^{-1}), respectively; V is the volume of the experimental system (L), and m is the mass of the adsorbent used in the experiment (g).

3.3.3. Analytical procedure

After 12 hours of agitation (time fixed preliminary tests), aliquots of each solution were filtered with a 0.45 µm pore syringe filter and conditioned and analyzed. The atrazine, simazine and multicomponent concentrations were monitored using LC-ESI-MS (LC 2020, Shimadzu®). The separation of components was carried out on a C18 VDSpher column (50 x 4.6mm x 5µm), mobile phase methanol and water (70:30). The monitored ion has a m/z ratio equal to 216 in positive mode. The analysis time was 7 min, and the method presented LOQ equal to 5 µg L-1, and linearity greater than 0.99.

3.3.4. Adjustment and selection of models

The experimental data obtained by the procedure reported above was used to adjustthe models presented in Table 2. Theoretically, the establishment of a specific model todescribe the experiments validates the hypothesis applied to obtaining it, improving the understanding of the nature of bicomponent adsoption. In this context, among several equations, we would be able to determine the best model.

The procedure used to select the best isotherm model was based on the one step adjustment, when all sets of experimental results were used to estimate the model parameters. The one step adjustment procedure involves the prediction evaluationof all systems (adsorption of atrazine and simazine, individually, and mixture of both) in all temperatures tested (20, 25, 35 and 45ºC).

To incorporate the effect of temperature in the models of Table 2 was used the Eq. (21) to describe the equilibrium constants ($K_{i,j}$), according to the thermodynamic principles.In this way, instead of one $K_{i,j}$ parameter for each temperature, is determined solely $\Delta H°_{i,j}$and $\Delta S°_{i,j}$, which are capable to describe $K_{i,j}$over the entire range of temperatures.

Considering a possible effect of the temperature over the maximum adsorbent capacity, the computational implementation considered one q_m parameter for each temperature.

The model's adjustment to the experimental data was made by non-linear means, using the trust-region-reflective optimization algorithm (COLEMAN and LI, 1996). The least-squares were employed as the objective function (F_{obj}) to be minimized, according with

Eq. (22). By this procedure were obtained the values of parameters that minimize F_{obj} for each isotherm of Table 3.All programming, algorithm and solvers used in this work were made in Matlab R2021b software.

$$F_{obj} = \sum_{s=1}^{3}\sum_{t=1}^{4}\sum_{p}\left(q_{A,e}\Big|_{exp}^{p,t,s} - q_{A,e}\Big|_{mod}^{p,t,s}\right)^2 + \sum_{s=1}^{3}\sum_{t=1}^{4}\sum_{p}\left(q_{B,e}\Big|_{exp}^{p,t,s} - q_{B,e}\Big|_{mod}^{p,t,s}\right)^2 \quad (22)$$

In Eq. (22): $q_{i,e}\Big|_{exp}^{p,t,s}$ and $q_{i,e}\Big|_{mod}^{p,t,s}$denote adsorption capacity of the “i” compound (A or B) of the point “p” of the data set relative to the temperature “t” of the system “s”, experimental and predicted by the model, respectively. The superscript “p” denotes the experimental point of the isotherm behavior, “t” denotes the temperature in which the data set was obtained (20, 25, 35 or 45°) and “s” indicates the system that refers toatrazine individually, simazine individually, or mixture. The subscripts “exp” and “mod” refer to the experimental data and values predicted by the model, respectively.

After the adjustment of each model of Table 2, the determination coefficient (R^2) and the corrected Akaike information criterion (AICc) were calculated. The AICcpermit to compare models with different number of parameters and consists in a correction of the Akaike information criterion (AIC)(AKAIKE, 1973) for small samples (n/np < 40) (HURVICH and TSAI, 1991). Where n is the number of experimental observations adjusted to the model (in this work $n = 176$), n_p is the number of parameters of the model.

$$AICc = n\,ln\left(\frac{F_{obj}}{n}\right) + 2\,(np + 1)\left(1 + \frac{np + 2}{n - np - 2}\right) \quad (23)$$

Thus, the model that presents the lowest AICc value theoretically corresponds to the most appropriate model to describe the system, taking into account the power of prediction and the number of parameters involved.

