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Adsorptive removal of nitrogen, phosphorus, and micropollutants in sewage wastewater by using different sorbents: application of ANOVA

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ABSTRACT

The present research work involved the effectiveness of seven different sorbents (three inorganics, three organic, and one biopolymer) in eliminating sixteen micropollutants (dyes, metals, organophosphates, pharmaceuticals, pesticides, food additives, surfactants, and cosmetics), nitrogen and phosphorus was investigated in batch mode study using wastewater. Three inorganic sorbents were silica gel/rice flour decorated biochar, Ca/rice flour decorated biochar and bentonite clay whereas organic materials comprised of organic charcoal, fruit peel (kiwi) and *Aloe vera* and one biopolymer was magnetic, silica gel chitosan beads. The maximum nitrogen (93%) and phosphorus (73%) were removed by inorganic sorbents efficiently as compared to other sorbents. Maximum dyes removal was occurred by magnetic, silica gel chitosan beads (96%), whereas the highest metals (93%) and pesticides (94%) removal were investigated by using inorganic sorbents. The surfactants and pharmaceuticals showed promising removal y using organic sorbents. Magnetic, silica gel chitosan beads showed the highest removal efficiency (93%–97%) for food additives. Whereas cosmetics and organophosphates were moderately eliminated by all sorbents. Analysis of variance was applied to data to calculate the difference in removal capacity. The results showed that both Langmuir and Freundlich's isotherms were best fitted to experimental data.

Keywords: Micro-pollutants; Sorbents; Equilibrium study; Analysis of variance; pH effect

1. Introduction

The presence of organic and inorganic micropollutants including natural and synthesized in sewage wastewater can affect the environment as well as the quality of water badly [1]. These micropollutants include pesticides, food additives, cosmetics, surfactants, dyes, metals, pharmaceuticals, and organophosphates pose a major problem for human beings and aquatic organisms [2]. Even minor concentration of these pollutants cause serious damage [3]. A large number of wastewater treatments have been investigated for the removal of micropollutants from sewage wastewater, including abiotic transformation, biodegradation [4], membrane bioreactors [5] and ozonation [6]. But some techniques are not cost-effective and others may generate toxic byproducts [7]. Micro-pollutants can be removed efficiently through sorption processes [8].

Sorption process of micropollutants in sewage wastewater depends upon various factors such as properties of wastewater (pH, micropollutants concentration), the characteristics of sorbents (surface area, size of particles) and physical interaction with sorbents [9]. The presence of dyes in wastewater affects human health seriously due to their carcinogenetic and toxic nature [10]. Metals intake can cause failure of the nervous and cardiac system as well as inhibition of enzyme activity [11]. Increased quantity of nutrients in water triggers the expansion of blue-green algae which leads to the deficiency of oxygen. Nitrogen along

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with phosphorus reduces the growth of plants. So wastewater treatments require the reduction of these nutrients in water [12]. Along with the above micropollutants, humans and aquatic organisms are also affected by pharmaceuticals pollution. Functions of hormones are disturbed by some pharmaceuticals [8]. Water contaminated with pesticides is also problematic as pesticides may cause mutation in living organisms [13]. The effect of food additives on our ecosystem is highly concerned because some of them are released unchanged and disturbed aquatic life [14]. Surfactants are widely used in our daily life. So, water becomes polluted due to the high consumption of surfactants [15]. Cosmetics and personal healthcare products are manufactured as persistent substances. Their concentration in groundwater has reached up to 100 μg L^{-1} that is alarming [16].

Activated carbon has been commonly and efficiently used sorbent for micropollutants uptake from wastewater [17]. Granular activated carbon is also a promising adsorbent but its effectiveness depends upon the type used and highly costly [18]. Some other adsorbents such as lignite, zeolite, and sand have been investigated and found good removal potential for many pollutants [19]. Chitosan, a polymer is also studied as a cost-effective sorbent for various dyes removal [20]. But alternative sorbents are always getting the interest of scientists.

The main objective of this study was to investigate better sorbent for uptake of micropollutants and nutrients from sewage water as these are harmful and toxic. In a batch study for removal of micropollutants (dyes, metals, organophosphates, pharmaceuticals, pesticides, food additive, surfactants, and cosmetics), and nutrients (nitrogen and phosphorus) various inorganic and organic sorbents were tested.

2. Materials and methods

2.1. Chemicals

Chemicals used in this study were of analytical grade and acquired from Sigma-Aldrich and Merck.

2.2. Sorbent materials

The choice of sorbent materials was based on their applicability and literature survey. Three inorganics, three organic and one biopolymer, consisting of natural and modified materials were investigated. Three inorganic sorbents were silica gel/rice flour decorated biochar, Ca/rice flour decorated biochar and bentonite clay whereas organic materials comprised of organic charcoal (OC), fruit peel (kiwi) (FP) and *Aloe vera* and one biopolymer was magnetic, silica gel chitosan beads (Table 1).

