

# Simultaneous adsorption of pollutants onto the adsorbent review of interaction mechanism between the pollutants and the adsorbent

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## Abstract

The contamination of the environment by the release of wastewater containing multi pollutants is one of the major environmental concern in the recent time. Adsorption using the adsorbent is an effective method for the removal of various pollutants from wastewater. In the simultaneous adsorption of a binary solution, the interaction among the pollutant molecules and the competition among the solutes for the adsorbent are complicated. Thus, it is important to understand the mechanism of the simultaneous adsorption of pollutants from the industrial point of view. Therefore the current work reviews the simultaneous adsorption of solutes from wastewater using different adsorbents. The interaction among the pollutants such as synergistic, antagonistic and non-interaction was determined. Different concepts used for understanding the interaction mechanism among the components and the adsorbent were discussed. The possible reason for the interaction formed among the pollutants is also investigated.

**Keywords:** Adsorption; Interaction; Simultaneous; Binary Solution; Affinity.

## 1. Introduction

The problem of water pollution by various pollutants is a serious problem of concern nowadays. Because of this, there is an increasing interest from all over to prevent the pollution of water by different chemicals and has also caused awareness among the public. The existence of the chemicals at very low values of concentration will be considered as toxic [1]. The group of these chemicals comprises of organic compounds, dyes, heavy metals and even some elements like radioactive elements. These are released from the wastewater of different industries [2]. These chemicals are harmful to both human beings and the aquatic bodies [3]. As per environmental protection agency there are strict regulations on the release of these pollutants into the environment [4]. Generally the pollutants are released from different industries like petroleum, paint, pharmaceutical, rubber, electroplating, iron and steel industries [5]. Different methods are available to treat these chemicals such as biodegradation, chemical oxidation, biosorption, solvent extraction, liquid membrane methods, coagulation and adsorbent using adsorbent [6].

Most of the work found in literature reports on the single component adsorption of pollutants. But real industrial wastewater which contains various pollutants requires simultaneous adsorption of two or more components. Thus it is significant to investigate on simultaneous adsorption of pollutants from the wastewater. Different equilibrium isotherm equations [7] which are used for single component system are modified for multicomponent system in order the behavior of the component. The interaction mechanism can also be found from these models.

Therefore the present review aims to explore on the simultaneous adsorption of the pollutants from wastewater. The various possible interactions such as synergism, antagonism and non-interaction

among the components were investigated from the available literature. Different concepts and terminologies were employed for determining how the components interacts with each other and with the adsorbent in the binary solution. It also focusses on finding the reason for the interaction among the components under different experimental conditions. The possible reason for the interaction formed among the pollutants is also investigated.

## 2. Simultaneous adsorption of pollutants

The industrial wastewater contains many pollutants such as organic compounds, dyes, heavy metals and suspended matter. Therefore interaction happens between the pollutants for the adsorbent sites and simultaneous adsorption of the pollutants takes place. The simultaneous adsorption studies describes the fraction of adsorbent sites occupied by each pollutant molecule on the adsorbent surface, their attraction towards the adsorbent surface and the interaction among the adsorbent molecules [2]. It also quantifies the interaction of one solute with the adsorbent surface in the presence of another solute [8]. The interaction can be synergic, antagonistic or non-interactive due to the presence of another molecule [9, 10]. The adsorption system becomes more complex when more than one pollutant is present. The literature available on the interaction among the molecules in a binary solution are limited. Therefore it is required to study the interactions among the molecules and the mechanism to understand the effectiveness of the process for wastewater treatment [10]. It is also important in optimizing the process so that it can be implemented at the industrial scale [9].

### 3. Interaction mechanism

In a binary solution having various pollutant molecules, three types of interactions are possible between the adsorbate molecules. The basic principle used to find the mechanism is by considering the adsorption capacity of the pollutant (i) in the binary solution  $(Q_{i,o})_b$  and the adsorption capacity of the component (i) in the solution containing only that particular component  $(Q_{i,o})_s$ .

The possible interactions are discussed below.

(a) Synergistic interaction: The adsorption capacity of a component increases when it is in association with another component in the solution  $((Q_{i,o})_b / (Q_{i,o})_s > 1)$ .

(b) Antagonistic interaction: The adsorption of an adsorbate molecule decreases when it is present in a solution having another component  $((Q_{i,o})_b / (Q_{i,o})_s < 1)$ .

(c) Non interaction: The adsorption capacity of a component is not dependent on the presence or absence of the other components in the solution  $((Q_{i,o})_b / (Q_{i,o})_s = 1)$  [11-21].

Various methods and concepts are used to determine the interaction between the components in a binary solution and are discussed below. The terminologies also describes how one component will inhibit the adsorption of another component in the solution.