3.4.RESULTS AND DISCUSSION

3.4.1. Adsorption equilibrium: models' adjustment and selection

The application of an isotherm model to the equilibrium of adsorption provides useful information about the processing mechanism. To understand the phenomenological basis of the bicomponent adsorption of atrazine and simazine in activated carbon, the models presented in Table 1 were investigated to adjust the equilibrium data for the temperatures of 20, 25, 35 and 45 °C and to the systems containing atrazine and simazine, individually, and mixture of both.

Table 4 presents the results of the non-linear minimization of the objective function for each one of the models proposed (see Table 1). Thenumber of parameters (n_p), number of experimental data adjusted by the model (n), determination coefficient (R^2) obtained for each systems (atrazine and simazine individually and mixture), considering all temperatures, and the correspondent Akaike information criteria (AICc) calculated by means of Eq. (22) are presented. The AICcis used to determine the most suitable model for the system, since it takes into account the accuracy, precision and ability of different models with different numbers of adjustable parameters. The criterion provides, therefore, a metric for comparison and selection of models, in which the smallest AICc value represents the highest quality and simplicity (AKAIKE, 1973).

Looking at the Table 4 it is possible to compare the quality of all the tested models and how well adjusted the experimental data was.For atrazine, when adsorbed in individual process, the best hypothesis according to the R^2 value was the one that considered two active sites, S1 and S2, n-orderand 17 parameters, showing a $R^2 = 0,8482$ (model 10). When analyzing the AICc, that was also the best adjusted model, resulting in the lowest value (492,2). About simazime in monocomponent condition, the best model was also the hypothesis number 10, with a $R^2 = 0,4287$ and AICc = 492,2. Considering the mixture of atrazine and simazine the same could be seen, the best model is number 10 with a total $R^2 = 0,7333$.What can be concluded from it, is that the model that considers that there is competition between the compounds for both active sites and takes into consideration the highest np describes the process the best.

Table 4 - Quality of the adjustment of by various equilibrium models: determination coefficients (R^2) and corrected Akaike information criteria (AICc).

Model/Hypothesis				**Adjustment indicators**							
Nº	**Number of active sites**	**Adsorption order**	**Nature of adsorption**	**Number of parameters (n_p)**	**Number of experimental data (n)**	**Determination coefficient (R^2)**					**Akaike information criteria (AICc)**
						Atrazine (mono-component)	**Simazine (mono-component)**	**Atrazine (mixture)**	**Simazine (mixture)**	**Total**	
1	One (S1)	Firstorder	Competitive	8	176	0.7968	-0.0518	0.6355	0.7832	0.6614	513.0
2	One (S1)	n-order	Competitive	10	176	0.7846	0.0778	0.6385	0.7265	0.6662	515.0
3	Two (S1 and S2)	Firstorder	Non-competitive	9	176	0.8175	-0.1120	0.7043	0.6305	0.6402	525.9
4	Two (S1 and S2)	n-order	Non-competitive	11	176	0.8193	0.0260	0.7202	0.6158	0.6618	519.6

Model/Hypothesis				**Adjustment indicators**							
Nº	**Number of active sites**	**Adsorption order**	**Nature of adsorption**	**Number of parameters (n_p)**	**Number of experimental data (n)**	**Determination coefficient (R^2)**					**Akaike information criteria (AICc)**
						Atrazine (mono-component)	**Simazine (mono-component)**	**Atrazine (mixture)**	**Simazine (mixture)**	**Total**	
5	Two (S1 and S2)	Firstorder	Partially-competitive (A)	11	176	0.8099	0.0665	0.6905	0.4396	0.6208	539.8
6	Two (S1 and S2)	n-order	Partially-competitive (A)	14	176	0.8244	0.0221	0.7179	0.6181	0.6625	526.3
7	Two (S1 and S2)	Firstorder	Partially-competitive (B)	11	176	0.8227	0.1048	0.6767	0.6732	0.6771	511.5

Model/Hypothesis				**Adjustment indicators**							
Nº	**Number of active sites**	**Adsorption order**	**Nature of adsorption**	**Number of parameters (n_p)**	**Number of experimental data (n)**	**Determination coefficient (R^2)**					**Akaike information criteria (AICc)**
						Atrazine (mono-component)	**Simazine (mono-component)**	**Atrazine (mixture)**	**Simazine (mixture)**	**Total**	
8	Two (S1 and S2)	n-order	Partially-competitive (B)	14	176	0.8395	0.1887	0.7208	0.7062	0.7110	499.0
9	Two (S1 and S2)	Firstorder	Competitive	13	176	0.8122	0.1145	0.6889	0.7412	0.6933	507.1
10	Two (S1 and S2)	n-order	Competitive	17	176	0.8482	0.4287	0.7296	0.6235	0.7333	492.2

Hypothesis number 10 was the one that showed the best results. This theory is a competitive one, which means that atrazine and simazine need to compete for the two available active sites (S1 and S2) and it also considers n-order of adsorption. Model parameters must have physical meaning and must provide some understanding of the real system.