Table 1
Sorbent materials used in batch study

Sorbent	Abbreviation	Particle size	Surface area pore size	
		(mm)	(m^2 g^{-1})	(nm)
Inorganic				
Silica gel/rice flour decorated biochar	SR-biochar	0.20–0.35	0.5	3.7
Barium/rice flour decorated biochar	BR-biochar	0.25–0.40	0.4	4.0
Bentonite clay	B-clay	3–5	2.0	24
Biopolymer				
Magnetic silica gel chitosan beads	MSG-beads	2–4	8.0	18
Organic				
Organic charcoal	OC	1.0–2.5	6.5	13.5
Fruit peel (kiwi)	FP	0.5–1.0	2.5	14.0
Aloe vera	AV	1–3	3.0	10.0

2.3. Preparation of sorbents

For the preparation of biochar, rice flour was obtained from the market and dried it at 100°C to remove all moisture contents. Silica gel/rice flour decorated biochar, calcium/rice flour decorated biochar were synthesized through carbonization at 800°C. Silica gel and rice flour, $Ca(OH)_2$ and rice flour were mixed in equal ratio. After the addition of distilled water, dilute gels were formed and stirred to form the homogeneous mixture. Then the mixture was put in an oven to remove moisture, the dried mixture was put in a furnace at 800°C in the presence of nitrogen for 2 h. The dried biochar was named as Sg-BC (Silica gel/rice flour decorated biochar) and Ca-BC (calcium/rice flour decorated biochar) [21].

Bentonite clay and OC were purchased from the market. Magnetic, silica gel chitosan beads were synthesized by Wang et al. [22]. Silica gel suspension was made by adding 3 g of silica gel in 40 ml of water with constant stirring of 30 min. Then 1.5 g of chitosan was mixed with constant stirring to silica gel suspension. Then 5 ml of $FeCl_3$ solution was added and stirred it continuously for 30 min to obtain a homogenous mixture. Then the mixture was added dropwise into a crosslinking solution prepared by mixing sodium citrate and sodium hydroxide. The obtained beads were washed and stored.

Kiwi FP was obtained from the market and then washed with distilled water to remove impurities. After that kept it under sunlight for 10 d and then it was dried in an oven for about 12 h at 70°C. Then the peel was ground, sieved and stored in plastic bottles.

Aloe vera leaves were obtained from a plant. After washing with water, the skin was removed carefully from the gel. First, the skin was dried in sunlight, then in an oven at 60°C. Then it was ground with a food processor, sieved and stored.

2.4. Micropollutants, preparation, and analysis

The micropollutants evaluated including dyes, metals, organophosphates, pharmaceuticals, pesticides, food additives, surfactants, cosmetics, phosphorus and nitrogen (Table 2). For the preparation of the sample solution, 8 μL of a standard solution of each chemical compound was added in 44 L of wastewater solution to make a concentration of 4 μg L^{-1} of each component. This wastewater sample was stored in dark glass bottles at 4°C–5°C. Instrument analysis

Table 2
Standard micro-pollutants used in batch study

Compound	Component	Abbreviation
Dyes	Reactive Red 22	RR22
	Direct Blue 17	DB17
Metals	Cu^{+2}	Cu^{+2}
	As^{III}	As^{III}
Organophosphates	Triphenyl phosphate	TPP
	Malathion	MT
Pharmaceuticals	Caffeine	CF
	Amocolline	AM
Pesticides	Hexafluorobenzene	HFB
	Atrazine	AZ
Food additives	α-Tocopheryl acetate	α-TPA
	Monosodium glutamate	MSG
Surfactants	Dodecyldimethylamine oxide	DDO
	Amide alcohol ethoxylates	AAE
Cosmetics	Galaxolide	HHCB
	Oxybenzone	OB

was done by using high-performance liquid chromatography which is coupled with a mass spectrometric technique.

2.5. Batch sorption studies

The effect of different parameters such as pH, wastewater concentration and contact time was evaluated through batch experiments. A wastewater solution containing micropollutants of known pH, concentration, sorbent dose was shaken for 4 h at 100 rpm at 25°C. The same conditions were given to a blank solution except for the sorbent. Selected pHs (2, 4, 6, 8, and 10) were used to study the pH effect. Isotherm's study was conducted by applying various isotherm models such as Langmuir [23], Freundlich [24] and Harkins–Jura [25] isotherm models. The percentage of sorption was evaluated through the following equation,

$$\%\text{sorption} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

C_0 is the initial and C_e are the equilibrium concentrations of a sample solution, respectively. The mean values of results are reported after conducting triplicate experiments.

2.6. Statistical analysis (ANOVA)

Analysis of variance (ANOVA) is a statistical analysis tool which divides the variation into different parts and every part is linked with different variation source [26]. ANOVA and the least significance difference test were applied to data to calculate the difference in removal capacity. The removal capacity was tested as a dependent variable and various sorbents and micropollutants were considered as independent variables.

3. Results and discussions

3.1. Effect of pH changes

Nitrogen removal from the sample is affected by a change in pH value. Inorganic sorbents eliminated nitrogen more effectively as compared to organic sorbents. The maximum nitrogen was removed (87%–90%) at pH 8 with Ca/rice flour decorated biochar and silica gel/rice flour decorated biochar. Nitrification is inhibited at high pH value which decreased the nitrogen removal efficiency [27]. Maximum phosphorus removal (73%) was achieved by Ca/rice flour decorated biochar at alkaline pH. Calcium-containing sorbents facilitated the formation of calcium-phosphorus precipitates [28]. Whereas other sorbents showed an average removal rate of phosphorus.