#### 3.1. Additive rule

The interaction effect can be found by using additive rule i.e. comparing the total adsorption capacity of all the components in binary solution and single solution mode. The total adsorption capacity of all the components in the single component solution mode is obtained from the equation

$$\sum_{j=1}^2 ((Q_{j,o})_s) = (Q_{i,o})_s + (Q_{j,o})_s \quad (1)$$

The total adsorption capacity in the binary solution mode is given by

$$\sum_{j=1}^2 ((Q_{j,o})_b) = (Q_{i,o})_b + (Q_{j,o})_b \quad (2)$$

Where  $(Q_{j,o})_s$  and  $(Q_{j,o})_b$  are the adsorption capacity of the pollutant j in the mono component and the binary solution.

The synergistic interaction plays a role when  $\sum_{j=1}^2 ((Q_{j,o})_b) > \sum_{j=1}^2 ((Q_{j,o})_s)$ . The antagonistic mechanism becomes important when  $\sum_{j=1}^2 ((Q_{j,o})_b) < \sum_{j=1}^2 ((Q_{j,o})_s)$ .

If the value of  $\sum_{j=1}^2 ((Q_{j,o})_b) = \sum_{j=1}^2 ((Q_{j,o})_s)$ , it signifies non interaction between the components in the solution [22].

#### 3.2. Selectivity ratio (S(i/j))

The ratio indicates the affinity of an adsorbent towards a component in a binary solution. It also helps to investigate the selective preference of an adsorbent to a component based on the surface structure, morphology and the pore distribution [23-26]. It is given by the equation

$$S(i/j) = \frac{(Q_{i,o})_b}{(Q_{j,o})_b} = \frac{(Q_{i,o})_s}{(Q_{j,o})_s} \quad (3)$$

The value of S(i/j) greater than one explains that the adsorbent has more affinity towards component i than component j.

#### 3.3. Relative percent adsorption $R_{Qi}$

The relative adsorption of a component in a binary solution is measured from the following expression [27]

$$R_{Qi} = \frac{(Q_{i,o})_b}{(Q_{i,o})_s} \times 100 \quad (4)$$

The value of  $R_{Qi}$  greater than 100 shows that synergistic interaction and a value lesser than 100 describes antagonistic interaction. The value of 100 signifies non interaction between the components in a solution.

#### 3.4. Sorption affinity $k_s^*$

It denotes the attraction of an adsorbent to a solute molecule in a binary solution [28]. It is helpful for comparing the adsorption capability of the adsorbents in a binary system. It is represented by the expression

$$k_s^* = \frac{(C_{i,o})}{(C_{i,s})_b} \quad (5)$$

where  $C_{i,o}$  is the initial concentration of component and  $(C_{i,s})_b$  is the concentration of solute in solid phase in binary solution. The lower the value of  $k_s^*$ , the stronger the affinity of the adsorbent to the solute molecule.

#### 3.5. Interaction factor $\theta_{ij}$ from sheindorf-rebuhn-sheintuch (SRS) equation [29-30]

The interaction factor from the SRS equation can be used to investigate the inhibition of adsorption of a component in a binary solution by another component. The equation is given as

$$(Q_{i,e})_b = k_i (C_{i,e})_b \left( \sum_{j=1}^N (\theta_{ij} (C_{j,e})_b) \right)^{(1/n_i)-1} \quad (6)$$

$(Q_{i,e})_b$  The equilibrium adsorption capacity for component i (mg/g),  $(C_{i,e})_b$  the equilibrium concentration of component i (mg/L) in the binary solution,  $k_i$  the Freundlich constant,  $n_i$  the adsorption intensity and  $N = 2$  for binary solution. The interaction factor  $\theta_{ij}$  shows the inhibition of adsorption of component i by another component j. The higher value of  $\theta_{ij}$  than  $\theta_{ji}$  signifies that component j will have strong inhibition on adsorption of component i. It also infers that component i may exhibit weak inhibition on the adsorption of component j [25].

#### 3.6. Interaction factor $\eta_i$ from modified competitive Langmuir isotherm (MCLI) equation [5-31]

The interaction factor from the MCLI equation is helpful in determining the interaction of a solute with the adsorbent in binary system. It also shows the competition among the adsorbates in a solution and is dependent on the concentration of the components in the solution. The equation is given by

$$(Q_{i,e})_b = \frac{(Q_{i,o})_b b_i ((C_{i,e})_b / \eta_i)}{1 + \sum_{j=1}^N (b_j ((C_{j,e})_b / \eta_j))} \quad (7)$$

$b_i$  Langmuir constant for component i (L/mg),  $\eta_i$  the interaction factor for component i and  $N = 2$  for binary solution. The higher the value of  $\eta_i$  shows the the lower the affinity of the solute i to the adsorbent [13-32].

