APPENDIX

APPENDIX A

DETERMINATION OF MAXIMUM WAVELENGTH AND CHROMIUM STANDARD CURVE

A.1. Determination of Maximum Wavelength

Maximum wavelength of Cr(VI) was determined by measuring the absorbance of the solution using survey scan of UV-Vis Genesys 10v spectrophotometer in the range of wavelength of 300-400 nm

Table A.1. λ and Absorbance of 20 mg/L Cr(VI) Solution

Wavelength (nm)	Absorbance
300	1.166
310	1.298
320	1.335
330	1.278
340	1.411
350	1.704
351	1.769
352	**1.788**
353	1.724
354	1.636
355	1.511
358	1.422
359	1.329
360	1.287
370	1.228
380	1.112
390	1.287
400	1.177

From figure A.1, it can be ssen that the maximum wavelength for Cr(VI) solution is 352 nm.

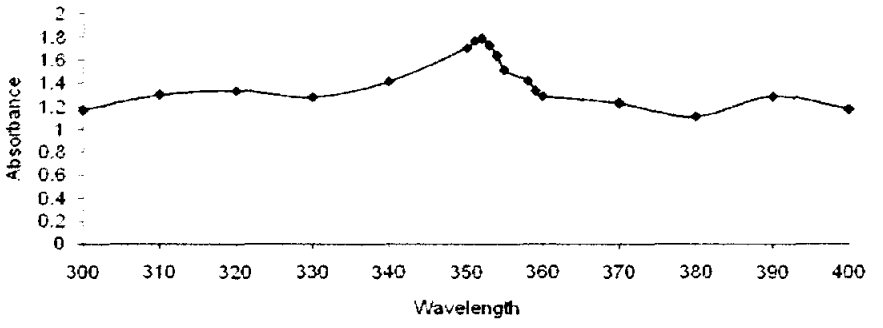

Figure A.1. Maximum Wavelength of Chromium (VI) Solution

From Table A.1, it can be seen that the maximum wavelength for Cr(VI) analysis is at 352 nm.

A.2. Preparation of Standard Curve

Absorbance of all solution was measured using UV-Vis Genesys 10v spectrophotometer at maximum wavelength which has been obtained from step A.1. Standard curve between absorbance versus dyes concentration was prepared and then linear regression was determined by Sigma Plot software.

Table A.2 Relationship between Concentration and Absorbance of Cr(VI)

Concentration (mg/L)	Absorbance
5	0.527
10	1.058
15	1.470
20	1.735

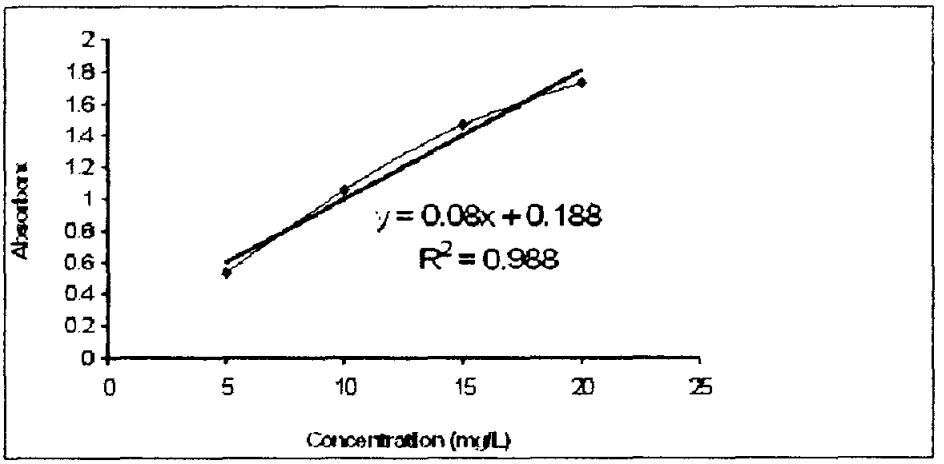

Figure A.2. Standard Curve of Cr(VI) Solution

The linear regresion equation from figure A.2 is :

$$y = 0.08\ x + 0.188$$

Where : y is the absorbance of Cr(VI) solution

x is the concentration of Cr(VI) solution

APPENDIX B

DATA ANALYSES

B.1. Boehm Titration

Assumptions used:

1. $NaHCO_3$ only neutralizes carboxylic groups
2. Na_2CO_3 neutralizes carboxylic and lactonic groups
3. NaOH neutralizes carboxylic, lactonic, and phenolic groups

The results are shown below.

Table B.1. Results of Boehm's titration

Sample	mL HCl			mL NaOH
	$NaHCO_3$	Na_2CO_3	NaOH	HCl
Durian shell	9.1	7.8	8	8.6

Below is the example of Boehm's titration calculation:

N $NaHCO_3$ = 0.049607 N
N Na_2CO_3 = 0.049547 N
N NaOH = 0.052657 N
N HCl = 0.050237 N

(i) Acidity analysis

N*V HCl + meq carboxylic groups = N*V $NaHCO_3$

0.050237*9.1 + meq carboxylic groups = 0.049607*10

meq carboxylic groups = 0.038918

meq carboxylic groups/g AC = 0.038918/0.5 = 0.077835 meq/g = 77.835 μeq/g

N*V HCl + meq carboxylic groups + meq lactonic groups = N*V Na_2CO_3

0.050237*7.8 + 0.038918 + meq lactonic groups = 0.049547*10

meq lactonic groups = 0.0647034

meq lactonic groups/g AC = 0.0647034/0.5 = 0.129416 meq/g = 129.416 μeq/g

N*V HCl + meq carboxylic groups + meq lactonic groups + meq phenolic groups = N*V NaOH

0.050237*8 + 0.038918 + 0.0647034 + meq phenolic groups = 0.052657*10

meq phenolic groups = 0.021051

meq phenolic groups/g AC = 0.021051/0.5 = 0.042102 meq/g = 42.102 μeq/g

(ii) Basicity analysis

N*V NaOH + meq basic groups = N*V HCl

0.052657*8.6 + meq basic groups = 0.050237*10

meq basic groups = 0.049517

meq basic groups/g AC = 0.049517/0.5 = 0.099033 meq/g = 99.033 μeq/g

The summary of all calculation can be seen at Table 3.

B.2. BET (Brunauer-Emmett-Teller) Method

Make a plot of BET equation:

$$\frac{1}{V\left[\left(\frac{P_0}{P}\right)-1\right]} = \frac{C-1}{V_m C}\left(\frac{P}{P_0}\right) + \frac{1}{V_m C}$$

with the value of $\left(\frac{P}{P_0}\right)$ and from the nitrogen sorption data at relative pressure between 0.05 – 0.25

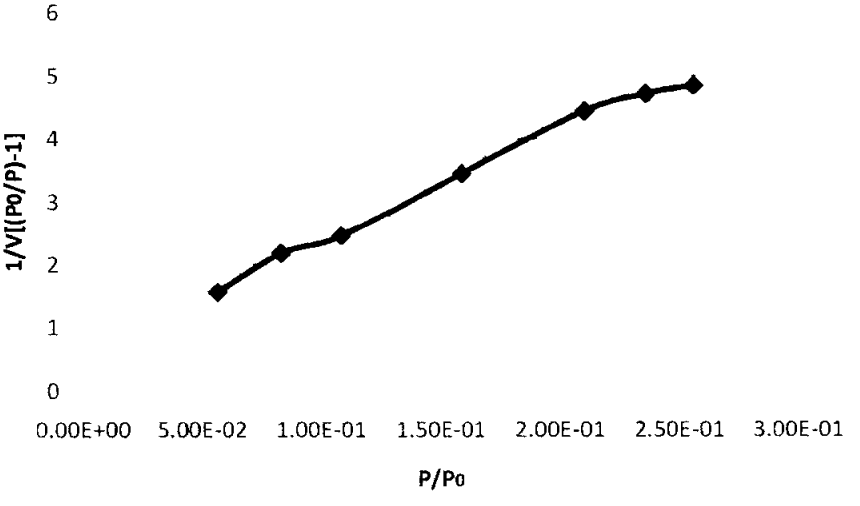

Figure B.1. BET (Brenauer-Emmett-Teller) method plot

Using Sigma Plot software, found the value of $V_m = 0.0567$ cm^3 g^{-1}

S_{BET} calculated using equation :

$$S_{BET} = \frac{V_m N S}{V}$$

Where N is Avogadro's number, S is adsorption cross section (0.16 nm^2 for nitrogen) and V is molar volume of nitrogen (6153 cm^3 mol^{-1} at 77 K and 1 atm)

$S_{BET} = 0.888$ m^2 g^{-1}

B.3. pH Drift

From pH drift experiments by several pH_{init}, several pH_{final} could be obtained as follows:

Table B.2 pH Final of durian shell

pH_{init}	pH_{final}
2	2.51
2.6	2.93
3.23	3.84
3.86	5.36
4.22	5.55
5.4	6.32
5.7	6.82
6.4	6.4
7.21	6.51
8.2	6.62

From the data given in the table, pH_{PZC} of the durian shell could be determined as illustrated in the Figure below.