Maximum dyes removal was occurred by magnetic, silica gel chitosan beads and FP sorbents. The adsorption process was high due to chelating and ion-exchange reactions of chitosan which enhanced the sorption function of silica gel [29]. The maximum dye removal (90%–96%) was gained at low pH value and decreased with an increase in pH value up to 10%. At high pH value, there was a decrease in protonating sites that interacted with dye's functional groups [10]. The highest metal concentration was removed (92%–96%) at pH 4 by bentonite clay and about 93% by silica gel/rice flour decorated biochar at pH 10. Krstic et al. [30] studied the copper ion sorption and found the optimum pH value around 3–8. The sorption potential decreased with an increase in pH value in all other sorbents which may be due to an increase in repulsion between sorbent surfaces and ionic Arsenic species [31].

The chemicals such as cosmetics and organophosphates were moderately eliminated by all sorbents with 63%–75% removal at lower pH value. Whereas the removal efficiency of pesticides was maximum with inorganic sorbents. Bentonite clay and silica gel/rice flour decorated biochar showed the highest removal (94%–96%) at pH 2. The highest sorption was might be due to hydrophobic forces of attraction between chemicals and sorbent materials [2]. The pharmaceuticals were absorbed mostly by organic sorbents as compared to inorganic and biopolymer sorbents. Charcoal exhibited the highest sorption capacity of about 93%–97% at low pH value. This seemed the occurrence of functional groups on the sorbent's surface [32]. Two types of food additives were tested on various sorbents. Magnetic, silica gel chitosan beads showed the highest removal efficiency (93%–97%) for both food additives. This efficiency decreased with an increase in the pH value. Whereas charcoal was the promising sorbent for the removal of surfactants at pH 2 with removal efficiency up to 96%. This could be explained by the hydrophobic interactions between chemicals and sorbents [33]. The effect of pH on the removal of pollutants by various sorbents are shown in Figs. 1–10. The sorbents affect the sorption efficiency ($p < 0.05$, ANOVA) of micropollutants, which is illustrated in Table 3. The sorption efficiency of FP was lowered as compared to other sorbents.

3.2. Sorption isotherm behavior

Isotherm model study is carried out to optimize various parameters. In this study three isotherm models Langmuir, Freundlich, and Harkins–Jura were interpreted.

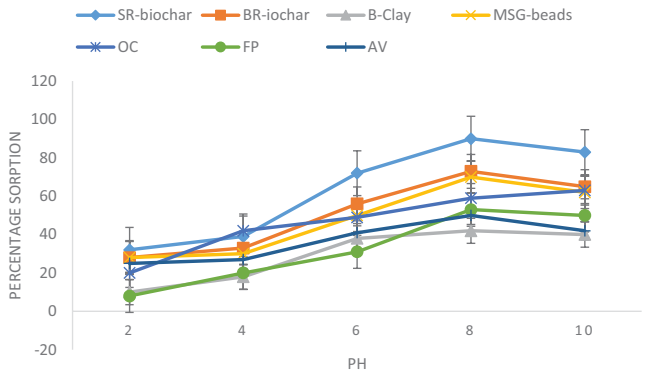

Fig. 1. Effect of pH on the removal of N_2 by various sorbents.

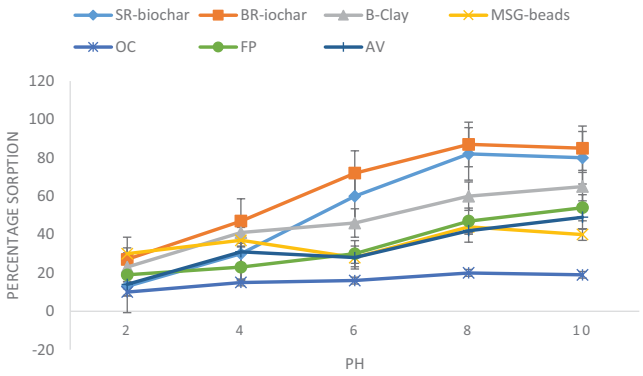

Fig. 2. Effect of pH on the removal of P by various sorbents.

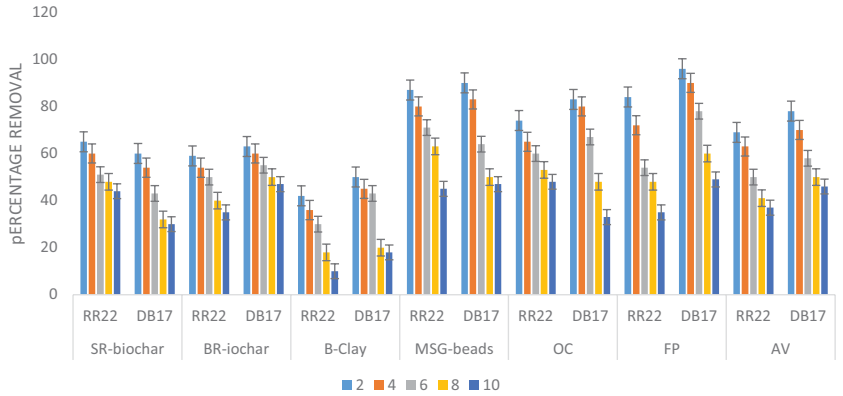

Fig. 3. Effect of pH on the removal of dyes by various sorbents.