#### 3.7. P factor

The comparison of mono component equilibrium data and the binary component data can be done using P factor. It describes the competitive adsorption of the components in a binary solution [11, 23-30]. It also explains how the adsorption of a component is in-

hibited by another component in a binary solution. It is given by the expression

$$P_{fi} = \frac{(Q_{i,o})_s}{(Q_{i,o})_b} \tag{8}$$

Where  $(Q_{i,o})_s$  and  $(Q_{i,o})_b$  are the adsorption capacity of the component  $i$  in the mono component and the binary system. The value of  $P_{fi}$  will determine the inhibition of adsorption of a component by another component in a binary solution [23]. The value of  $P_{fi}$  greater than one shows that the adsorption of component  $i$  is inhibited in the presence of another component. If  $P_{fi}$  is lower than unity, then it signifies that the adsorption of component  $i$  is enhanced in the presence of another component in the binary solution. The value of  $P_{fi}$  equal to unity suggests that the adsorption of the component is not hindered by any other component.

### 3.8. Inhibitory effect

The adsorption of an adsorbate may be inhibited by another component and is described by the inhibitory effect ( $\Delta IE$ ) [23], [24], [33]

$$\Delta IE = \frac{(Q_{i,o})_s - (Q_{i,o})_b}{(Q_{i,o})_s} \tag{9}$$

where  $(Q_{i,o})_s$  and  $(Q_{i,o})_b$  are the adsorption capacity of the pollutant  $i$  in the mono component and the binary solution. The higher value of  $\Delta IE$  shows that the adsorption of component  $i$  is suppressed to the maximum extent in the presence of other components.

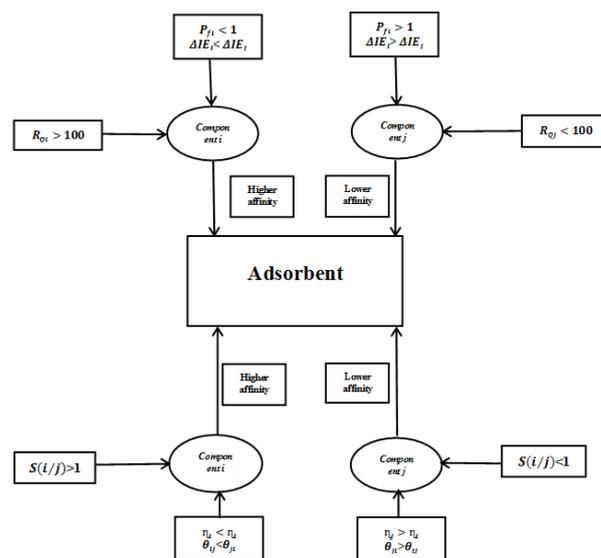


Fig. 1: The Schematic Representation of the Affinity of the Adsorbate to the Adsorbent Based on the Various Properties.

From the literature, various works are available which are carried out to study the interaction among the solute molecules in a binary solution. The works emphasize the adsorption of the adsorbate molecules onto the adsorbent, the adsorption capacity of the adsorbate in single and binary solution mode and the type of interaction. It also discusses the possible reason for the interaction among the components. Therefore the current study investigates the simultaneous adsorption of the various works available from the literature. The interaction effect among the components in the above investigation are determined from the additive rule. The components involved in simultaneous adsorption, the adsorption capacity for each component and the interaction mechanism are discussed below. The summarization of all the parameters involved in the study are listed in the Table 1.

Table 1: The Summarization of Simultaneous of the Pollutants by Different Adsorbents, their Adsorption Capacity in Single and Binary Solution Mode, Interaction Effect and the Reason for Interaction

Sl. No	Adsorbent	Pollutant 1	Pollutant 2	Experimental conditions	Ads capacity of 1 (single) (mg/g)	Ads capacity of 2 (single) (mg/g)	Ads capacity of 1 (binary) (mg/g)	Ads capacity of 2 (binary) (mg/g)	Interaction effect	Reason	Reference
1	Chitosan hydrogel	Erchrome black T	Reactive blue 2	Co 50-400 mg/L, pH 2-10, ads 0.02-0.065, 55°C,	184.6	178.3	90.99	73.54	Antagonistic	Affinity constant of the solute to the adsorbent	[6]
2	Ziziphus mauritiana	Basic Yellow 28	Basic Blue 41	Co 25-100 mg/L, ads 0.2 g/L, 30 min	200	217.39	133.15	190.83	Synergistic	Affinity constant	[8]
3	Coconut shell	Phenol	Cyanide	Co 100-1000 mg/L phenol 10-100 mg/L cyanide, ads 5-60 g/L, 120 rpm, 30°C	6.67	1.09	239.85	5.30	Synergistic	Freundlich constant	[11]
4	Tea waste biomass	Chromium	Phenol	Co 100-450 mg/L cr 50-225 ph, ads 2.5-20 g/L, pH 2-9, 30°C	33.328	7.50	199.52	9.48	Synergistic	Molecular structure, type of attractive forces	[12]