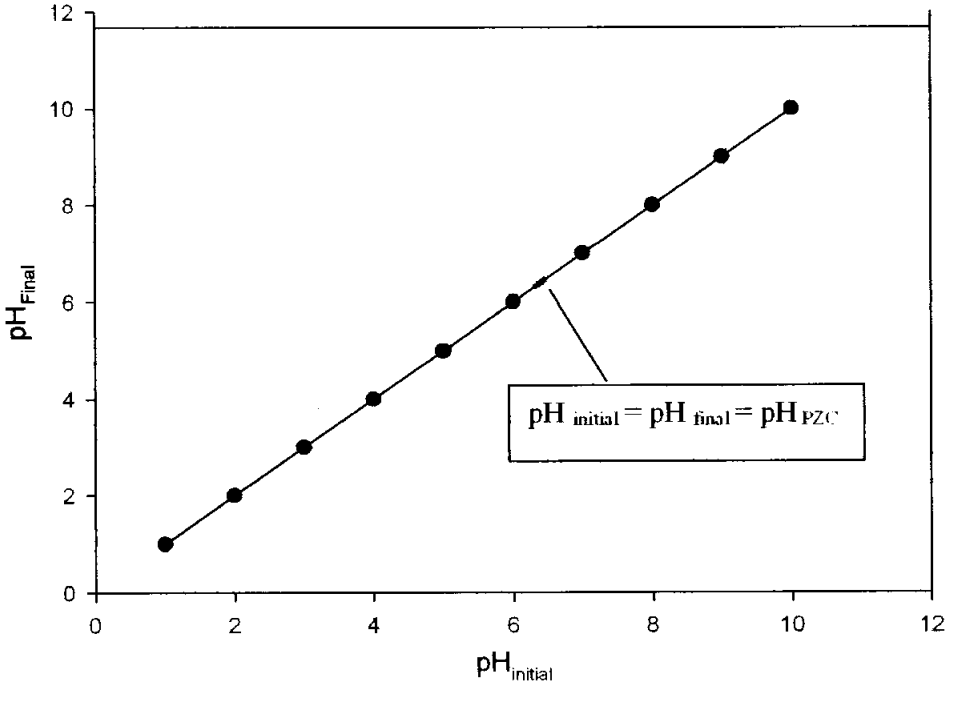

Figure 8. pH_{PZC} Determination Using pH Drift

B.4. Cr(VI) Adsorption

B.4.1. Cr(VI) Equilibrium Time

In a preliminary experiment, the sample durian shell with the weight of 5 gram and solution of Cr(VI) with the concentration 20 mg/L were shaken at room temperature. The equilibrium time was obtained when the absorbance of the solution was not decreasing again in the time length of 1 hours.

Table B.3. Experiment Data for the Determination of Cr(VI) Equilibrium Time

	Absorbance (A)						
	10 minutes	20 minutes	30 minutes	40 minutes	50 minutes	60 minutes	70 minutes
Sample	0.894	0.739	0.673	0.569	0.543	0.518	0.538

B.4.2. Cr(VI) Adsorption Isotherm of durian shell as Adsorbent

The example calculation:

pH= 2.5 , T= 30°C

Mass of durian shell = 0.9985 gram

Initial concentration (Co) = 20 mg/L

V = 0.05 L

$$q_e = \frac{Co-Ce}{m} \times V$$

$$q_e = \frac{20-8.2}{0.9985} \times 0.05$$

$$q_e = 0.5908\ mg/g$$

For the other variations are listed in table B.4

Table B.4. Data Analyses of Adsorption Isotherm of durian shell at Different pH

pH	Temperature (°C)	Weight (g)	Absorbance (A)	C_e (mg/L)	q_e (mg/g)
2.5	30	10.005	0.284	1.2	0.0895
		9.012	0.292	1.3	0.0969
		8.024	0.308	1.5	0.1117
		6.8805	0.332	1.8	0.1338
		6.0592	0.348	2	0.1466
		5.0313	0.380	2.4	0.1775
		4.0081	0.420	2.9	0.2015
		2.9909	0.484	3.7	0.2725
		1.9971	0.596	5.1	0.3730
		0.9985	**0.844**	**8.2**	**0.5908**
	40	9.9166	0.252	0.8	0.0952
		8.7758	0.260	0.9	0.1088
		7.8631	0.268	1	0.1188
		7.1163	0.276	1.1	0.1328
		5.9672	0.292	1.3	0.1567
		5.1244	0.308	1.5	0.1947
		3.9706	0.340	1.9	0.2279
		3.0686	0.380	2.4	0.2656
		1.9897	0.468	3.5	0.4146
		1.0040	0.668	6	0.6871
	50	10.0252	0.188	0	0.0911
		8.9078	0.228	0.5	0.1092
		7.9808	0.236	0.6	0.1288
		6.8061	0.244	0.7	0.1453
		5.8480	0.252	0.8	0.1725
		4.9451	0.260	0.9	0.1992
		3.9814	0.276	1.1	0.2489
		2.9926	0.292	1.3	0.3057
		1.9632	0.324	1.7	0.4676
		1.0149	0.388	2.5	0.7685
	60	10.0417	0.212	0.3	0.0798
		9.1936	0.220	0.4	0.0961
		8.1247	0.228	0.5	0.1292
		6.7453	0.236	0.6	0.1438
		5.7599	0.244	0.7	0.1775
		5.0208	0.252	0.8	0.1912
		3.9859	0.268	1.0	0.2484
		3.0302	0.292	1.3	0.3086
		2.0235	0.340	1.9	0.4514
		0.9902	0.476	3.6	0.8338
	30	9.8998	0.588	5	0.0716
		9.1592	0.612	5.3	0.0802
		8.0945	0.652	5.8	0.0814
		7.0357	0.7	6.4	0.0967
		6.0255	0.756	7.1	0.1070

		4.9851	0.828	8	0.1197
		3.9911	0.916	9.1	0.1366
		3.0246	1.028	10.5	0.1558
		2.0152	1.188	12.5	0.1861
		1.0100	1.42	15.4	0.2262
	40	10.0149	0.444	3.2	0.0830
		9.0935	0.468	3.5	0.0884
		7.9756	0.5	3.9	0.1009
		7.0651	0.532	4.3	0.1110
		5.9771	0.58	4.9	0.1263
		5.0012	0.636	5.6	0.1440
		4.0537	0.708	6.5	0.1611
		3.0057	0.82	7.9	0.2013
		1.9784	0.988	10	0.2527
		1.0093	1.252	13.3	0.3303
	50	9.9992	0.372	2.3	0.0890
		9.0600	0.388	2.5	0.0901
		7.9640	0.412	2.8	0.1080
		7.0797	0.436	3.1	0.1110
		5.9326	0.476	3.6	0.1382
		5.0644	0.516	4.1	0.1544
		4.0423	0.58	4.9	0.1868
		3.0089	0.676	6.1	0.2277
		2.0014	0.828	8	0.2998
		1.0050	1.108	11.5	0.4209
	60	10.0607	0.308	1.5	0.0893
		9.0579	0.324	1.7	0.1010
		8.0292	0.34	1.9	0.1101
		6.8363	0.364	2.2	0.1302
		5.9292	0.388	2.5	0.1476
		5.0109	0.42	2.9	0.1606
		4.0260	0.468	3.5	0.2049
		3.0500	0.54	4.4	0.2500
		1.9873	0.676	6.1	0.3497
		0.9901	0.948	9.5	0.5291
	30	9.9882	0.652	5.8	0.0711
		9.0878	0.684	6.2	0.0707
		8.1129	0.724	6.7	0.0820
		6.9685	0.78	7.4	0.0889
		6.0209	0.836	8.1	0.0988
		5.0178	0.908	9	0.1055
		4.0329	0.996	10.1	0.1227
		2.9881	1.116	11.6	0.1399
		1.9942	1.268	13.5	0.1630
		1.0084	1.476	16.1	0.1905
	40	10.0438	0.468	3.5	0.0814
		9.0926	0.492	3.8	0.0891
		8.0353	0.524	4.2	0.0973

		6.9659	0.564	4.7	0.1098
		5.9480	0.612	5.3	0.1236
		5.0166	0.668	6	0.1355
		4.0072	0.748	7	0.1622
		2.9948	0.86	8.4	0.1937
		1.9769	1.028	10.5	0.2398
		0.9932	1.292	13.8	0.3020
	50	10.0411	0.38	2.4	0.0855
		9.1734	0.396	2.6	0.0948
		8.0957	0.42	2.9	0.1007
		6.9631	0.452	3.3	0.1199
		6.0746	0.484	3.7	0.1341
		5.0509	0.532	4.3	0.1554
		4.0590	0.596	5.1	0.1811
		3.0406	0.692	6.3	0.2253
		1.9920	0.852	8.3	0.2905
		1.0001	1.132	11.8	0.4100
	60	10.0113	0.316	1.6	0.0901
		8.9924	0.332	1.8	0.0998
		8.0170	0.348	2	0.1123
		7.0187	0.364	2.2	0.1211
		5.9899	0.396	2.6	0.1452
		4.8987	0.436	3.1	0.1725
		3.9774	0.484	3.7	0.2049
		3.0440	0.556	4.6	0.2530
		2.0035	0.692	6.3	0.3419
		1.0039	0.964	9.7	0.5105