The parameters (or variables) can be evaluated separately and the extension of a parameter affects the response of the whole system. In a positive way, priorities are obtained that suggest which environment or which parameters on the real world must be modified to bring good result (SODRÉ, 2007). H10 has 17 parametersthat were explainedpreviously.

Considering the best model (H10), that corresponds to the general form (two-sites, competitive and with adsorption order different from 1), also as result of the adjustment, in the Table 5 are presented the determination coefficients for the adsorption systems dismembered for the temperatures of 20, 25, 35 and 45ºC. The temperature that shows the best result when evaluating atrazine monocomponent is 25ºC, and the worst is 45ºC. That could be explained because the molecule is not a rigid structure and its atoms, at room temperature, vibrate around their equilibrium positions. When exposed to higher temperatures, due to greater agitation of molecules, it becomes more difficult to stabilize in their equilibrium positions (CARVALHO, 2010). It could also explain why the 25º happened to be the best result. Simazine individually showed 35ºC as the best temperature, with the highest $R^2 = 0,9176$. Atrazine in the mixture also showed 35ºC with a highest $R^2 = 0,9401$ and 45ºC as the worst one. Simazine in multicomponent adsorption presented the best temperature as 35ºC and worst 25ºC.

Tabela 5 - Determination coefficients (R^2) obtained from the adjustment of the best model (H10) to the adsorption runs on different temperatures and systems (mono component and bicomponent).

Adsorption run	Temperature				Total
	20ºC	25ºC	35ºC	45ºC	
Atrazine	0.8231	0.9249	0.7891	-0.1106	0.8482

(mono-component)					
Simazine (mono-component)	-2.6806	-0.0378	0.9176	0.8883	0.4287
Atrazine (mixture)	0.8734	0.9352	0.9401	0.3306	0.7296
Simazine (mixture)	0.2108	-4.9519	0.7706	0.4517	0.6235
Total					0.7333

In the Fig.5, the performance of the isotherm model H10 (two-sites, competitive and with adsorption order different from 1) is presented the form of model prediction vs experimental plot. In this figure, all experimental data are presented - for individual and bicomponent adsorption in all the different temperatures (20, 25, 35 and 45°). By analyzing it, can be concluded that the data is well adjusted considering that all the experimental values were taken off from the same experiments instead of separated batches, that is, data integration was carried out and they are being used to adjust all the data at once. It is possible using the parameters and using the thermodynamic principles, that relates the temperature to the equilibrium constant, so the effect of the temperature is embedded in the equilibrium constant and also in the different *qn*'s. The orders of adsorption (adsorption intensities) were used to adjust all experimental conditions. All this can justify a relatively lower R^2 value (0.7333) when comparing with some other studies (YOU, *et al.*,2021; LI, *et al.*,2021).

The values for atrazine show a smaller error bar when comparing with the ones for simazine, specially comparing the monocomponent condition, which means that the compound A reacts better to this experiment and B might need some adjustments to fit in the process ans demonstrate better results. Regarding to the temperatures, in general, 35°C showed the best R^2 values (0.9176, 0.9401 and 0.7706 for B monocomponent, A in the mixture and B in the mixture, respectively). Only for A monocomponent, the temperature that showed the best result was 25°C, which can be explained by the influence that simazine causes in the process.