5	Bentonite	copper	cadmium	Co 50-700 mg/L, pH 5-6, ads 1g/30ml	5.30	5.22	4.70	4.96	Antagonistic	Ionic radius, ability to form stable complex	[16]
6	Leonardite	Cadmium(II)	Zinc(II)	Co 5-30 mg/L, ads 0.1g/100 ml, pH 6, 120 rpm	26.39	19.16	10	5	Antagonistic	Ionic properties, covalent index	[18]
7	Red mud	Remazol brilliant blue (RBB)	Disperse orange(DO)	Co RBB 50 mg/L, DO 130 mg/L, ads RBB 2.05g/L DO 0.88g/L	111	116	52	95	Antagonistic	Alteration of adsorbent surface, displacement effect	[20]
8	Natural clay	Copper	Zinc	Co 150-1600µL, pH 6, 200 rpm, 60 min	434.7	344.8	370.3	38.16	Antagonistic	Precipitation of metal	[23]
9	Magnetic iron oxide/ nano-composite (MNP3)	Methyl orange	Phenol	Co 20-100 mg/L, ads 0.5-4 g/L, 25°C, 200 rpm	72.67	42.34	71.01	19.02	Antagonistic	Electrostatic and non-electrostatic interactions	[26]
10	Rice husk ash	Cadmium (II)	Nickel (II)	Co Cd 0.8897 mmol/L	0.0256	0.0764	0.0083	0.0233	Antagonistic	Size of the metal ions	[29]
11	Biochar	Methyl red	Methylene blue	Co Ni 1.7036 mmol/L	156.25	256.41	97.85	174.19	Antagonistic	Size and ionization of molecules	[34]
12	Iron oxide-vermiculite composite	Copper	Nickel	Co MR 150 mg/L MB 200 mg/L	53.14	94.69	59.7	101.3	Synergistic	Affinity constant and binding energy of solute with adsorbent	[35]
13	Activated carbon	Chromium	Fluoride	Co 1000 mg/L, Vmt 10 g/L, contact time 30 min, rpm 500 pH 4.5	3.136	2.922	49.07	2.740	Synergistic	Electrostatic attraction of ions	[36]
14	Cyanoguanidine-Crosslinked Chitosan	Food yellow 4	Food blue 2	Co 10- 100 mg/L, pH 7.2	915.36	825.55	667.98	565.14	Antagonistic	Molecular weight and molecular polarity	[37]
15	Cystoseira indica	Uranium	Nickel	Co 50 to 400 mg/g, pH 3, ads 25 mg, 100 rpm, 24 h, 298 K	334.34	53.47	208.79	47.63	Antagonistic	Electro negativity of solute	[38]
16	Clinoptilolite	Methyl orange	Cadmium	Co 90mg/L, flow rate 0.7 mL/min, Co 0-1.24 mmol/L, ads 2g/L, 360 min, 298 K	0.305	0.282	0.52	0.566	Synergistic	Distribution coefficient	[39]
17	Rice straw biochar	cadmium	Sulfamethoxazole (SMX)	Co cd 5-100 mg/L, Co SMX 5-200 mg/L, pH 6, ads 0.05 g/L, Co 10-125 mg/L, pH 5, ads 50 mg	34129.69	35919.54	1827.82	9182.74	Antagonistic	Sorption affinity based on metal complex	[40]
18	Ferrihydrite	Arsenic (III)	Arsenic (V)	Co 50 mg/L, ads 0.1 g/100 mL, 150 rpm, 30°C	87.43	42.39	71	35.85	Antagonistic	Electrostatic interaction	[41]
19	Bottom ash	cadmium	zinc		11.34	12.08	6.06	7.72	Antagonistic	Ionic radius of metal ions	[42]