B.4.3. Cr(VI) Adsorption Kinetic of durian shell as Adsorbent

The example calculation:

pH= 2.5 , T= 30°C

Particle size = $^{-30}/_{+40}$

Mass of durian shell = 25 gram

Initial concentration (Co) = 20 mg/L

V = 0.25 L

$$q_t = \frac{Co-Ct}{m} \times V$$

$$q_e = \frac{20-7.8}{25} \times 0.25$$

$$q_e = 0.122\ mg/g$$

For the other variations are listed in table B.5

Table B.5. Data Analyses of Adsorption Kinetic of durian shell at Different pH

Temperature (°C)	**pH**	**Particle size (mesh)**	***t* (min)**	**Absorbance (A)**	**C_t (mg/L)**	**q_t (mg/g)**
30	2.5	-30/+40	0	1.788	20	0.0000
			5	0.812	7.8	0.1220
			10	0.632	5.55	0.1445
			15	0.5552	4.59	0.1541
			20	0.5136	4.07	0.1593
			25	0.4872	3.74	0.1626
			30	0.4688	3.51	0.1649
			35	0.4552	3.34	0.1666
			40	0.4448	3.21	0.1679
			45	0.4368	3.11	0.1689
			50	0.4304	3.03	0.1697
			55	0.4248	2.96	0.1704
			60	0.4208	2.91	0.1709
	2.5	-40/+60	0	1.788	20.00	0.0000
			5	0.796	7.61	0.1239
			10	0.619	5.38	0.1462
			15	0.544	4.45	0.1555
			20	0.504	3.94	0.1606
			25	0.478	3.62	0.1638
			30	0.460	3.40	0.1660
			35	0.447	3.24	0.1676
			40	0.437	3.11	0.1689
			45	0.429	3.01	0.1699
			50	0.423	2.94	0.1706
			55	0.418	2.87	0.1713
			60	0.413	2.82	0.1718
	2.5	-60/+80	0	1.788	20.00	0.0000
			5	0.773	7.31	0.1269
			10	0.595	5.09	0.1491
			15	0.521	4.17	0.1583
			20	0.481	3.66	0.1634
			25	0.455	3.34	0.1666
			30	0.438	3.12	0.1688
			35	0.425	2.96	0.1704
			40	0.415	2.84	0.1716
			45	0.407	2.74	0.1726
			50	0.401	2.67	0.1733
			55	0.396	2.60	0.1740
			60	0.392	2.55	0.1745
40	2.5	-30/+40	0	1.788	20.00	0.0000
			5	0.803	7.69	0.1231
			10	0.621	5.41	0.1459

			15	0.550	4.52	0.1548
			20	0.503	3.94	0.1606
			25	0.482	3.68	0.1632
			30	0.459	3.39	0.1661
			35	0.451	3.29	0.1671
			40	0.435	3.09	0.1691
			45	0.429	3.01	0.1699
			50	0.421	2.91	0.1709
			55	0.419	2.89	0.1711
			60	0.411	2.79	0.1721
	2.5	-40/+60	0	1.788	20.00	0.0000
			5	0.790	7.52	0.1248
			10	0.606	5.23	0.1477
			15	0.538	4.38	0.1562
			20	0.492	3.80	0.1620
			25	0.470	3.52	0.1648
			30	0.449	3.27	0.1673
			35	0.439	3.14	0.1686
			40	0.427	2.99	0.1701
			45	0.418	2.88	0.1712
			50	0.413	2.81	0.1719
			55	0.409	2.76	0.1724
			60	0.404	2.69	0.1731
	2.5	-60/+80	0	1.788	20.00	0.0000
			5	0.763	7.19	0.1281
			10	0.581	4.92	0.1508
			15	0.497	3.86	0.1614
			20	0.471	3.54	0.1646
			25	0.442	3.17	0.1683
			30	0.430	3.03	0.1697
			35	0.427	2.99	0.1701
			40	0.408	2.76	0.1724
			45	0.403	2.69	0.1731
			50	0.395	2.59	0.1741
			55	0.390	2.52	0.1748
			60	0.386	2.48	0.1752
50	2.5	-30/+40	0	1.788	20.00	0.0000
			5	0.776	7.34	0.1266
			10	0.609	5.26	0.1474
			15	0.527	4.24	0.1576
			20	0.491	3.79	0.1621
			25	0.462	3.42	0.1658
			30	0.444	3.21	0.1679
			35	0.441	3.16	0.1684
			40	0.422	2.93	0.1707
			45	0.419	2.89	0.1711
			50	0.408	2.75	0.1725
			55	0.405	2.71	0.1729

			60	0.399	2.64	0.1736
	2.5	-40/+60	0	1.788	20.00	0.0000
			5	0.751	7.04	0.1296
			10	0.586	4.98	0.1502
			15	0.510	4.03	0.1597
			20	0.477	3.61	0.1639
			25	0.448	3.25	0.1675
			30	0.434	3.08	0.1692
			35	0.419	2.89	0.1711
			40	0.413	2.81	0.1719
			45	0.407	2.74	0.1726
			50	0.402	2.67	0.1733
			55	0.392	2.55	0.1745
			60	0.388	2.50	0.1750
	2.5	-60/+80	0	1.788	20.00	0.0000
			5	0.731	6.79	0.1321
			10	0.557	4.61	0.1539
			15	0.496	3.85	0.1615
			20	0.451	3.29	0.1671
			25	0.434	3.07	0.1693
			30	0.412	2.80	0.1720
			35	0.405	2.71	0.1729
			40	0.391	2.54	0.1746
			45	0.387	2.49	0.1751
			50	0.379	2.38	0.1762
			55	0.376	2.35	0.1765
			60	0.370	2.28	0.1772
60	2.5	-30/+40	0	1.788	20.00	0.0000
			5	0.746	6.97	0.1303
			10	0.565	4.72	0.1528
			15	0.498	3.88	0.1612
			20	0.456	3.35	0.1665
			25	0.435	3.09	0.1691
			30	0.415	2.84	0.1716
			35	0.406	2.72	0.1728
			40	0.393	2.57	0.1743
			45	0.389	2.51	0.1749
			50	0.380	2.40	0.1760
			55	0.379	2.39	0.1761
			60	0.371	2.29	0.1771
	2.5	-40/+60	0	1.788	20.00	0.0000
			5	0.725	6.71	0.1329
			10	0.550	4.53	0.1547
			15	0.487	3.74	0.1626
			20	0.443	3.18	0.1682
			25	0.434	3.07	0.1693
			30	0.402	2.68	0.1732
			35	0.396	2.60	0.1740

			40	0.381	2.42	0.1758
			45	0.375	2.34	0.1766
			50	0.368	2.26	0.1774
			55	0.364	2.20	0.1780
			60	0.360	2.15	0.1785
	2.5	-60/+80	0	1.788	20.00	0.0000
			5	0.701	6.41	0.1359
			10	0.530	4.28	0.1572
			15	0.470	3.52	0.1648
			20	0.426	2.97	0.1703
			25	0.398	2.63	0.1737
			30	0.387	2.49	0.1751
			35	0.382	2.42	0.1758
			40	0.367	2.24	0.1776
			45	0.364	2.20	0.1780
			50	0.354	2.08	0.1792
			55	0.352	2.05	0.1795
			60	0.346	1.97	0.1803
60	6.6	-30/+40	0	1.788	20.00	0.0000
			5	0.866	8.48	0.1152
			10	0.685	6.21	0.1379
			15	0.603	5.19	0.1481
			20	0.564	4.70	0.1530
			25	0.532	4.30	0.1570
			30	0.516	4.10	0.1590
			35	0.498	3.88	0.1612
			40	0.491	3.79	0.1621
			45	0.479	3.64	0.1636
			50	0.477	3.61	0.1639
			55	0.469	3.51	0.1649
			60	0.462	3.42	0.1658
	6.6	-40/+60	0	1.788	20.00	0.0000
			5	0.847	8.23	0.1177
			10	0.719	6.64	0.1336
			15	0.590	5.02	0.1498
			20	0.550	4.53	0.1547
			25	0.525	4.21	0.1579
			30	0.502	3.92	0.1608
			35	0.494	3.82	0.1618
			40	0.478	3.62	0.1638
			45	0.475	3.59	0.1641
			50	0.463	3.44	0.1656
			55	0.461	3.41	0.1659
			60	0.453	3.31	0.1669
	6.6	-60/+80	0	1.788	20.00	0.0000
			5	0.829	8.01	0.1199
			10	0.659	5.89	0.1411
			15	0.575	4.83	0.1517