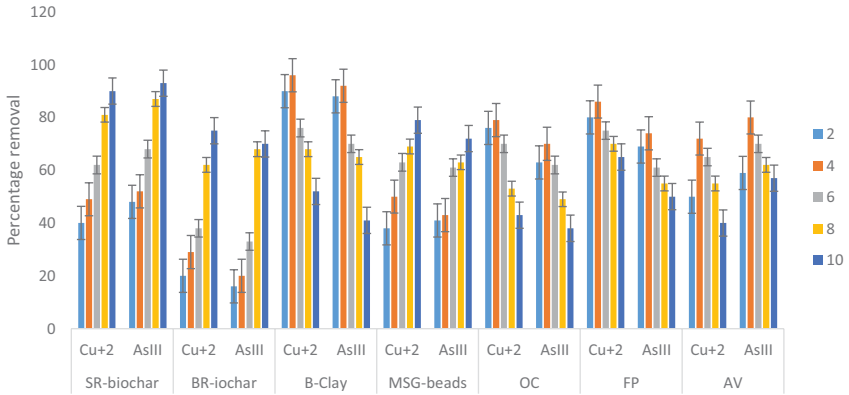

Fig. 4. Effect of pH on the removal of metals by various sorbents.

3.2.1. Langmuir sorption isotherm model

The Langmuir model suggests the homogenous monolayer sorption on sorption surface sites and when the saturation level is achieved, then no further sorption occurs [33].

The Langmuir model is expressed as:

$$\frac{C_e}{q_e} = \frac{1}{K_a q_m} + \frac{C_e}{q_m} \quad (2)$$

According to equation q_e is the amount of micropollutants sorption (mg g^{-1}), C_e is the concentration at equilibrium, q_m is the highest sorption capacity (mg g^{-1}) and K_a is sorption constant (L mg^{-1}). The values of various constants are illustrated in Table 4. The R^2 values described the best applicability of this model.

3.2.2. Freundlich sorption isotherm model

The Freundlich model explains the heterogeneous sorption. This isotherm shows the empirical relationship between liquid and solid [31].

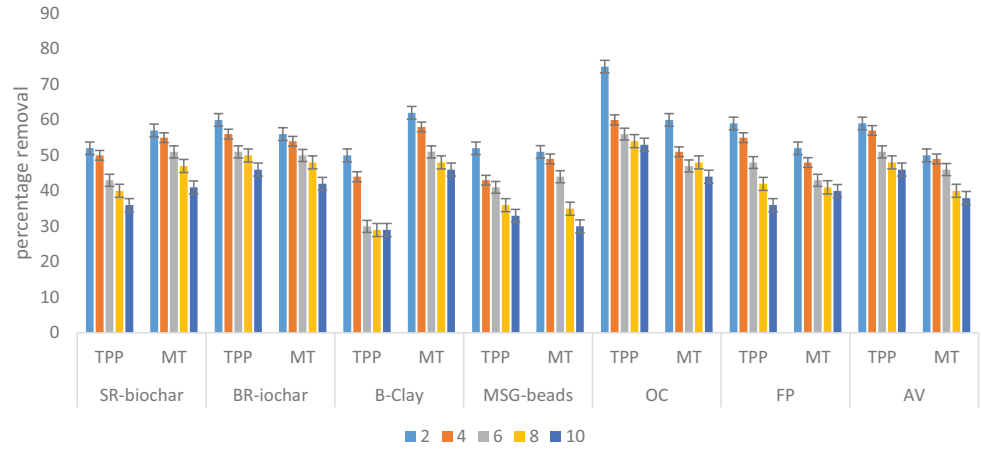

Fig. 5. Effect of pH on the removal of organophosphates by various sorbents.

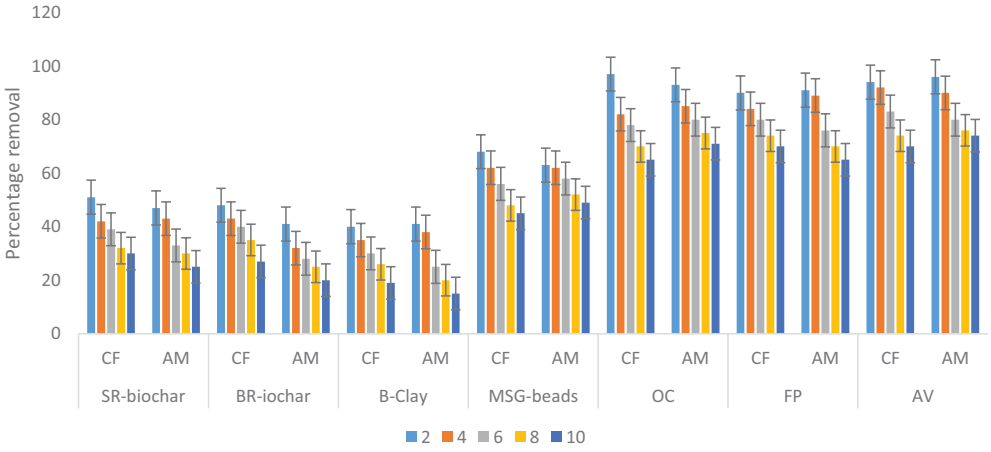

Fig. 6. Effect of pH on the removal of pharmaceuticals by various sorbents.