20	Leonardite	copper	nickel	Co 0.0314-4.409 mmol/dm <sup>3</sup> , ads 1g/dm <sup>3</sup> , 25°C, 2h	0.33 mmol/g	0.26 mmol/g	0.30 mmol/g	0.10 mmol/g	Antagonistic	Ionic potential	[43]
21	Pistichio shells	Methylene blue	Rhodamine B	Co 0-60 mg/L, ads 0.1 g/100 cm <sup>2</sup> , Co 25-250 mg/dm <sup>3</sup> , ads 10cm <sup>3</sup> in 90 cm <sup>3</sup> , 24 h, 5000 rpm, 25°C	124	79	56.5	74.7	Antagonistic	Molecular diameter, weight, volume	[44]
22	Chlorella vulgaris	Chromium	Iron	Co 500µg/L arsenic, 10000 µg/L fluoride, pH 5, ads 20 g/L, 300 min	27.27	24.49	18.7	11.8	Antagonistic	Affinity constant	[45]
23	Laterite	arsenic	fluoride	Co 5 mg/L atrazine 30 mg/L	0.769	0.526	5.98	0.413	Synergistic	Surface charge of the metal ions	[46]
24	Carbon nanotube	Atrazine	Copper	copper ads 0.2 g/L, pH 3-9	40.16	38.91	17.75	18.85	Antagonistic	Electrostatic attraction and steric effect	[47]
25	Beidellite	cadmium	lead	Co lead 100 mg/L, cadmium 50 mg/L, ads 0.2 g/50ml, 45°C, 250 rpm	45.66	86.95	30	50	Antagonistic	Ionic radius, ionic potential	[48]
26	Pulp waste	Methylene blue	Methyl orange	Co 100 mg/L, ads 5-40 mg, 40°C, 180 rpm	251	285.71	157.48	142.85	Antagonistic	Electrostatic attraction, functional groups of the adsorbent	[49]
27	Rice husk ash	Resorcinol	Phenol	Co resorcinol 4.213 mmol/L phenol 5.305 mmol/L, ads 20g/L, 150 rpm, 30°C	0.103 mmol/g	0.096 mmol/g	0.061	0.066	Antagonistic	Affinity constant, π-π interaction	[50]
28	Ulva sp.	Chromium	Manganese	Co 10 mmol/L, ads 0.2g, 160 rpm, 25°C	2.75 mmol/g	0.75 mmol/g	1.75 mmol/g	0.25 mmol/g	Antagonistic	Electronegativity of the metal ions	[51]
29	Magnetic composite carbon	Lead	Aniline	Co 50 mg/L, ads 0.05g/50mL, 220 rpm, 300 min	67.1	90.91	99.8	206.6	Synergistic	Ionization of metal, electrostatic forces	[52]
30	Activated sludge	Chromium	Phenol	Co 50-500 mg/L, ads 1.5 g of activated sludge	18.4	8.0	9.0	2.1	Antagonistic	Affinity constant, inhibitory effect	[53]
31	Activated carbon and Saccharomyces cerevisiae	Copper	Lead	Co copper 20-250 mg/L, lead 25-300 mg/L, ads 0.5-5g	74.18	177.84	55.12	164.5	Antagonistic	Ion charge density, bonding, reduction potential	[54]
32	Activated carbon and chitosan composite	Phenol	Copper	Co phenol 20-250 mg/L, copper 100-600 mg/L ads	34.188	74.349	34.483	70.522	Synergistic	Ionization of the molecules, type of attractive forces	[55]

33	Anaerobic activated sludge	Phenol	Chromium	0.3g/50mL, Co 100 mg/dm <sup>3</sup> , ads 0.5 g/dm <sup>3</sup>	74.2	88.6	50.3	70.2	Antagonistic	Functional groups, ionic size	[56]
34	Activated carbon	Cadmium	Zinc	Co 0-50 mg/L, ads 0.5g/0.1L, 20°C	0.01 mmol/g	0.052 mmol/g	0.028 mmol/g	0.04 mmol/g	Synergistic	Size of metal ions	[57]
35	Activated carbon cloth	Lead	Phenol	Co Ph 0-0.4 mmol/L, Pb 0-0.8 mmol/L, ads 0.1 g	0.14 mmol/g	0.31 mmol/g	0.13 mmol/g	0.54 mmol/g	Synergistic	$\pi$ - $\pi$ interaction, dipole attractions	[58]
36	Tea fibre waste	Phenol	Nickel	Co Ph 0-100 mg/l, Ni 0-40 mg/l, ads 0.25-2 g/250 ml, pH 4-8, 8 hrs	5.17	10.49	5.75	13.25	Synergistic	Increase in the interfacial surface between solute and adsorbent	[59]
37	Lantana camara	Cobalt	Nickel	Co 10-50 mg/L, ads 1g/250 mL, pH 7, 12 hrs	5.2576	5.1308	7.4536	8.3420	Synergistic	Affinity of the metal to the adsorbent	[60]
		Lead	Cadmium		10.8459	7.2727	9.9706	6.2894	Antagonistic		

The adsorption of nickel and cadmium onto rice husk ash was carried out by Srivatsava et al. [29]. It was investigated that the adsorption of Ni(II) was higher than Cd(II). This is due to the size of the molecules. Nickel and cadmium are having molecular size of 1.62 Å and 1.71 Å respectively. Therefore the small sized nickel molecules can penetrate inside the pores of the adsorbent. Thus the adsorption capacity of nickel molecules are more. The system exhibits antagonistic type of interaction between the solute molecules [29].