			20	0.542	4.42	0.1558
			25	0.507	3.99	0.1601
			30	0.492	3.80	0.1620
			35	0.475	3.59	0.1641
			40	0.470	3.53	0.1647
			45	0.457	3.37	0.1663
			50	0.454	3.32	0.1668
			55	0.448	3.25	0.1675
			60	0.441	3.16	0.1684
60	7.2	-30/+40	0	1.788	20.00	0.0000
			5	0.896	8.84	0.1116
			10	0.708	6.49	0.1351
			15	0.629	5.51	0.1449
			20	0.580	4.90	0.1510
			25	0.554	4.58	0.1542
			30	0.531	4.29	0.1571
			35	0.518	4.12	0.1588
			40	0.505	3.96	0.1604
			45	0.496	3.85	0.1615
			50	0.491	3.79	0.1621
			55	0.483	3.68	0.1632
			60	0.477	3.62	0.1638
	7.2	-40/+60	0	1.788	20.00	0.0000
			5	0.878	8.62	0.1138
			10	0.696	6.35	0.1365
			15	0.614	5.33	0.1467
			20	0.566	4.73	0.1527
			25	0.541	4.41	0.1559
			30	0.518	4.12	0.1588
			35	0.508	4.00	0.1600
			40	0.492	3.80	0.1620
			45	0.486	3.72	0.1628
			50	0.476	3.61	0.1639
			55	0.473	3.56	0.1644
			60	0.466	3.47	0.1653
	7.2	-60/+80	0	1.788	20.00	0.0000
			5	0.853	8.31	0.1169
			10	0.672	6.05	0.1395
			15	0.592	5.05	0.1495
			20	0.551	4.54	0.1546
			25	0.521	4.17	0.1583
			30	0.507	3.99	0.1601
			35	0.489	3.76	0.1624
			40	0.482	3.67	0.1633
			45	0.470	3.52	0.1648
			50	0.467	3.49	0.1651
			55	0.457	3.36	0.1664
			60	0.452	3.31	0.1669

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Review

Recent Progress on Biosorption of Heavy Metals from Liquids Using Low Cost Biosorbents: Characterization, Biosorption Parameters and Mechanism Studies

A significant number of biosorption studies on the removal of heavy metal from aqueous solutions have been conducted worldwide. Nearly all of them have been directed towards optimizing biosorption parameters to obtain the highest removal efficiency while the rest of them are concerned with the biosorption mechanism. Combinations of FTIR, SEM-EDX, TEM as well as classical methods such as titrations are extremely useful in determining the main processes on the surfaces of biosorbents. Diverse functional groups represented by carboxyl, hydroxyl, sulfate and amino groups play significant roles in the biosorption process. Solution pH normally has a large impact on biosorption performance. In brief, ion exchange and complexation can be pointed out as the most prevalent mechanisms for the biosorption of most heavy metals.

Keywords: Biosorption; Heavy metals; Biosorbent; Mechanism

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1 Introduction

Water contamination by toxic organic chemicals and heavy metals from the miscellaneous industrial wastewater discharges has become a worldwide environmental concern. Thus, heavy metal pollution is considered as a major problem of increasing magnitude. Heavy metals are persistent, and therefore, very difficult to eliminate naturally from the environment, even at a presence of trace amounts. Nearly all heavy metals are highly toxic, non-biodegradable, non-thermodegradable and readily accumulate to toxic levels [1–3]. Heavy metal removal from wastewater has progressed significantly and can now be applied for the protection of the environment and human health. Table 1 provides a short summary of the negative effects of heavy metals on human health [4–11].

To date, several treatment methods for metal ion removal from aqueous solutions have been established, i.e., chemical precipitation, chemical oxidation and reduction, ion exchange, filtration, electrochemical treatment, reverse osmosis, evaporative recovery and solvent extraction [12–14]. Biosorption processes still retain quite a few advantages overt all of the other techniques mentioned. To begin with, it is selective, effective, cheap and works well at very low concentrations [15]. In addition, it is eco-friendly, since the biosorption processes do not generate toxic sludge, which offers further possibilities for metal recovery and potential biosorbent regeneration [16–19]. Biosorption is an alternative technology for the removal of metal ions and organic pollutants from dilute aqueous solutions by employing biomass as the adsorbent, e.g., agricultural and fermentation wastes and various kinds of microorganisms [20–29].

Extensive studies have been undertaken in recent years with the aims of finding alternative and economically feasible adsorbents for wastewater and water treatment. At a large scale, economic sorbents can be defined as materials which are abundant in nature or can be found as a by-product or waste from industry, and which normally do not require pre-processing. Recent studies on the removal of heavy metals using numerous types of biomass are the subject of this review.

During the past ten years, some reviews have been published that mainly focused on different aspects of heavy metal biosorption [30–48]. Shukla et al. [30] emphasized a summary of the functioning of sawdust for the removal of various pollutants from water while Romera et al. [32] directed their review towards statistical methods for heavy metal biosorption by utilizing algae. Liu and Liu [37] recently published a review detailing the isotherms, kinetics and thermodynamics involved in biosorption. The derivations of several popular equations for gas- and liquid-phase adsorption including their application in biosorption systems were briefly featured in the paper. Sud et al. [38] also reviewed the prospective use of agricultural waste to sequester heavy metal ions from aqueous solutions. In parallel with the increasing attractiveness of biosorption research, its pace of advance is also boosted.

At this stage, a requirement to encompass all the latest accomplishments and studies is apparent. For that reason; this review is intended to cover most studies published between 2000 and 2008 that centered on the capabilities of biosorbents and the mechanisms involved for the extraction of metal ions from solutions. As a starting point, the review details the characteristics of biosorbents followed by the presentation of biosorption mechanisms for the

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Table 1. The effects of heavy metals on human health.

Heavy metal	Toxicities	References
Cr (VI)	Headache, nausea, severe diarrhea, vomiting, epigastric pain, hemorrhage, carcinogenic and has an adverse potential to modify the DNA transcription process	[4, 5, 7, 9]
Cr(III)	Allergic skin reactions and cancer	[6]
Zn(II)	Depression, lethargy, neurologic signs such as seizures and ataxia, and increased thirst	[4, 5]
Cu(II)	Liver damage, Wilson's disease, insomnia	[4, 5]
Cd(II)	Kidney damage, renal disorder, Itai-Itai (excruciating pain in the bone), hepatic damage, cancer, and hypertension	[4, 5, 10]
Pb(II)	Encephalophathy, seizures and mental retardation, reduces haemoglobin production	[7, 10]
Ni (II)	Dermatitis, nausea, chronic asthma, coughing, bronchial hemorrhage, gastrointestinal distress, weakness and dizziness	[4–6, 11]

removal of a variety of metals on diverse types of biosorbents. The influence of different process parameters, e.g., pH, temperature and initial concentration, on the biosorbent capacity are considered significant, and therefore, are also the subject of discussion.

2 Biosorbents Characteristics and the Influence on the Metal Binding Process

The physical and chemical characteristics of biosorbents are important for understanding the metal binding mechanism on the biomass surface. The characterization of the structure and surface chemistry of the biosorbent is of considerable interest for the development of adsorption and separation processes. Depending on the nature of the biosorbents, a variety of techniques are useful for this purpose, e.g., Fourier Transform Infra-Red (FTIR) spectroscopy, X-ray Photo Electron Spectroscopy (XPS), Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), Energy Dispersive X-ray (EDX) fluorescence spectrophotometry, nitrogen sorption, etc. These methods are commonly utilized in together to obtain a complete description of the structure, morphology and composition of the biosorbents.

2.1 FTIR Spectroscopy

One important characteristic of a biosorbent is the surface functional groups present, which are largely characterized by the FTIR spectroscopy method. This technique is only capable of providing a qualitative description. Table 2 lists the typical functional groups present in biosorbents [13, 14, 19, 49–85]. Specifically, most biosorption studies utilize FTIR just to determine the availability of certain surface functional groups as part of the structure of biosorbents, although further probing the influence of these groups towards the metal binding process is also possible. Several research groups have provided good discussions about the metal binding mechanism on functional groups based on FTIR results [53, 57, 66, 70, 71, 86, 87].

Pavasant et al. [57] studied the relationship between functional groups on the dried marine green macroalga *Caulerpa lentillifera* and its heavy metal adsorption capability. The authors utilized FTIR to analyze the functional groups in both fresh and dried marine green macroalga. The results indicate that carboxylic acid, amine, amide, amino, sulfonyl and sulfonate groups are dominant in the *Caulerpa lentillifera* structure. In addition, the transmission spectra shift at certain wavenumbers confirms that several surface functional groups are involved in the binding of Cu(II), Cd(II), Pb(II) and Zn(II). As an example, the most plausible explanation behind the shift in