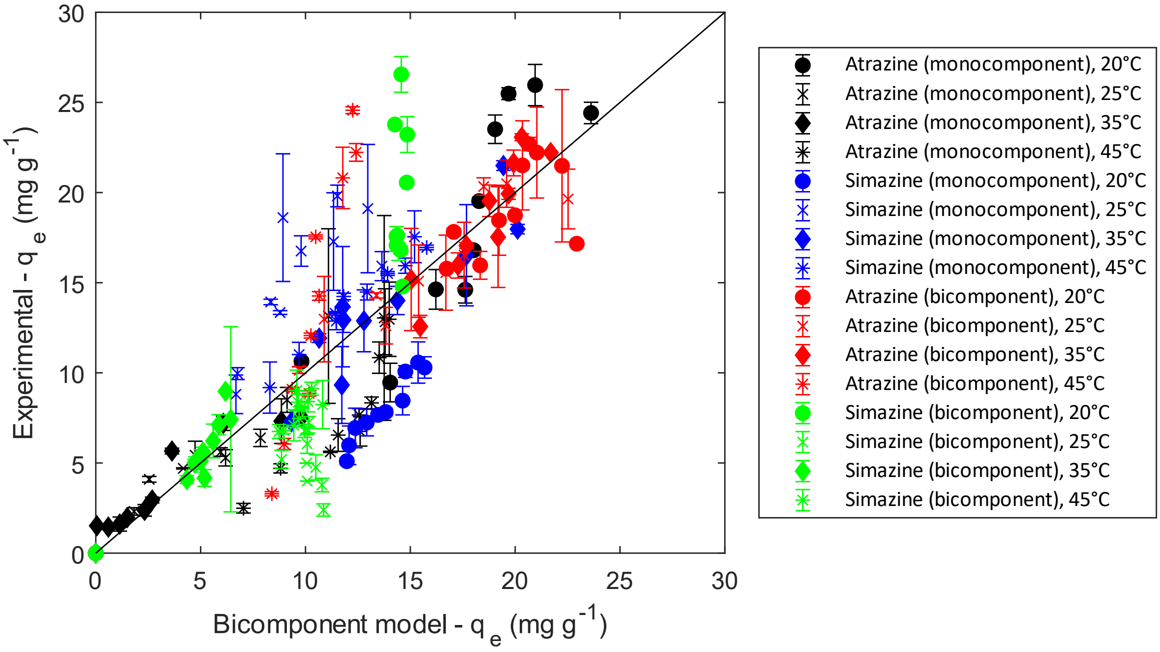

Figure 3 – Isotherm model H10 prediction *vs* experimental results for mono and bicomponent adsorption of simazine and atrazine in various temperatures (R^2=0.7333).

3.4.2. Model H10 (competitive bicomponent adsorption in two active sites with η-order): isotherm and thermodynamics

The Table 6 brings theparameters of the model H10 (competitive bicomponent adsorption in two active sites with η-order), such as the maximum adsorption capacity(q_m) for each temperature tested, faction of S1 sites in the adsorbent surface, the thermodynamic parameters ($\Delta H°$ and $\Delta S°$) involved on the equilibrium constants and the adsorption order.

Looking at the q_m values, is notable that for the temperatures 20, 25 and 35°C, the capacities were similar, which are numbers that agree with the ones found in other studies (WEI, *et al.*, 2018; SANINO, *et al.*, 2013; JIA, *et al.*, 2017). However, a smaller value can be seen for 45°C, what can be explained by the thermal effect. As it is a high temperature, the pores of the solid adsorbent (AC) could close and decrease the access of the superficial area that is capable of adsorbing the compound. It could also cause a bending or a blocking in the solid adsorbent, changing its form and causing the same consequence, decreasing the access of the adsorbate to the active sites.

Tabela 6 - Parameters values for the model H10 (competitive bicomponent adsorption in two sites with η-order).

Parameter		**Unity**	**Value**
Capacity parameters			
Maximum adsorption capacity of monolayer adsorption (q_m)	20°C	$mg\ g^{-1}$	42.69
	25°C		41.84
	35°C		44.53
	45°C		27.72
Faction of S1 sites in the adsorbent surface (r_{S1})		adm	0.5270
Thermodynamic parameters			
Equilibrium constant for atrazine (A) adsorption in active site S1 (K_{S1A})	Standard state enthalpy change ($\Delta H°$)	$kJ\ mol^{-1}$	153.7
	Standard state entropy change ($\Delta S°$)	$kJ\ mol^{-1}K^{-1}$	0.6946
Equilibrium constant for atrazine (A) adsorption in active site S2 (K_{S2A})	$\Delta H°$	$kJ\ mol^{-1}$	-294.7
	$\Delta S°$	$kJ\ mol^{-1}K^{-1}$	-0.865
Equilibrium constant for simazine (B) adsorption in active site S1 (K_{S1B})	$\Delta H°$	$kJ\ mol^{-1}$	-54.45
	$\Delta S°$	$kJ\ mol^{-1}K^{-1}$	-0.1247