In the work reported by Wang et al. [34] on the adsorption of methyl red and methylene blue onto biochar, the adsorption of the molecules happens by size and ionization of molecules. Because of the variation in the above factors at equilibrium and different states was used to determine the interaction between the molecules [34].

The simultaneous adsorption of nickel and copper onto iron oxide-vermiculite composite was investigated by Gharin Nashtifan et al. [35]. It was reported that the affinity constant for nickel and copper towards the adsorbent was 0.0048 L/mg and 0.0044 L/mg respectively. The binding energy of the metal ions with the functional groups of the adsorbent was found to be 114.3 J/mol and 298.2 J/mol for nickel and copper respectively showing that nickel had more adsorption towards the adsorbent. It was reported that affinity constant and binding energy were used for determining the interaction factor. The system exhibited synergic type of interaction [35].

The adsorption capacity of erichrome black T was higher compared to reactive blue [2] over chitosan hydrogel because of the varying values of affinity constant. The values of affinity constant were found to be 1.121L/mg and 0.897 L/mg for erichrome black T and reactive blue respectively. The antagonistic type of interaction was observed for the system [6].

The electrostatic attraction was found to enhance the adsorption of chromium over activated carbon electrode when compared to fluoride. The hydrated radius of Fluoride and chromium were reported as 3.52 Å and 3.75 Å respectively. Therefore, the electrosorption selectivity of the divalent chromate ions were stronger compared to monovalent fluoride ions [36].

The adsorption of reactive orange 16 and reactive brilliant blue R onto polyaniline polysaccharide composite was carried out. The selectivity ratio was used for finding the affinity of the solute towards the adsorbent. The selectivity ratio of reactive brilliant blue

with respect to reactive orange was obtained as 1.08-1.31 showing that reactive brilliant blue has more affinity to the adsorbent compared to reactive orange. This may be due to the reason that sulfonated species in the reactive brilliant blue combines with the amine group of the adsorbent faster compared to reactive orange [31].

It was studied that the adsorption happens because of the molecular weight and the molecular polarity of the solute molecules. Food Yellow 4 showed higher adsorption compared to Food Blue 2 because it possessed one carboxylic group and two sulfonated groups, high molecular weight and high solubility. It showed antagonistic type of behavior [37].

Based on the electronegativity of nickel (1.91) and uranium (1.38) it was studied that the oxygen containing groups on the adsorbent surface like carboxylic, sulfonic and hydroxyl groups repels with the molecule having high electronegativity value. Therefore nickel molecule will repel with the adsorbent. Antagonistic interaction was observed in the solution [38].

The adsorption of methyl orange and cadmium onto clinoptilolite was carried out by Zou et al. The interaction between the solutes was formed due to difference in the distribution coefficient value. The distribution coefficient value for methyl orange was obtained in the range of 1.1 to 2.5 L/g and for cadmium 0.8 to 1.1 L/g. The binary solution exhibited synergic behavior between the solutes [39].

Han et al. studied the simultaneous adsorption of cadmium and sulfamethoxazole (SMX) onto rice straw biochar. Cadmium showed higher adsorption over sulfmethoxazole (SMX) because of  $\pi$ - $\pi$  electron donor acceptor mechanism. Antagonistic interaction was investigated from the binary system [40].

Qi and Picher reported the adsorption of arsenic (III) and arsenic (V) onto ferrihydrite as adsorbent. It was observed that the adsorption of arsenic (III) was more compared to arsenic (V). This was mainly because of the electrostatic attraction present and also because of coulombic force and Lewis acid-base interactions existing between the solute and the adsorbent [41].

The binary adsorption of cadmium and zinc to leonardite was studied by Terdputtakun et al. It was noted that the system is showing antagonistic type of interaction. Cadmium is said to adsorb more quantity when compared to zinc because of the ionic properties, high affinity towards the adsorbent, electronegativity and covalent index. The higher the covalent index value of the

solute, the better the ability to build covalent bonds with adsorbent. The system showed antagonistic type of behavior [18].

Natural clay was used to remove copper and zinc from wastewater. The adsorption of copper was more when compared to zinc the formation of  $\text{CuCO}_3$  was more because of precipitation. The copper carbonate formed due to the presence of carbonates in clay and the binary solution interacted antagonistically [23].

The ionic radius of cadmium and zinc affected the binary adsorption of the metal ions from wastewater. The ionic radius of cadmium and zinc were found to be 97 pm and 74 pm respectively. The radius values in the hydrated form were 430 pm and 426 pm for cadmium and zinc respectively. Therefore smaller the radius, more easily it will penetrate inside the adsorbent. Thus the adsorption of zinc was more compared to cadmium ions [42].