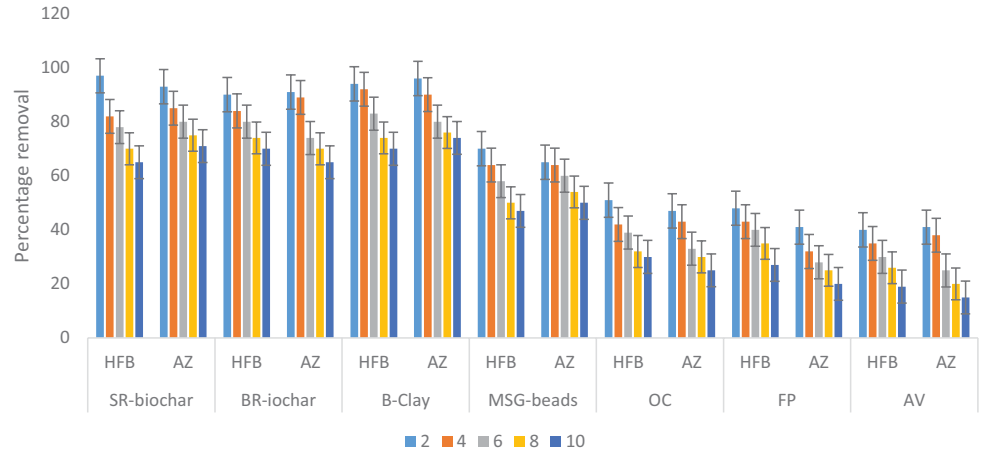

Fig. 7. Effect of pH on the removal of pesticides by various sorbents.

The Freundlich model is defined as:

$$\ln q_e = \frac{1}{n}\ln C_e + \ln K_F \quad (3)$$

In the equation, K_F is the Freundlich model constant described the bonding energy (mg g^{-1}). The values of R^2, K_F, and n are described in Table 4. The values of n are more than 1 showing that the sorption process is favorable.

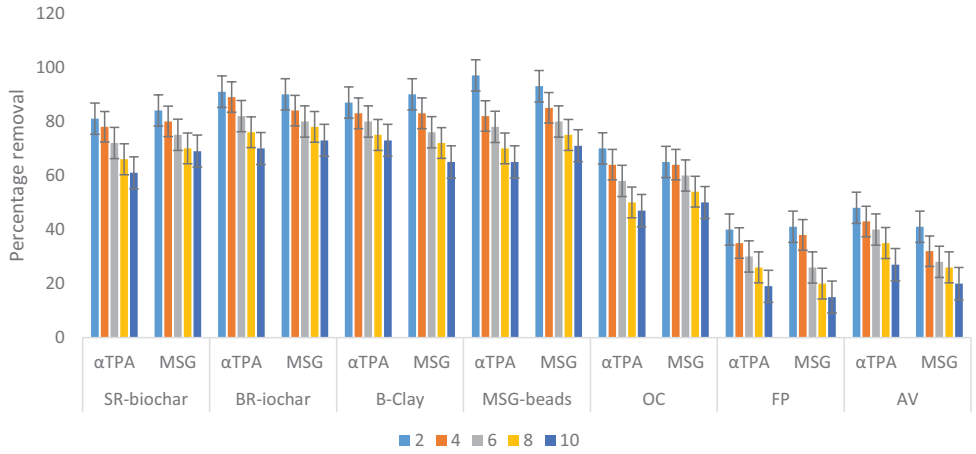

Fig. 8. Effect of pH on the removal of food additives by various sorbents.

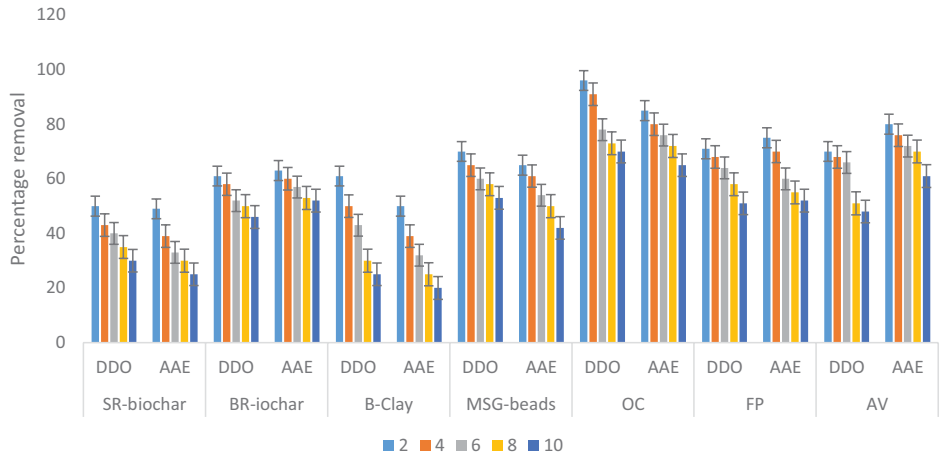

Fig. 9. Effect of pH on the removal of surfactants by various sorbents.