Parameter		Unity	Value
Equilibrium constant for simazine (B) adsorption in active site S2 (K_{S2B})	$\Delta H°$	$kJ\ mol^{-1}$	184.3
	$\Delta S°$	$kJ\ mol^{-1}K^{-1}$	0.7586
Adsorption order			
Atrazine (A) adsorption in active site S1 (α_1)		adm	2.002
A in site S2 (α_2)			1.375
Simazine (B) in site S1 (β_1)			0.587
B in site S2 (β_2)			1.884

Regarding to the value of r_{S1}, 52.7% of active sites correspond to S1 type and, on the other hand, 47.3% of S2 type. These numbers help to explain why the competition model with two active sites was the one that represented the process the best. Having the fraction well divided in proportional portions supports the hypothesis that atrazine and simazine have to compete to get a spot in the active sites and explain why the two compounds can be well adsorbed in this experiment.

Analyzing the thermodynamic parameters, entropy is a thermodynamic quantity that measures the disorder of a system and the spontaneity of physical processes. The greater the disorder of the system, the greater the entropy (MARINESCU; MARINESCU, 2012). The change in entropy is directly proportional to the change in free energy, and this proportionality is given by the temperature T (LIN; ZHAO, 2021). The standard state entropy change ($\Delta S°$) for $K_{S1,A}$, as a positive value (0.6946) demonstrates that atrazine adsorption has their spontaneity improved in S1 site with increase of temperature, which cannot be observed when adsorbing atrazine in S2, showing that this compound connects better with S1 than S2. For simazine, the opposite is observed, $K_{S1,B}$ shows a negative value (-0.1247) and $K_{S2,B}$ a positive one (0.7586), demonstrating that simazine has their spontaneity improved in S2 and not in S1 with the increase of temperature.

Enthalpy variation is a physical quantity that indicates the amount of energy absorbed or released by a process. An endothermic reaction is when energy is absorbed (the result will be a positive number) and an exothermic reaction occurs when energy is released (showing a negative value as a result) (LIN; ZHAO, 2021). ForK_{S1A}, $\Delta H°$ shows a positive result (153.7kJ mol^{-1}), indicating that it is an endothermic event, which absorbs energy. K_{S2A}, presents a negative number (-294.7kJ mol^{-1}), so the reaction in this case is exothermic and releases energy. K_{S1B}has a $\Delta H° = -54.45\ kJ\ mol^{-1}$, indicating and exothermic reaction and for last, K_{S2B} indicates an endothermic reaction with $\Delta H° = -184.3 kJ\ mol^{-1}$. So, these numbers complement the entropy ones, because it shows that when the reaction is spontaneous, the disorder is elevated, and energy is being released by the process (YU, *et al.*, 2020).To complement it, the positive results for $\Delta H°$ indicate physical adorption, that occurs by a difference in energy or forces of attraction, called *Van der Waals*, that make the flags physically attached to the adsorbent. These interactions have a long reach, but they are weak. On the other hand, when the adsorption process takes place through forces of a chemical nature, it is called chemical adsorption. In this type of interaction, the adhesion of the adsorbent to the surface of the adsorbate is established by chemical bonds, in general, covalent. Once chemical bonds are formed, it is an exothermic process ($\Delta H°$ presenting negative values) (BREEUWSMA; LYKLEMA, 1973).

As a complement for the thermodynamic parameters of Table 6, the Figure 6 presents the standard state Gibbs free energy change (ΔG°), calculated by the Eq. (19), and equilibrium constant, evaluated by Eq. (20), for each compound-active sitelink. To a process be able to happen from a thermodynamic point of view, ΔG° needs to present itself as a negative value (BANGHAM, 1937). Such situation is observed in the Figure 6 (b), all four situations show negative values. Interpreting the values, the smaller the ΔG°, the more spontaneous is the process, it means that with the increasing of the temperature, the adsorption of atrazine in S1 and simazine in S2 becomes more favorable, whereas the adsorption of atrazine in S2 and simazine in S1 become less spontaneous and less favorable (VIEIRA, *et al.*, 2022; HARIKA, *et al.*, 2020).

The Figure 6(a) is regarding tothe equilibrium constants over the temperature variation. It is notable that, with the temperature increasing, the adsorption of atrazine in S1 begins to be more favorable, and the same happens with simazine in S2 (positive values for ΔS°). However, the process is less favorable for simazine in S1 and atrazine in S2 (negative Δ*S*°). This reassure once again, the competitiveness in the process between the two compounds, seeing that, when the adsorption starts being more favorable for one compound in one active site, in the same active site it starts to be less favorable for the other one, depending on the increase of the temperature.