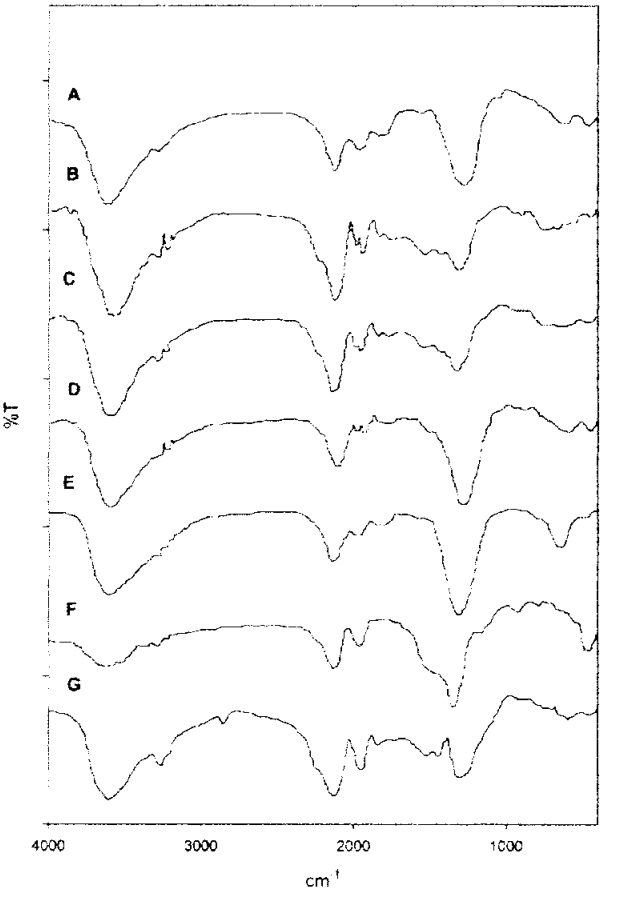

Figure 1. Infrared spectra of (a) Live *Spirulina* sp., and treated with Cd^{+2} ions for different lengths of time, viz. (b) 0.5 (c) 1.5, (d) 2.5, (e), 3.5, and (f) > 12 h. and (g) Dead *Spirulina* sp. after treatment with Cd^{+2} ions for > 12 h. (Taken from [66]).

terms of wavenumber for the –OH bending groups' contained on the carboxylic acid was that these groups were included in the binding of heavy metals. In the case of the amine groups, N–H stretching was found to be responsible for Cu(II) and Pb(II) binding while C–N stretching was detected for all four metals. Another observation revealed that for the amide groups, the C–O bond played an important role for all metal sorption, whereas N–H bending was largely

Table 2. Surface functional groups found in biomass obtained by the FTIR method.

Biomass	Type of Biomass	Surface Functional Groups	Wavenumber (cm^{-1})	Reference
Aerobic granules		–OH and –NH stretching	3200 – 3600	[49]
		$-CH_2$ asymmetric stretching	2928	
		$-CH_2$ symmetric stretching	2850	
		C=O stretching	1725	
		C=O stretching, C–N (amide I)	1648	
		C–N stretching, N–H deformation	1520	
		C=O deformation	1261	
		C–O–C stretching	1130 – 1160	
		C–O bending	1082	
		–OH stretching	1056	
Aspergillu niger		Bonded hydroxyl groups (OH–)	3425 – 3437	[50]
		C–H stretching	2925 – 2926	
		NH_2^+, NH^+, NH	2341 – 2361	
		Amide I, NH_2 bending	1633 – 1639	
		P–O alkyl	1036 – 1037	
		NO^{3-}	851 – 862	
Aspergillus niger	Fungal biomass by pretreatment	Bonded hydroxyl groups (OH–), N–H stretching	3430 – 3400	[51]
		C–H stretching	2930 – 2900, 2860 – 2850	
		C=C groups	2200 – 2050	
		C=O amide, N–H bending, Imines and oximes	1650 – 1640	
		N–H bending	1550 – 1540	
		C–H bending ($-CH_3$)	1460 – 1450	
		Sulfamide bonds (SO)	1380 – 1370	
		C–O stretching of COOH	1260 – 1230	
		Amines (C–N stretching)	1317.74, 1160 – 1150, 1079, 1040 – 1030	
		C–H bending	900 – 850, 785 – 750	
Bacillus cereus	Bacteria	–OH, –NH	3306.48	[52]
		–CH	2930.84	
		COO^-, C=O	1728.68	
		C=O	1655.19	
		COO , –C(=O)–NH–, C=O	1544.20	
		–CH	1453.60	
		COO–, C–N	1381.11	
		–C–N–, P=O, S=O, COO–	1291.09	
		C–N, P–O–C	1184.29	
		P–O	1055.95	
Baker's yeast		O–H	1071	[53]
		C–N stretching	1240	
		C=O	1652	
		N–H stretching	1541	
		CH stretching	2928.7	
Bio-functional magnetic beads (contain *Rhizopus cohnii*)	Mixture of fungus, Fe_3O_4 particle coating with alginate and PVA	Hydroxyl group; N–H stretching	3410	[54]
		C=C	3020	
		C–H stretching	2920	
		NH_2^+, NH^+, C=NH^+–C=O chelate s tretching; amide I band	2350 1650	
		–N=N– of aromatic compounds	1490	
		=C–O–C= ; C=S, C=O stretching, N–H of aliphatic compound	1200	
		=C–O–C=	1080	
Cassia fistula	–	–OH stretching	3300 – 2500	[55, 56]
		–CH stretch	2851.45	
		Carbonyl group stretching	1632 – 1623	
		–NH band	1443.12	
Caulerpa lentillifera	Marine green macroalga	O–H stretching	2922	[57]
		C–O strectching	1244	
		O–H bending	1414	
		N–H stretching	3408	
		N–H bending	1544, 1650	
		C–N stretching	1324	
		S=O stretching	1366	
		S–O stretching	908	

Table 2. Continued.

Biomass	Type of Biomass	Surface Functional Groups	Wavenumber (cm^{-1})	Reference
Cephalosporium aphidicola	Filamentous fungus	–NH and bonded –OH groups	3268	[58]
		$-CH_3$ stretching	2856	
		$-CH_2$ stretching	2925	
		$-CH_3$ bending	1380	
		$-CH_2$ bending	1458	
		Carbonyl stretching	1745	
		C–O stretching	1650, 1077	
		C=N deformation	1558	
		$-SO_3$ stretching	1239	
Chlamydomonas reinhardtii	Microalgae	–OH stretching, –NH stretching	3400–3200	[59]
		Stretching band of carboxyl groups	1652–1544	
		C–O stretch	1232	
		C–H stretching vibrations	2924	
		N–H bending	1544	
		$-CH_3$ wagging	1398	
		C–OH stretching vibrations	1061	
		C–N–C scissoring	530, 470	
Chlorella miniata	Microalgal isolate	Amide I	1654	[60]
		Amide II	1540	
		O–H stretching, N–H stretching	3200–3500	
		C–H stretching vibration		
		C–H stretching deformation	3000–2800	
		Symmetric vibrational COO–	1300–1470	
		P=O	1400	
		C–O	1240, 1076	
Cicer arientinum	Agricultural waste	OH groups	3000 and 3750	[61]
		C–H	2918.18	
		Amide	1634.34	
		C=O	1115.57	
Cladophora fascicularis	Green alga	–OH, $-NH_2$	3376.39	[62]
		C=O	1660.12	
		C–O, C–O–C	1062.26	
Cladophora fascicularis	Green algae	C=O	1660.12	[63]
		Sulfate	1246.96	
		OH stretching	3376.39	
		C–O	1062.26 and 1116.93	
Cotton cellulose	Biomass material	–OH group	3400	[64]
		C=O group	1630	
		C–O–C group	1160	
Dead *Spirulina*	Algal bloom	O–H bending	~3305	[65, 66]
		C–O stretching	1040	
Dried activated sludge		–OH and –NH stretching	3224	[67]
		–CH asymmetric vibration	2925	
		C–O stretching	1651	
		–CN stretching	1532	
		–OH and –C–O stretching	1424	
		–COO stretching	1396	
		–C–O–C and –OH	1027	
Eichhornia crassipes	Water hyacinth	Bonded hydroxyl	3419	[68]
		C=C	1646	
Fucus serratus	Brown algae	Amide and the stretching vibration of C–N included in peptidic bound of proteins	1636 and 1540	[69]
		vibrations of carboxylate and carboxylic acid groups	1384 and 1265	
		vibration of polysaccharides (C–O–C and O–H)	1168	
		Phosphate groups	629	
		Sulfur groups	825	

Table 2. Continued.

Biomass	Type of Biomass	Surface Functional Groups	Wavenumber (cm^{-1})	Reference
Green taro	Aquatic weeds	OH stretch	3763	[70]
		CH antisym and asym stretch	3000	
		NH_2 stretch	2325	
		Several bands from overtone and combination	1920	
		C=O stretch	1707, 1624	
		Ring stretch	1487	
		Antisym stretch	1404	
		C – O stretch	1281	
		SO_3 stretch	1184	
		C – O – C stretch	4	
		C – O stretch	1019	
		CH – CH_2 in vinyl compounds	903, 898	
		C – CO – C bend	655	
Lathyrus sativus	Agricultural waste	Overlapping of O – H and N – H stretching vibration	3200 – 3600	[71]
		C – O	1033.8	
		C – N stretching	1332.7	
		C=O	1660.6	
		N – H stretching	1631.7	
Lignin	–	Stretching vibrations of aromatic and aliphatic OH groups	3412	[72]
		C – H stretching	2925, 2849	
		Carboxyl and carbonyl stretching	1703, 1648	
		Aromatic skeletal vibrations	1600, 1514, 1425	
		Aromatic methyl group vibrations	1463	
		C – O stretching	1329, 1217	
		Syringyl units	1114, 827	
Lignin	Lignocellulosic biomasses	– OH group	3600 – 3000	[73]
		C – O, C – C and C – OH bonds	1000 – 1300	
Live *Spirulina*	algal bloom	C=O stretching	1740	[66]
Mangrove leaves	Aquatic weeds	OH stretch	3389	[70]
		CH antisym and asym stretch	2929	
		NH_2 stretch	2308	
		C=C stretch	2114	
		Several bands from overtone and combination	1907	
		C=O stretch	1706, 1622	
		Ring stretch	1493	
		Antisym stretch	1375	
		NO_2 antisym stretch	1342	
		C – O stretch	1250	
		SO_3 stretch	1192	
		CH – CH_2 in vinyl compounds	909	
Neurospora crassa	Fungal biomass	– OH and – NH_2 groups	3340	[74]
		C – H groups	2928	
		C=O groups	1705	
		NH – groups	1647	
		Amid or sulfamide groups	1408	
Nutshells	Lignocellulosic biomasses	– OH group	3600 – 3000	[73]
		C – O, C – C and C – OH bonds	1000 – 1300	
Olive solid residue	Agricultural waste	g(O – H)	3400	[13]
		g(C – H)	2900	
		g(– NH)	1500	
		g(C=C)	1700	
		g(COO –, C=O)	1037	
Populus tremula	The litter of natural trembling poplar forest	C=O or C=C stretching	1645	[14]
		Carboxylate functional group	1387	
		– C – C – group	782	
Protonated sewage sludge	Various types of dried sludge	– OH	3800 – 2500	[75]
		– COO	1384	
		N – H bending	1662	
		C – N stretching	1238	
		P=O stretching	1164	
		P – OH stretching	941	
		P – O – C stretching	1047	