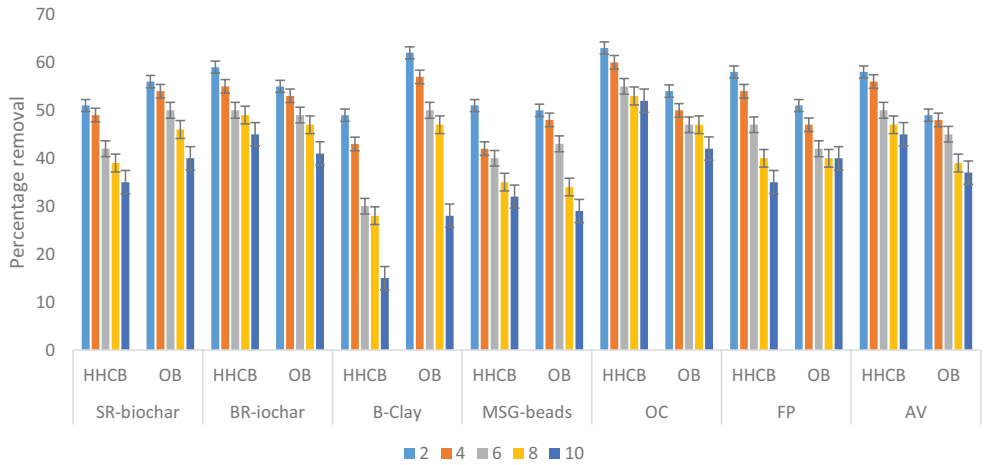

Fig. 10. Effect of pH on the removal of cosmetics by various sorbents.

Table 3
Least significance difference test for sorbents

Sorbent	Sorbent	Mean difference	Standard error	Sigma
(a)	(b)		(a–b)	
SR-biochar	BR-biochar	0.341	0.9842	0.001
	B-clay	0.211	0.9842	0.024
	MSG-beads	0.429	0.9842	0.126
	OC	0.237	0.9842	0.145
	FP	0.110	0.9842	0.000
	AV	–0.215	0.9842	0.120
BR-biochar	SR-biochar	0.427	0.9842	0.010
	B-clay	0.234	0.9842	0.025
	MSG-beads	0.422	0.9842	0.041
	OC	0.101	0.9842	0.110
	FP	–0.128	0.9842	0.062
	AV	0.266	0.9842	0.044
B-clay	SR-biochar	0.356	0.9842	0.102
	BR-biochar	0.415	0.9842	0.001
	MSG-beads	0.311	0.9842	0.000
	OC	0.233	0.9842	0.137
	FP	0.348	0.9842	0.141
	AV	0.241	0.9842	0.012
MSG-beads	SR-biochar	0.355	0.9842	0.011
	BR-biochar	0.432	0.9842	0.039
	B-clay	0.343	0.9842	0.040
	OC	0.284	0.9842	0.022
	FP	–0.209	0.9842	0.021
	AV	–0.257	0.9842	0.126
OC	SR-biochar	–0.321	0.9842	0.000
	BR-biochar	0.438	0.9842	0.054
	B-clay	0.277	0.9842	0.062
	MSG-beads	0.421	0.9842	–
	FP	0.244	0.9842	0.011
	AV	0.459	0.9842	0.072
FP	SR-biochar	–0.237	0.9842	0.033
	BR-biochar	–0.100	0.9842	0.041
	B-clay	–0.366	0.9842	0.023
	MSG-beads	–0.112	0.9842	0.000
	OC	–0.210	0.9842	0.011
	AV	0.331	0.9842	0.000
AV	SR-biochar	0.235	0.9842	0.038
	BR-biochar	–0.213	0.9842	0.051
	B-clay	0.187	0.9842	0.072
	MSG-beads	0.356	0.9842	0.148
	OC	0.321	0.9842	0.001
	FP	0.111	0.9842	0.061

Dependent variable is removal.
Mean square error is 0.982.

Table 4
Isotherm study for removal of micropollutants onto various sorbents

	Sorbents						
Micro-pollutants	SR-biochar	BR-biochar	B-clay	MSG-beads	OC	FP	AV
Langmuir q_m (mg g^{-1})							
RR22	195	187	147	352	266	467	232
DB17	201	184	131	290	243	265	185
Cu^{+2}	472	193	182	211	120	156	99
As^{III}	498	187	116	202	97	124	119
TPP	436	237	91	167	179	268	401
MT	420	261	112	87	193	245	387
CF	489	467	451	174	109	86	67
AM	478	475	476	169	93	75	61
HFB	73	80	126	159	398	417	436
AZ	71	68	101	184	367	422	452
α-TPA	348	459	446	480	356	74	86
MSG	357	440	473	469	330	69	55
DDO	117	143	139	245	459	357	232
AAE	96	137	126	213	426	382	297
HHCB	134	166	110	150	175	119	123
OB	148	135	188	147	149	105	98
R_L							
RR22	0.04	0.07	0.14	0.08	0.03	0.09	0.21
DB17	0.09	0.06	0.08	0.23	0.14	0.04	0.11
Cu^{+2}	0.13	0.07	0.02	0.16	0.26	0.03	0.07
As^{III}	0.09	0.08	0.12	0.04	0.01	0.11	0.03
TPP	0.17	0.13	0.06	0.05	0.09	0.04	0.07
MT	0.12	0.11	0.14	0.09	0.04	0.12	0.03
CF	0.05	0.08	0.01	0.01	0.04	0.07	0.05
AM	0.11	0.06	0.04	0.16	0.12	0.06	0.13
HFB	0.06	0.03	0.01	0.02	0.05	0.04	0.02
AZ	0.17	0.12	0.07	0.23	0.06	0.11	0.05
α-TPA	0.06	0.06	0.12	0.07	0.01	0.08	0.07
MSG	0.08	0.04	0.01	0.03	0.04	0.01	0.03
DDO	0.13	0.16	0.23	0.01	0.05	0.11	0.07
AAE	0.08	0.04	0.04	0.01	0.03	0.02	0.19
HHCB	0.06	0.02	0.07	0.13	0.06	0.08	0.02
OB	0.06	0.11	0.05	0.06	0.07	0.03	0.01
R^2							
RR22	0.99	0.98	0.9	0.93	0.96	0.97	0.99
DB17	0.98	0.99	0.96	0.94	0.93	0.96	0.91
Cu^{+2}	0.96	0.98	0.98	0.95	0.99	0.94	0.98
As^{III}	0.99	0.99	0.96	0.97	0.99	0.98	0.99
TPP	0.94	0.93	0.99	0.97	0.99	0.93	0.97
MT	0.98	0.98	0.99	0.98	0.99	0.99	0.98
CF	0.99	0.97	0.98	0.96	0.95	0.97	0.96
AM	0.93	0.95	0.97	0.99	0.96	0.94	0.91
HFB	0.97	0.97	0.98	0.94	0.96	0.96	0.97
AZ	0.96	0.98	0.98	0.95	0.99	0.94	0.98