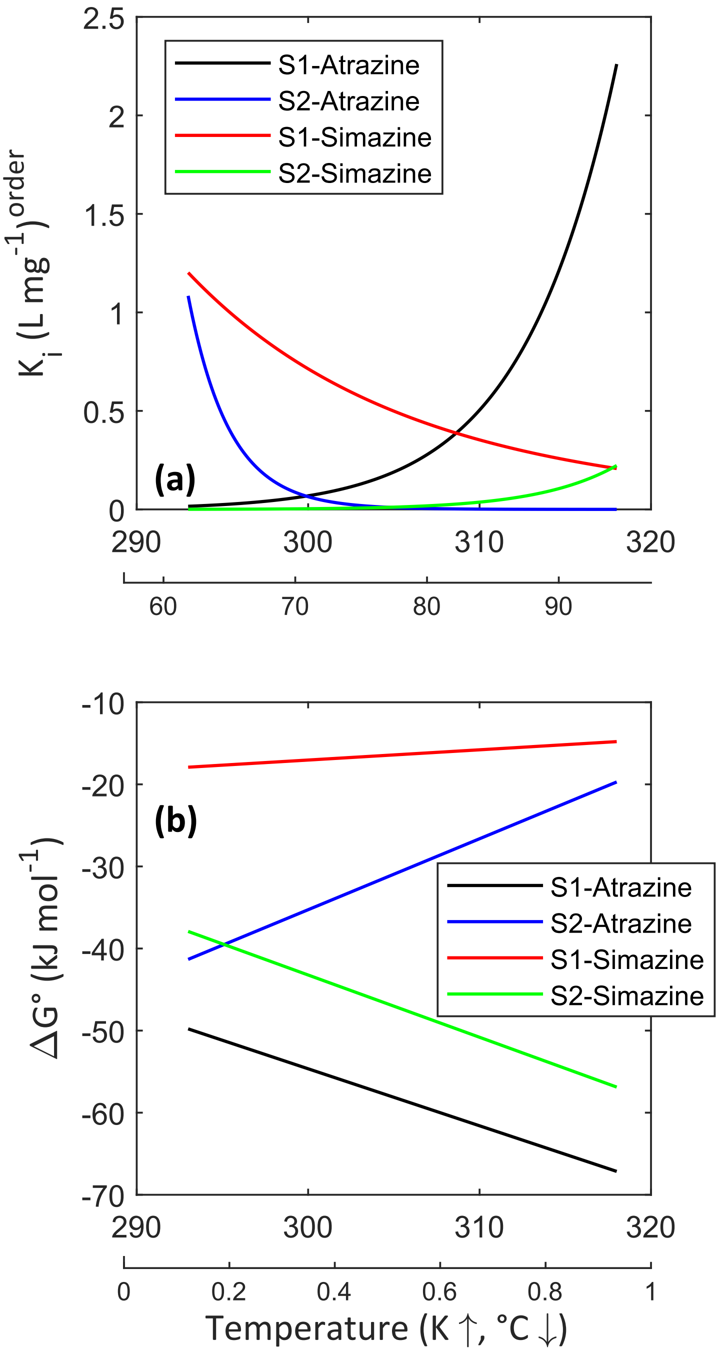

Figure 4 - Equilibrium constants and standard state Gibbs free energy of adsorption of atrazine and simazine in active sites S1 and S2.

Regarding to the adsorption order values, and analyzing the equation H10 in Table 2 for the model that fitted the best, there is a combination of Langmuir and Freundlich isotherm models. For the monocomponent adsorption this combinationit's known as the Sips isotherm model, which is deduced to predict not just the heterogeneity of the adsorption systems, but also transpass the limitations associated with the increased concentrations of the adsorbate of Freundlich model. This leads to the production of an expression that has a finite limit at a high concentration (AL-GHOUTI; DA'ANA, 2020). Sips model has the validity in localizing the adsorption without the adsorbate-adsorbate interaction (SAADI *et al.*, 2015). Operating conditions such as alteration of the concentration, pH, and temperature, governs the parameters of the equation.