The ionic potential or electronegativity value of the metal ions was used as the basis for finding the interaction mechanism in the adsorption of nickel and copper onto leonardite. The ionic potential of nickel and copper was 2.50 and 2.89. Copper having the highest electronegativity value was found to adsorb on the specific functional groups present on the adsorbent surface. The system followed antagonistic type of interaction [43].

The adsorption of methylene blue and rhodamine B onto pistachio shells were carried out by Attia et al. [44]. The adsorption system antagonistic type of behavior. This may because of molecular diameter, molecular weight and due to solubility of the molecules [44].

In the work reported Aksu et al. [45] on the adsorption of iron and chromium onto *Chlorella vulgaris*, antagonism was observed. The affinity constants were obtained as 0.052 and 0.028 for chromium and iron respectively. Therefore chromium had more affinity towards the adsorbent [45].

Olu-Owolabi et al. investigated the removal of copper and cadmium from wastewater onto bentonite. The interaction of the solutes with adsorbent was defined based on the ionic radius and the ability of the metal ions to form stable complexes with the surface of the adsorbent. It was reported that the ionic radius of copper and cadmium were found to be 0.73 Å and 0.97 Å respectively. It was also studied that cadmium forms complexes like sulfhydryl and amino groups, while copper forms carbonate, phosphate, hydroxyl complexes. Thus copper is having more adsorption capacity compared to cadmium [16].

The simultaneous removal of arsenic and fluoride onto lanterite was discussed in the work reported by Rathore et al. [46]. The interaction between the solutes and the adsorbent was explained based on the surface charges formed on the metal ions and the adsorbent surface. It was found that the adsorption of arsenic was more compared to fluoride. The synergism was found with the interaction of solutes in the system [46].

In the adsorption of basic yellow 28 and basic blue 41 onto *Persea americana* nuts, the interaction effects were described by affinity constants of the solute to the adsorbent. The affinity constants for the solutes in the binary system reported were 0.12 and 0.07 L/mg for basic blue 41 and basic yellow 28 respectively. The basic blue 41 showed higher adsorption over basic yellow 28 and the system exhibited synergic type of behavior [8].

Magnetic walled carbon nanotubes were used for the simultaneous adsorption of atrazine and copper from wastewater. It was thought the formation of metal complexes were formed on the surface of the adsorbent. The system showed higher adsorption when the components are present in single component solution model [47].

The adsorption of methyl orange and phenol onto Magnetic iron oxide based nanocomposite (MNP3) was investigated by Istrate et al. The adsorption of methyl orange was higher compared to phenol because methyl orange adsorption was explained by both electrostatic and non electrostatic forces but phenol adsorption was due to non electrostatic forces. It was explained based on the solubility of the solute (i.e. methyl orange 5 g/L and phenol 83 g/L) [26].

The research carried by Etcı et al. showed the simultaneous adsorption of lead and cadmium onto beidellite. The interaction mechanism was discussed by various parameters such as ionic

radius, ionic potential. The ionic radius of lead and cadmium were 1.21 Å and 0.97 Å respectively. The metal ions attract water molecules and forms complex of hydrated radius which is smaller for lead than cadmium. Therefore the complex with smaller hydrated radius can penetrate inside the pores of the adsorbent. The electronegativity values for lead and cadmium were 2.33 and 1.69 respectively. This also contributed to enhanced adsorption of lead over cadmium [48].

The work presented by Ahmaruzzaman and Reza discussed the simultaneous adsorption of methylene blue and methyl orange onto the pulp waste source. The interaction between the solutes was explained based on various aspects such as electrostatic interaction, the functional groups present on the adsorbent, surface chemistry with respect to adsorbent. The system exhibited antagonistic type of interaction [49].

The binary mixture of resorcinol and phenol was adsorbed onto rice husk ash and discussed in the work. The interaction formed between the solutes and the adsorbent was defined by the affinity constant and  $\pi$ - $\pi$  interaction. The values of affinity constants were calculated as 0.0624 and 0.0468 for resorcinol and phenol respectively, showing stronger affinity of resorcinol towards the adsorbent. The substitution of hydroxyl group takes place with resorcinol, thus the  $\pi$ - $\pi$  interaction leads to adsorption of resorcinol with the adsorbent [50].

In the work reported by Singh and Balomajumder on the adsorption of phenol and cyanide to coconut shell as adsorbent the Freundlich constant was used as the determining factor for investigating the interaction. The Freundlich constant was found to be 2.38 and 0.41 for phenol and cyanide respectively. Thus the adsorption of phenol was more compared to cyanide. The system showed synergistic type of interaction [11].

Tea waste biomass was used as adsorbent to remove chromium and phenol from binary solution. The adsorption of chromium was higher than phenol. The possible reason may be because of various factors such as functional groups, structure of the adsorbent, size, shape and molecular nature of solutes present. It was also explained that chromium gets attracted to the functional groups present on the adsorbent, while phenol gets attached to the adsorbent surface through weak van der Waals forces and  $\pi$ - $\pi$  interaction. The binary system represents synergic type of behavior [12].