α-TPA	0.98	0.98	0.99	0.98	0.99	0.99	0.98
MSG	0.99	0.97	0.98	0.96	0.95	0.97	0.96
DDO	0.99	0.98	0.9	0.93	0.96	0.97	0.99
AAE	0.98	0.99	0.91	0.99	0.95	0.96	0.95
HHCB	0.96	0.96	0.99	0.98	0.96	0.94	0.97
OB	0.96	0.98	0.98	0.94	0.97	0.99	0.96
Freundlich							
K_F							
RR22	25.8	34.2	12.9	21.7	12.7	17.5	29.2
DB17	44.7	17.9	10.1	15.8	37.5	41.7	31.9
Cu^{+2}	25.7	15.4	24.8	14.9	37.3	18.9	22.9
As^{III}	18.6	21.6	29.3	10.6	40.8	24.1	14.4
TPP	49.6	33.7	41.8	26.9	22.7	20.1	33.6
MT	17.8	18.5	11.5	43.1	32.6	19.2	29.5
CF	37.8	30.3	23.6	36.1	17.2	19.8	24.5
AM	48.4	43.6	26.3	35.9	31.4	25.1	19.9
HFB	9.4	17.9	39.4	11.6	28.7	22.6	17.9
AZ	18.9	39.5	36.1	29.8	14.8	11.5	21.0
α-TPA	38.6	30.8	27.8	26.5	19.6	16.8	43.9
MSG	27.6	23.3	17.6	18.9	24.6	29.9	24.6
DDO	15.7	19.4	16.4	22.5	19.5	35.1	18.7
AAE	44.7	17.9	10.1	15.8	37.5	41.7	31.9
HHCB	25.5	9.6	23.8	34.1	33.8	31.3	12.6
OB	17.8	27.4	29.5	31.8	27.9	33.9	32.1
n							
RR22	3.5	2.1	2.7	4.7	2.9	5.4	2.0
DB17	2.0	2.7	2.2	2.8	3.1	2.7	2.5
Cu^{+2}	3.7	3.6	4.1	2.3	4.8	3.0	3.7
As^{III}	2.9	3.4	3.8	3.5	3.1	2.7	4.1
TPP	2.1	2.7	2.2	2.0	2.4	2.5	2.3
MT	2.9	3.2	4.1	3.6	3.8	3.8	2.2
CF	3.0	2.2	2.8	2.4	3.0	2.5	2.1
AM	3.1	3.1	3.0	2.7	2.5	2.6	2.7
HFB	4.6	5.0	5.2	2.8	4.2	3.8	4.0
AZ	2.6	2.7	2.0	2.1	2.6	2.6	3.1
α-TPA	2.9	2.0	3.4	3.0	2.8	2.0	2.4
MSG	3.8	4.1	4.6	4.0	3.2	3.1	2.9
DDO	3.0	2.2	2.8	2.4	3.0	2.5	2.1
AAE	2.6	5.3	3.0	3.1	2.6	2.8	2.7
HHCB	2.6	3.8	2.2	2.4	3.3	3.1	3.6
OB	3.5	2.7	2.0	2.2	2.6	2.8	2.7
R^2							
RR22	0.91	0.95	0.89	0.91	0.92	0.99	0.95
DB17	0.89	0.95	0.96	0.99	0.95	0.94	0.93
Cu^{+2}	0.97	0.99	0.93	0.87	0.94	0.95	0.99
As^{III}	0.99	0.95	0.96	0.94	0.96	0.99	0.89
TPP	0.97	0.97	0.98	0.94	0.96	0.96	0.97
MT	0.98	0.98	0.99	0.98	0.99	0.99	0.98
CF	0.86	0.89	0.97	0.98	0.95	0.96	0.99
AM	0.91	0.94	0.93	0.99	0.98	0.89	0.91

(continued)

Table 4 (*continued*)