The Sips model becomes the Langmuir model when the order equal to one ($\eta = 1$) and becomes the Freundlich model at low concentrations (WANG; GUO, 2020).The adsorption order parameter is usually>1, and therefore the larger is this parameter the moreheterogeneous is the system. Values close to (or exactly) 1 indicate asolid with relatively homogeneous binding sites. If order is unity, theLangmuir equation applicable for ideal surfaces is recovered (DO, 1998). Observing the results of Table 4 forα_1, α_2, β_1 and β_2 that were found in the experiment (2.002, 1.375, 0.587 and 1.884), three out of four values are >1, indicating a heterogeneity of the system. Only simazine in site S1 (β_1) shows a number <1 indicating that in that case, there is a homogeneity of the system. The interpretation for these results could be that the higher thevalues, the higher will bethe intensity of adsorption and the smaller, the lower will be the intensity of adsorption.

About the isotherm curves adjusted by the model H10, it can be found on Figure 7, where there is the comparison of the modeled and experimental results of all conditions tested in this work, including monocomponent and bicomponent conditions for both pollutants in all the tested temperatures.

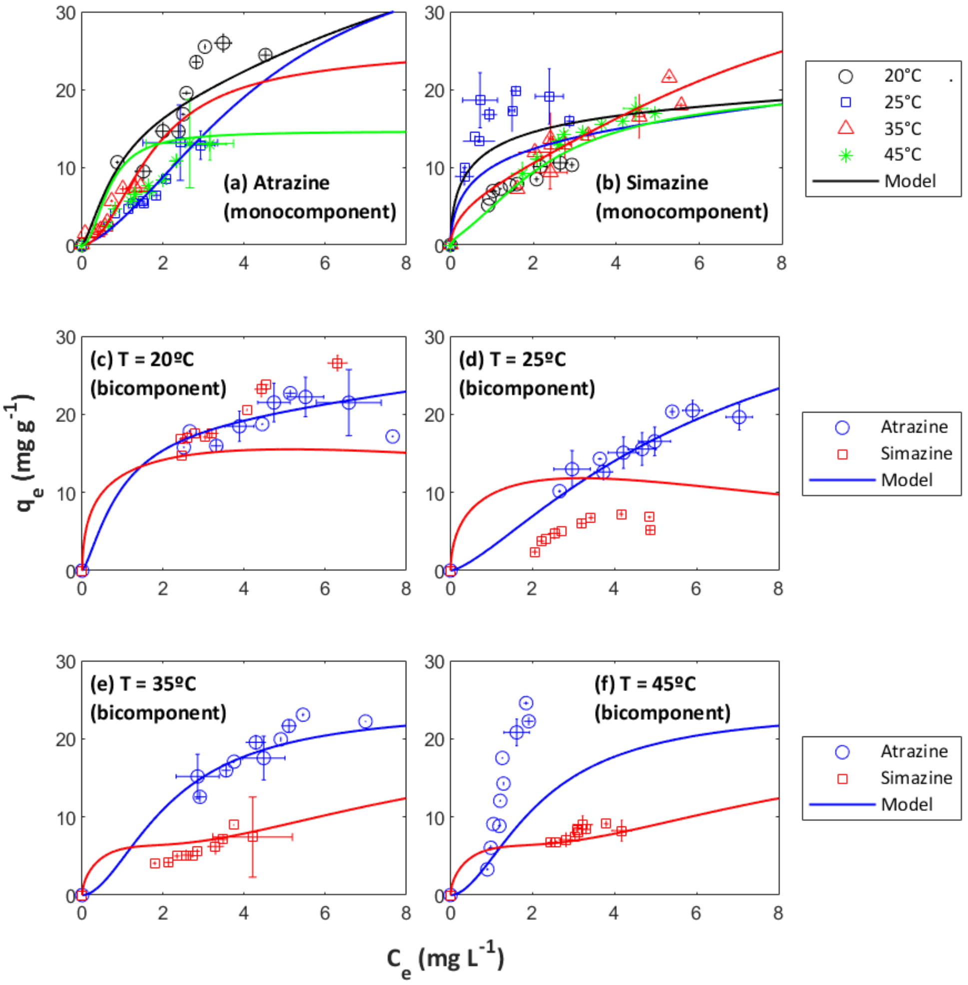

Figure 5 - Adsorption isotherms of bicomponent adsorption: (a) Atrazine monocomponent in all the temperatures; (b) Simazine monocomponent in all the temperatures; (c) Atrazine and simazine bicomponent at 20°C; (d) Atrazine and simazine bicomponent at 25°C;(e)Atrazine and simazine bicomponent at 35°C and; (f) Atrazine and simazine bicomponent at 45°C.