The removal of metal ions chromium and manganese on Ulva sp. were studied Vijayaraghavan and Joshi. Chromium had more affinity to the adsorbent compared to manganese because of electronegativity. The values of electronegativity were 1.66 and 1.55 for chromium and manganese respectively. The binary solution showed antagonistic type of behavior [51].

The simultaneous adsorption of lead and aniline onto magnetic composite material was carried out by Kakavandi et al. It was studied that the ionization of the ions and the electrostatic attractive and repulsive forces were considered responsible for the interaction between the solutes present in the solution. The synergistic type of interaction was obtained in the binary system [52].

Activated sludge was used as the adsorbent for the removal of chromium and phenol from wastewater. The chromium adsorption was more compared to the adsorption of phenol. It may be because of the reason that the affinity constant of chromium to the adsorbent was higher compared to phenol. It is also because of chromium had inhibitory effect on the adsorption of phenol in the binary system [53].

The adsorption of Remazol brilliant blue and Disperse orange dye onto red mud was investigated. The adsorption of disperse orange dye was superior compared to remazol brilliant blue and the system was exhibiting antagonistic type of interaction inside the system. The interaction is because of various reasons such as alteration of the adsorbent surface after adsorption, displacement effect where one component replaces another component from the active sites and blocking of adsorbent sites to enhance adsorption [20].

The combined activated carbon and *Saccharomyces cerevisiae* was used as adsorbent for the simultaneous removal of copper and lead from the binary solution. Various factors such as Ion charge density, bonding, reduction potential, ionic size of the components

and adsorbent properties were considered for finding the interaction between the components. The system shows antagonistic type of behavior [54].

In the work reported by Liu et al. activated carbon and chitosan composite was used for the adsorption of copper and phenol from binary solution. The adsorption capacity of copper was higher over component phenol. The ionization of the components was an important factor in determining the interaction factor. It was also explained that the adsorption between phenol and adsorbent was due to van der Waals forces (physical adsorption) and that between copper and the carbon was because of chemical adsorption [55].

The potential of anaerobic activated sludge as adsorbent for the removal of phenol and chromium was investigated by Aksu and Akpınar. Various parameters like functional groups and structure of the adsorbent, ionic size and molecular structure of solutes were considered for determining the interactive force between the components. The adsorption of chromium was better in comparison with phenol adsorption. The system shows antagonistic type of interaction [56].

The adsorption of zinc and cadmium onto activated carbon was discussed by Erto et al. It was reported that the interaction mechanism was because of size of the metal ions which penetrates into the pores of the adsorbent. The size of the zinc ions are smaller compared to cadmium ions. Therefore, the adsorption of zinc was more in the binary solution and the system exhibits synergism [57].

Activated carbon cloth was used as adsorbent for the simultaneous adsorption of lead and phenol. It was reported that the adsorption of phenol was superior compared to lead. This is probably due to the dipole attraction and  $\pi$ - $\pi$  interaction between the porous layers of the adsorbent and the benzene ring. It is also because of the reason that phenol causes steric hindrance on the adsorbent surface to lead adsorption. Synergistic type of behavior was obtained in the binary system [58].

The adsorption of phenol and nickel from wastewater was studied using tea fibre waste as adsorbent by Karania et al. It was reported that phenol showed synergism on nickel, while nickel was having synergistic influence on phenol adsorption. This may be because of the reason that by increasing concentration, the interfacial area between the component and the solid surface increases [59].

The removal of cobalt, nickel, cadmium and lead from wastewater using Lantana camara was studied by Robert and Girish. It was investigated that cobalt and nickel when present in binary solution with other components exhibited synergistic effect. Cadmium and lead in binary combination with other metals showed antagonistic effect. The possible reasons for the interaction are affinity of the adsorbent towards the adsorbent and the competition of the metal ions for the active sites on the adsorbent surface [60].

#### 4. Conclusion

The present study showed that adsorption can be used efficiently for the removal of pollutants from a binary solution. The interaction among the components in the simultaneous adsorption of the pollutants is important in understanding the efficacy of the process for the treatment of industrial wastewater. The study was able to determine the interactive mechanism using various concepts. It was investigated that various factors such as ionic size, ionic potential, affinity constant of the solute, the functional groups present on the adsorbent and porous nature of the adsorbent and also the electrostatic attractive and repulsive forces between the adsorbent and the pollutant molecules play an important role in determining the interaction mechanism. It was found from the review that both synergistic and antagonistic type of interaction happens between the components in the solution under different experimental conditions. Therefore it is helpful in finding the dominating pollutant present in wastewater, when the system becomes complicated.

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