	Sorbents						
Micro-pollutants	SR-biochar	BR-biochar	B-clay	MSG-beads	OC	FP	AV
HFB	0.98	0.99	0.91	0.99	0.95	0.96	0.95
AZ	0.96	0.97	0.95	0.95	0.97	0.94	0.97
α-TPA	0.97	0.99	0.95	0.94	0.99	0.98	0.87
MSG	0.99	0.98	0.97	0.95	0.94	0.94	0.95
DDO	0.96	0.98	0.98	0.95	0.99	0.94	0.98
AAE	0.87	0.89	0.91	0.96	0.85	0.95	0.93
HHCB	0.97	0.94	0.94	0.99	0.94	0.94	0.95
OB	0.94	0.93	0.99	0.97	0.99	0.93	0.97
Harkins–Jura							
A							
RR22	987	875	989	943	767	775	453
DB17	887	899	991	765	564	776	321
Cu^{+2}	674	751	633	981	673	544	784
As^{III}	992	980	342	338	845	981	922
TPP	768	887	721	653	532	321	387
MT	543	553	411	496	433	844	643
CF	690	901	850	532	998	431	781
AM	731	890	287	431	790	879	560
HFB	678	907	850	889	541	506	217
AZ	774	632	609	662	731	642	965
α-TPA	531	560	885	893	832	890	881
MSG	954	566	761	776	240	338	421
DDO	764	981	993	805	901	780	553
AAE	669	890	931	690	651	690	783
HHCB	678	761	552	219	810	128	210
OB	345	762	611	443	120	542	559
B							
RR22	1.9	2.7	2.7	2.0	2.1	1.6	1.7
DB17	2.0	2.1	2.0	1.7	1.4	1.0	1.5
Cu^{+2}	1.6	2.6	2.4	2.3	1.9	2.0	2.4
As^{III}	1.1	1.6	1.3	1.0	1.8	1.1	1.2
TPP	2.2	2.8	1.9	1.6	2.4	2.1	1.7
MT	1.0	1.4	1.8	1.7	1.5	1.6	1.9
CF	1.8	2.3	2.2	2.0	2.1	1.0	1.1
AM	2.7	2.0	2.0	1.9	2.5	2.2	2.6
HFB	2.0	2.1	1.6	1.1	2.3	1.3	1.0
AZ	1.7	1.5	2.5	2.3	1.1	1.9	1.4
α-TPA	1.6	2.6	2.0	2.3	1.9	2.2	2.4
MSG	1.0	1.8	1.3	2.8	2.5	1.5	0.9
DDO	2.0	2.5	2.3	2.6	2.7	2.2	2.1
AAE	1.5	2.3	0.5	2.0	2.1	1.0	2.8
HHCB	1.8	1.7	1.1	1.0	1.7	1.9	1.5
OB	2.8	2.1	1.1	1.1	2.3	1.3	1.5
R^2							
RR22	0.77	0.72	0.85	0.79	0.71	0.82	0.84
DB17	0.81	0.75	0.79	0.69	0.77	0.83	0.81
Cu^{+2}	0.71	0.8	0.81	0.78	0.72	0.70	0.76
As^{III}	0.77	0.72	0.85	0.80	0.79	0.76	0.70

TPP	0.81	0.68	0.69	0.75	0.78	0.79	0.84
MT	0.83	0.70	0.79	0.81	0.77	0.83	0.81
CF	0.84	0.78	0.74	0.80	0.71	0.75	0.69
AM	0.81	0.81	0.84	0.76	0.67	0.69	0.71
HFB	0.67	0.71	0.79	0.81	0.77	0.83	0.84
AZ	0.65	0.67	0.71	0.67	0.79	0.81	0.63
α-TPA	0.77	0.78	0.83	0.61	0.80	0.80	0.66
MSG	0.63	0.71	0.79	0.66	0.77	0.83	0.74
DDO	0.85	0.81	0.84	0.78	0.79	0.61	0.64
AAE	0.67	0.65	0.60	0.76	0.71	0.68	0.82
HHCB	0.66	0.81	0.76	0.82	0.82	0.81	0.80
OB	0.65	0.83	0.84	0.60	0.79	0.61	0.64

Table 5
Comparison of the present study with previously reported data

Sorbent	Percentage removal (%)	References
Lignite	76	[1]
Iron coated peat	80	[34]
Sorbent	–	–
Activated sludge	91	[4]
Tetraselmis suecica (microalgae)	64	[35]
Biological activated carbon	84	[36]
Silica gel/rice flour decorated biochar	90	Present study
Bentonite clay	93	Present study
Magnetic, silica gel Chitosan beads	96	Present study

The R^2 values of pollutants showed that data was also good fitted to the Freundlich model.

3.2.3. Harkins–Jura sorption isotherm model

The Harkins–Jura model describes a multi-layer sorption process. The Harkins–Jura model is presented as:

$$\frac{1}{q_e^2} = \frac{B}{A} - \left(\frac{1}{A}\right)\log C_e \quad (4)$$

The values of various constants of this model are presented in Table 4. The values of correlation coefficients described that experimental data was poorly fitted to this model.

The comparison of the present study with previously reported data is presented in Table 5.

4. Conclusions

This study conducted to evaluate seven different sorbents that either these were promising for micropollutants removal or not. It was observed that nitrogen, phosphorus, metals, and pesticides were removed efficiently by inorganic sorbents. While surfactants and pharmaceuticals were eliminated by organic sorbents more effectively. Sorption of micropollutants by various sorbents was strongly affected by the change in pH values. Inorganic, biopolymer and organic sorbents except FP exhibited significantly higher removal capacity (ANOVA, $p < 0.05$). The results depicted that Langmuir and Freundlich's isotherms were best fitted to experimental data.

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