In Fig. 7 is shown the thermal effect on equilibrium of adsorption by atrazine and simazine isotherms. According to Giles *et al.* (1960), the isotherms are type H subtype 2, indicating high affinity to activated carbon for both compounds in the evaluated concentration range. The best adsorption capacities were 25,96 mgg^{-1} and 21,45 mgg^{-1}for atrazine (Fig. 7 a) and simazine (Fig. 7 b), respectively, in monocomponent condition (VIEIRA, *et al.*, 2022; SANINO, 2013; SAMUEL, *et al.*, 2023; ANDRUNIK, 2023; OLIVEIRA *et al.*, 2023). The results also show low variation between the amounts adsorbed in relation to the increase in temperature, mainly at lower concentrations.

When evaluating the bicomponent isotherms, the presence of atrazine in the solution decreases the adsorption of simazine in all the temperatures tested, while the adsorption of atrazine kept the best adsorption capacity of 24,57 mgg^{-1}. It can be explained by the fraction of active sites, 52,70% is S1, which shows more affinity with atrazine, although, the adsorption of simazine still happens in lower numbers when comparing with monocomponent adsorption. These numbers prove once again that the adsorption between atrazine and simazine by activated carbon follows a competitive model, being that atrazine doesn’t suffer any significant decrease in its adsorption and simazine, while still adsorbed, present less efficiency in the process when comparing to single adsorption.

3.5.CONCLUSIONS

Commercial activated carbon was tested to remove atrazine and simazine from aqueous means, in monocomponent and bicomponent conditions. Four temperatures were tested to evaluate different performances (20, 25, 35 and 45°C) in a sequence of several batches of experiments. Was developed a general bicomponent equilibrium model considering two types of active surface sites with adjustable order of adsorption. From the general model, several hypothesis were assumed, generating different mathematical models that were compared among them to find the most appropriate to describe the system. Using the corrected Akaike information criteria, the conclusion that the best model to describe the process is the competitive with two active sites (S1 and S2) was reached. From the models parameters was found that the adsorption of atrazine is more favorable in S1 site and simazine in S2, according to the increase of the temperature. The maximum adsorption capacity (q_m) was observed for 35°C ($44.53 mg\ g^{-1}$), when the adsorbent reaches its maximum adsorption power, and the lowest q_m was detected for 45°C ($27.72 mg\ g^{-1}$), when the adsorbent is exposed to a too high temperature that it loses adsorption capacity due to thermal effects. Thermodynamic parameters and equilibrium constants showed that the process is more favorable and spontaneous for atrazine in S1 and for simazine in S2, showing that, even though there is a competition for the sites and simazine suffers a small decrease in the adsorption capacity, the two compounds can be satisfactorily adsorbed when mixed in the same solute and exposed to the same process. Finally, the study contributes to the knowledge of bicomponent mathematical models of adsorption equilibrium, considering atrazine and simazine, but it can be extended and used for different pollutants.

3.6.ACKNOWLEDGEMENTS

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4. CONSIDERAÇÕES FINAIS

Carvão ativado comercial foi testado para remover atrazina e simazina de meios aquosos, em condições monocomponentes e bicomponentes. Quatro temperaturas foram testadas para avaliar diferentes desempenhos (20, 25, 35 e 45°C) em uma sequência de várias bateladas experimentais. Diferentes teorias para modelos matemáticos foram criadas e testadas no Software Matlab, chegando-se a conclusão que o melhor modelo para descrever o equilíbrio do processo foi o competitivo com dois sítios ativos (S1 e S2), em que a adsorção de atrazina é mais favorável em S1 e a de simazina em S2, de acordo com o aumento da temperatura. A capacidade máxima de adsorção (q_m) foi observada para 35°C (44,53mg g^{-1}), quando o adsorvente atinge seu poder máximo de adsorção. Já o menor q_m foi detectado para 45°C (27,72mg g^{-1}), quando o adsorvente é exposto a uma temperatura muito alta que perde a capacidade de adsorção devido aos efeitos térmicos. Parâmetros termodinâmicos e constantes de equilíbrio mostraram que o processo é favorável e espontâneo para atrazina em S1 e para simazina em S2, mostrando que, embora haja uma competição pelos sítios e a simazina sofra uma pequena diminuição na capacidade máxima de adsorção, os dois compostos podem ser satisfatoriamente adsorvidos quando misturados no mesmo soluto e expostos ao mesmo processo. Por fim, o estudo contribui para o conhecimento de modelos matemáticos bicomponentes de adsorção, considerando abrasivos, mas pode ser estendido e testado para diferentes poluentes.

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