Table 2. Continued.

Biomass	Type of Biomass	Surface Functional Groups	Wavenumber (cm^{-1})	Reference
Pseudomonas aeruginosa	Bacteria	–OH, –NH, and NH_2	3200–3550	[76]
		C=O stretching	1620–1690	
		C–O stretch of –OH bends	1020–1100	
Pseudomonas aeruginosa		–OH and –NH stretching	3430	[77]
		–CH stretch	2938	
		C=O stretch	1660	
		–NH stretch	1551	
		C=O stretch	1468	
		C=O stretch	1414	
		$-SO_3$ stretching	1246	
		–CN stretching	1080	
Quercus ithaburensis	Waste acorn	Bonded –OH groups	3413	[78]
		C–H stretching	2914	
		C=O stretching	1729, 1626	
		Secondary amine group	1511	
		Carboxyl groups	1447, 1367, 1323	
		$-SO_3$ stretching	1242	
		C–O stretching of ether groups	1158, 1094	
		–C–C– group	1033, 587	
Reed mat	Aquatic weeds	NH stretch	3442	[70]
		CH antisym and asym stretch	2988	
		NH_2 stretch	2369	
		C=C stretch	2120	
		Several bands from overtone and combination	1898	
		C=O stretch	1678, 1624	
		Ring stretch	1510	
		Antisym stretch	1350	
		C–O stretch	1298	
		SO_3 stretch	1146	
		C–O–C stretch	1219	
		C–O stretch	1050	
		CH–CH_2 in vinyl compounds	911, 879	
Rhodococcus opacus		Bonded hydroxyl group, –NH stretching	3354	[19]
		C–H stretching	2927, 2854	
		C=O stretching	1655	
		Amide II band	1541	
		P=O	1240	
		–CN stretching	1076	
Salvinia cucullata	Waste weed	H bonds and OH groups	3350	[79]
		Aliphatic	2930	
		Unsaturated C=C	1630	
		C–O stretch	1420	
		C–O stretch, Si–O stretch	1020	
		Amide bond	1560	
		Aromatic CH	880	
Sawdust from *Arundo donax*	Lignocellulosic biomasses	–OH group	3600–3000	[73]
		C–O, C–C and C–OH bonds	1000–1300	
Sawdust from *Prosopis ruscifolia* wood	Lignocellulosic biomasses	–OH group	3600–3000	[73]
		C–O, C–C and C–OH bonds	1000–1300	
Seed hulls	Lignocellulosic biomasses	–OH group	3600–3000	[73]
		C–O, C–C and C–OH bonds	1000–1300	
Sour orange residue	agricultural waste	–OH groups	3423	[80]
		CH stretching	2925.88	
		C=O band	1631	
		C–O carboxyl band	1257–1244	
Sphaeroplea Algae	Algae	N–H stretching	3419	[81]
		C–H stretching	2918	
		C=O stretching	1718, 1687	
		C–O stretching	1040	
		P=O stretching	1143	
		P–O stretching	910	
		Amide I	1613	
		Amide II	1548	
		C–N stretching	1225	

Table 2. Continued.

Biomass	Type of Biomass	Surface Functional Groups	Wavenumber (cm^{-1})	Reference
Spirogyra sp.	Green algae	O – H stretch	3408	[82]
		Carboxylic/phenolic stretching bands	2925	
		C=N, C=C and C=O stretch		
		N – H bending	1538 and 1442	
		– CH_3 wagging	1353	
		C – OH stretching	1078	
		C – N – S scissoring	1028	
			524 and 467	
Sugarcane bagasse	Lignocellulosic biomasses	– OH group	3600 – 3000	[73]
		C – O, C – C and C – OH bonds	1000 – 1300	
Tamarindus indica	Agricultural waste	– OH or – NH groups	3400 – 3550	[83]
		C=O stretching	1730 – 1750	
Tea waste		Bonded – OH groups	3420	[84]
		Aliphatic C – H group	2915, 2848	
		C=O stretching	1631, 1546	
		Secondary amine group	1511, 1448, 1435	
		Symmetric bending of CH_3	1345	
		– SO_3 stretching	1232	
		C – O stretching of ether groups	1141	
		– CN stretching	634	
Termitomyces clypeatus	biomass of different moulds and yeasts.	N – H and O – H stretching	3500 – 3000	[85]
		Alkyl chains	2920 – 2850	
		C=O stretching	1745.5, 1643.2	
		C=O	1708.1	
		N – H bending, C – N stretching	1550	
		COO –	1541, 1413.7	
		P=O stretching	1150	
		P – O – C stretching	1050 – 970	
		P – OH stretching	1040 – 910	
Twigs from *Ilex paraguaiensis*	Lignocellulosic biomasses	– OH group	3600 – 3000	[73]
		C – O, C – C and C – OH bonds	1000 – 1300	
Water hyacinth	Aquatic weeds	NH stretch	3403	[70]
		OH stretch	3738	
		CH antisym and asym stretch	2997	
		NH_2 stretch	2310	
		C=C stretch	2122	
		Several bands from overtone and combination	1911	
			1705, 1622	
		C=O stretch	1496	
		Ring stretch	1397	
		Antisym stretch	1343	
		NO_2 antisym stretch	1282	
		C – O stretch	1188	
		SO_3 stretch	1043	
		C – O stretch	903, 849	
		CH – CH_2 in vinyl compounds	628	
		C – CO – C bend		
Water lily	Aquatic weeds	NH stretch	3432	[70]
		OH stretch	3785	
		CH antisym and asym stretch	2924	
		NH_2 stretch	2309	
		C=C stretch	2107	
		Several bands from overtone and combination	1907	
			1704, 1636	
		C=O stretch	1489	
		Ring stretch	1353	
		Antisym stretch	1334	
		NO_2 antisym stretch	1235	
		C – O stretch	1180	
		SO_3 stretch	1230	
		C – O – C stretch	1046	
		C – O stretch	909, 859	
		CH – CH_2 in vinyl compounds	549	
		C – CO – C bend		

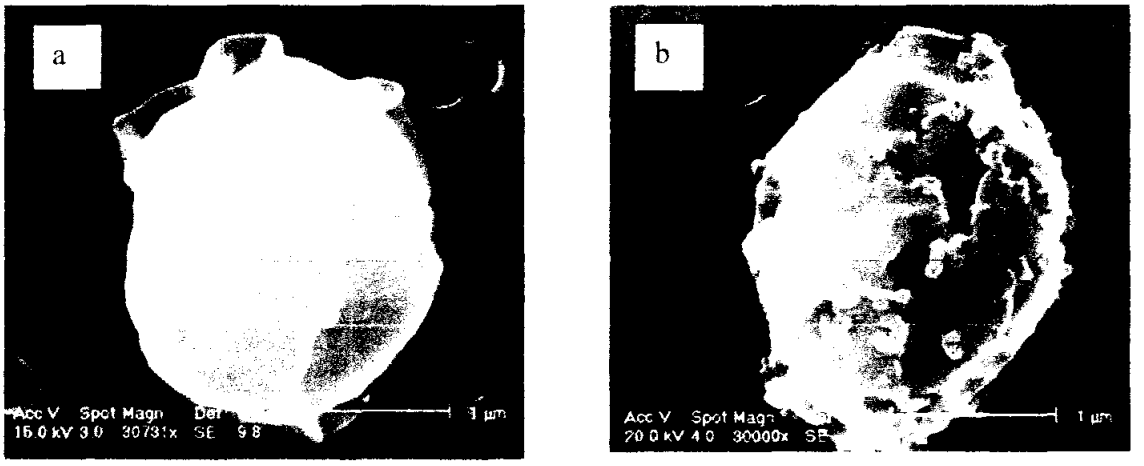

Figure 2. SEM pictures of *Chlorella miniata*: (a) Control cell without Cr(*n*) treatment, and (b) Algae cell treated with 100 mg L^{-1} Cr(III) at pH 4.5 for 24 h. (Taken from [91]).

accountable for the attachment of only Zn(II). Likewise, another important bond within the binding of these four heavy metals was S=O within sulfonyl and sulfonate groups.

The FTIR spectroscopy technique was employed to expose the sorption binding mechanism of Cd(II) by live and dead *Spirulina* [66]. Figure 1 shows the FTIR spectra of live and dead *Spirulina* including its treated forms. The participation of phosphate, carboxylic and amide/amine in Cd(II) binding is evident. However, in live *Spirulina*, the amino group makes a more contribution for metal uptake than carboxylic and phosphate groups.

Baker's yeast is an inexpensive biomass and is readily available. Numerous researchers have devoted their time to verifying the applicability of this material for remediation of heavy metals [53, 86, 88, 89]. Yu et al. [53], used FTIR results to detect the presence of various functional groups on the surface of modified baker's yeast, which explains its surface mechanism complexity. The authors observed that after metal adsorption, a significant shift of the N–H stretching vibration peaks take place, which verifies the chemical interactions between Cd(II), Pb(II) and the amide groups on the biomass surface. The alteration of several peaks due to hydroxyl- and carboxyl-groups after biosorption of the heavy metals, were also noticed. These phenomena highlighted the fact that carboxyl, hydroxyl and amide groups were all engaged in the adsorption of metals.

The plant's cell wall has a very large number of constituents that make the determination of its exact composition difficult. It consists of a large number of complex organic components, e.g., cellulose, lignin, hemicelluloses, proteins and lipids, as well as other inorganic materials such as Ca, K, Mg, etc. By employing FTIR spectra, Yazici et al. [87] made a comparison between the surface structure of *Marrubium globosum*, which was loaded or unloaded with Cu(II), as well being treated or untreated. They claimed that the spectral shift in terms of wavenumber was mainly due to chemical pretreatment, pH and metal binding. Furthermore, they also argued that the solution pH was not as responsible for the radical structural change on the *Marrubium globosum* surface as the chemical pretreatment. The solution pH merely alters the –OH bonds due to H^+ ions binding to the functional groups.

In order to understand the surface binding mechanism, it is therefore essential to identify the functional groups on the biomass. Li et al. [54] developed a practical technique for the recovery of Cr(VI) from wastewater using bio-functional magnetic beads. In their work, FTIR results showed that the $-NH^{3+}$, $-NH^{2+}$, and >NH– groups played an important role in the Cr(VI) adsorption. Raize et al. [90] studied the biosorption mechanism of Cd(II), Ni(II) and Pb(II) by brown marine macroalga. The main groups detected were carboxyl, amino, sulfhydryl, and sulfonate. Das and Guha [85] examined the biosorption of Cr(VI) onto fungal species, e.g., *Termitomyces clypeatus*. They claimed that amino, carboxyl, hydroxyl, and phosphate groups formed chemical bonding with the chromate ion. Moreover, a report by Gupta and Rastogi [82] stated that the presence of amino, carboxyl, hydroxyl and carbonyl groups on the surface of the green algae *Spirogyra* could be accountable for the binding of lead.

2.2 Scanning Electron Microscopy

In general, the characterization of biosorbents by scanning electron microscopy (SEM) offers topographical and elemental information of the solids with a virtually large depth of field, allowing different specimen parts to stay in focus at a time. SEM also has high resolution, making higher magnification possible for closely spaced materials. In addition to its capability to produce an actual clear image, it is also useful for obtaining the topographical aspects of biosorbents [82, 85, 90–93]. However, the SEM technique also has limitations on its lowest detectable particle size and its inability to detect trace elements in a substance.

In the mechanistic study of heavy metal removal by *Sargassum vulgaris*, Raize et al. [90] utilized SEM to acquire the surface topology of unloaded and loaded biosorbent. Heavy metal-loaded biomass had different morphology to the unloaded samples. In the case of loaded samples, the matrix layers of the cell wall were seen to shrink and stick. This structural change was attributable to the strong cross-linking of metal (Cd) and negatively charged chemical groups on the cell wall polymers.

The mechanism of metal biosorption varies according to the metal species and type of biosorbent [91]. SEM was one of several methods used by Han et al. [91] to probe the surface complexation

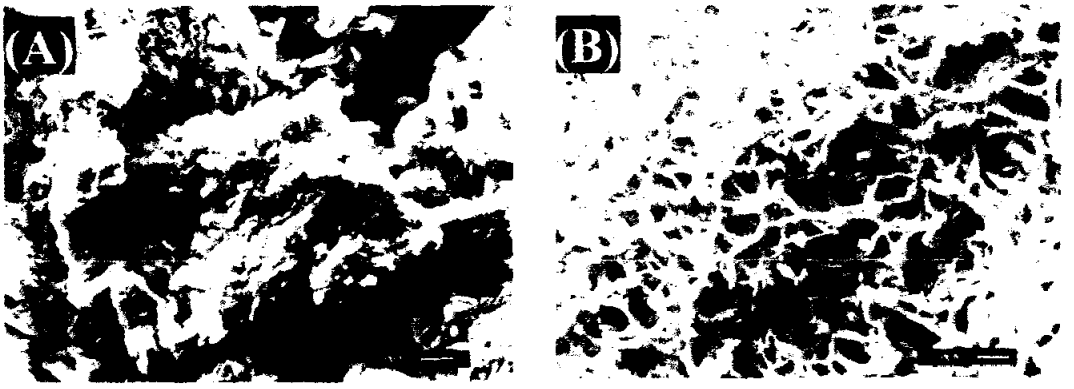

Figure 3. SEM pictures of (a) Pristine (protonated) biomass, and (b) Chromium adsorbed biomass (Taken from [85]).

mechanism in Cr(III) biosorption by *Chlorella miniata*. Figure 2 shows SEM pictures of the algal cell, before and after loading with Cr(III) [91]. The pristine algal cell had a plump shape with a transparent external layer on the outer cell surface, which become wrinkled after the cell adsorbed Cr(III). This observation indicates that the primary Cr(III) sequestering sites are on the cell wall surface instead of the intracellular sites.

Yavuz et al. [92] also used SEM to characterize magnetically modified yeast cells. The modified biomass was chosen to remove mercury ions from artificial wastewater. SEM examination revealed that the surface of the magnetically modified yeast cells was quite rough, supplying a large exposed surface area for biosorption of mercury ions. Accordingly, they concluded that the magnetic yeast cells can effectively be utilized for specific removal of Hg(II) ions from aqueous solutions as they have high biosorption rate and capacity.

The assessment of morphological changes as a result of chromium accumulation within the bacterial strain, *Acinetobacter* sp. has also been conducted using SEM by Srivastava and Thakur [93]. Using SEM pictures, they claimed that chromium was uniformly bound on the cell wall surface of the bacteria. A morphology transformation due to the exposure of the cells to chromate was also evident. Das and Guha [85] conducted another study using chromium as a heavy metal model. A cage-like structure was formed during the interaction of Cr(VI) ions with several functional groups on the surface structure of *Termitomyces clypeatus* as portrayed in Fig. 3 [85]. Other studies using SEM that contrasted the surface structure and morphology of biomass, before and after heavy metal biosorption, are also available for consultation [65, 66, 94].

Gupta and Rastogi [82] probed the biomass in their experiments using SEM with different magnifications, although their SEM pictures just featured the surface texture and morphology of pristine *Spirogyra*. No comparison was shown with lead adsorbed biomass. Surface texture and morphology of the initial (pristine) biomass was also evidenced by using the SEM technique by several research groups [95 – 100].

Meanwhile, some researchers [19, 50, 71, 101 – 110] have also performed surface morphology characterization of biomass with the assistance of SEM-EDX methods, e.g., Chen and Wang [110] have investigated the interaction mechanism between zinc and *Saccharomyces cerevisiae* using this technique. SEM pictures and EDX spectra of the intact yeast cells, before and after zinc uptake, substantiated the existence of covalent interactions between Zn(II) and surface groups of *Saccharomyces cerevisiae*. Gonzalez-Chavez et al. [102] provide another example of the usefulness of the SEM-EDX combination. They scrutinized Cu accumulation in the extraradical mycelium of three arbuscular mychorrhizal fungi. More detail of the bonding formations was acquired, which showed that these fungi are capable of accumulating Cu within their mucilaginous outer hyphal wall zone, cell wall as well as inside the hyphal cytoplasm. SEM pictures and EDX spectra taken, before and after Pb(II) biosorption onto heat inactivated *Botrytis cinerea*, clearly verified the existence of Pb particles that looked like "billiard balls" in the biomass' surface [103].

2.3 Transmission Electron Microscopy (TEM)

The ability of transmission electron microscopy (TEM) to provide information on crystalline structures as well as density maps that reach subatomic resolution is of great interest and widely applicable for the characterization of miscellaneous biomass [91, 93, 96, 102, 11]. With regards to its subatomic resolution, this technique can offer clearer evidence on the internal structure of the biomass. However, since TEM is very costly, its utilization to probe the internal structure of biomass is uncommon. A well-featured TEM image (see Fig. 4), has been shown by Han et al. [91] for Cr(VI) adsorption on *Chlorella miniata*. Figure 4a) demonstrates that the algae cell surface is transparent and the cell wall can be easily distinguished. After loading with Cr ions, a film of electron dense material was recognized on the cell wall surface, as depicted in Fig. 4b) [91].

2.4 X-ray Photoelectron Spectroscopy (XPS) Analysis

X-ray photoelectron spectroscopy (XPS) is a special chemical analysis technique used to resolve the elemental composition, empirical formulae, chemical and electronic states of the elements that exist within the surface region of a sample. For each particular element, a certain characteristic binding energy can be associated with each core atomic orbital. This technique is surface-specific due to the short range of photoelectrons excited from the solid.

In the biosorption field, XPS has been used to scrutinize the surface chemical structure of biosorbents [49, 53, 86, 90, 96, 101, 112 – 117]. In the mechanism investigation of Cd(II), Ni(II), and Pb(II) biosorption by *Sargassum vulgaris*, XPS provided valuable information

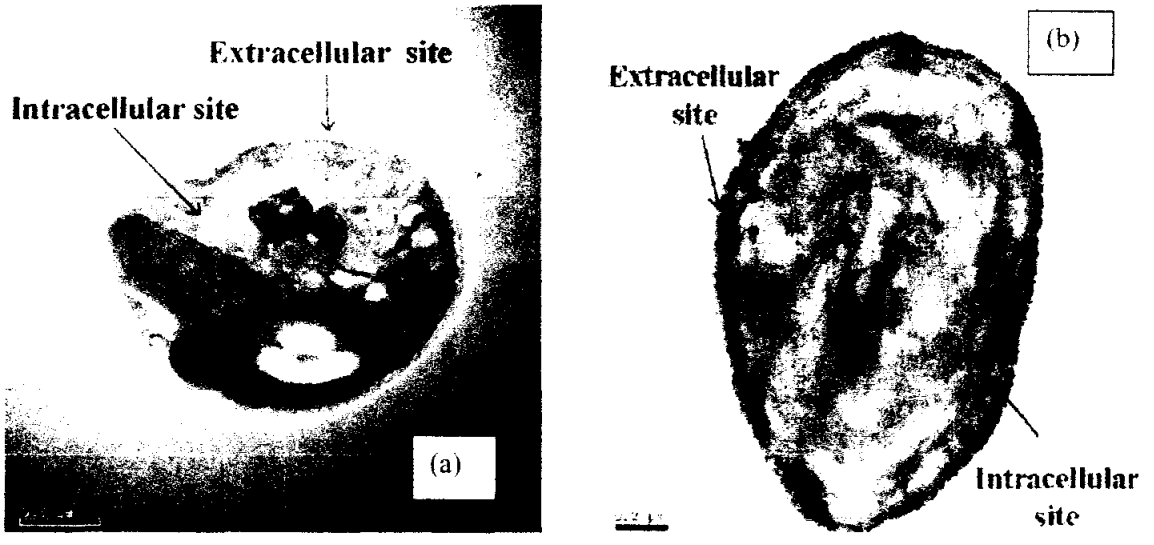

Figure 4. TEM pictures of *Chlorella miniata*: (a) Control cell without Cr(III) treatment, and (b) Algae cell treated with 100 mg L^{-1} Cr(III) at pH 4.5 for 24 h (Taken from [91]).

on heavy metal uptake by this brown marine macroalgae [90]. The resultant XPS spectra indicated that heavy metal binding was accompanied by changes in sulfur, nitrogen, oxygen, and carbon binding. Sulfur containing groups, e.g., thiol and sulfonate, as well as oxygen containing groups, e.g., carboxyl, were involved in cadmium and lead biosorption. On the other hand, nickel cations mainly attached to functional groups containing oxygen [90].

Sheng et al. [113] deduced the chelating characteristics of metal coordination to the functional groups in the cell walls of brown algae from XPS spectra. The functional groups participating in Pb(II), Cu(II), Cd(II), Zn(II) and Ni(II) biosorption comprise carboxyl, ether, alcoholic and amino groups. Sulfonate groups did not contribute substantially in the binding mechanism of bivalent metals ions.

In another example to clarify the biosorption mechanism, XPS was employed to probe the surface structure change of baker's yeast grafted with polyamic acid prior and subsequent to Cd(II) and Pb(II) biosorption [116]. XPS results prove that the interaction of Pb(II) with amide and hydroxyl groups on the biomass surface takes place via ion exchange or electrostatic interaction despite the fact that a coordination mechanism might also occur between the metal and carboxylate groups.

2.5 Energy-Dispersive X-Ray Spectroscopy

Energy dispersive X-ray spectroscopy (EDX) is another useful technique for elemental analysis or chemical characterization of a sample. In biosorbent characterization, this method is routinely coupled with SEM analysis to achieve more complete results [19, 40, 71, 91, 93, 101, 103–110, 118]. EDX make use of X-rays emitted from the lower part of a sample's interaction volume during electron beam bombardment that carries a specific energy according to their molecular weight.

Liu and Xu [107] studied the equilibrium, thermodynamics and mechanisms of Ni^{2+} biosorption by aerobic granules. EDX analysis indicated that Ni^{2+} ions could penetrate into the aerobic granule core, and additionally on element mapping, the adsorbed Ni^{2+} distribution within the aerobic granule was seen to be uniform [107].

2.6 X-Ray Absorption Fine Structure Spectroscopy (XAFS)

X-ray absorption fine structure spectroscopy (XAFS) is a spectroscopic technique that utilizes X-rays to probe the physical and chemical structure of material at an atomic scale. XAFS is element-specific, in which X-rays are selected to be at and above the binding energy of a particular core electronic level of a certain atomic species. Chen and Wang [110] exploited XAFS to investigate the interaction between zinc and *Saccharomyces cerevisiae*. From the results, they found that the nearest neighboring atom of the attached zinc ion on the biomass is an oxygen atom. Moreover, adsorbed zinc ions on the intact cells of *S. cerevisiae* had a tetrahedron structure with a Zn–O bond length of 1.97 Å while the coordination number was only 3.2.

2.7 X-Ray Diffraction (XRD) Spectroscopy

X-ray diffraction (XRD) is a non-destructive technique used to provide detailed information on the crystallographic structure of materials. This method offers several advantages, e.g., non-destructive, high accuracy, capability to detect single crystals, polycrystalline or amorphous materials. Moreover, standards are readily accessible for thousands of material systems. Due to its versatility, XRD has been widely employed to assist in the characterization of biosorbents and in the verification of heavy metal biosorption mechanisms [49, 96, 107, 119]. As an example, in Pb(II) biosorption on cellulose/chitin beads [96], the XRD pattern of the Pb-loaded cellulose/chitin beads exhibited distinct and complex peaks, denoting the deposition of crystallized lead, which is likely to be caused by lead hydroxides and lead carbonate.

2.8 Characterization Based on Titration Methods

Originally developed to determine oxygenated surface groups on activated carbons, Boehm's titration method is based on the acid-base titration of carbon acidic or basic centers. This method gives a semi-quantitative measure of surface functionalities. The assessment of the quantity of acidic groups is subject to the assumptions that NaOH neutralizes carboxylic, lactonic and phenolic groups, while Na_2CO_3 neutralizes carboxylic and lactonic groups, whereas $NaHCO_3$ neutralizes only carboxylic groups. In addition, the amount of basic sites can be determined from the total HCl that reacts with the adsorbent [120]. This method is quite common for the characterization of activated carbons. However, in the biosorption field, only a small number of research groups have utilized Boehm's method [2, 121, 122], since this method only presents a semi-quantitative measure of functional groups. As a rule, a description of a biosorption mechanism cannot be verified by semi-quantitative data.

Another titration method that can resolve the nature of functional groups on the biomass surface is potentiometric titration [69, 72, 76, 77, 123]. Kang et al. [77] studied Cr(III) and Cr(VI) biosorption on *Pseudomonas aeruginosa*. They utilized this method for surface characterization of bacteria cells. The results showed that the biomass contains at least two main functional groups on its surface. Exploiting the chemical models that comprise reactions between different bacteria groups and protons in the solution, the equilibrium constants *pKa* and *pKb* resembled those of carboxyl and hydroxyl groups. Their reactions models are written as Eqs. (1) and (2):

$$AH \rightarrow A^- + H^+,\ Ka = \frac{[A^-][H^+]}{[AH]} \quad (1)$$

$$BH^+ \rightarrow B^- + H^+,\ Kb = \frac{[B^-][H^+]}{[BH^+]} \quad (2)$$

where $[A^-]$, $[B^-]$, and $[AH]$, $[BH^+]$ represent the concentration of deprotonated and protonated surface groups, respectively and $[H^+]$ signifies the proton activity in solution.

Guo et al. [72] used a nonelectrostatic surface complexation model to explain the potentiometric titration data. They approached the proton dissociation from ligands on lignin surface using Eq. (3):

$$S_iOH \rightarrow S_iO^- + H^+,\ Ka_i = \frac{[S_iO^-][H^+]}{[S_iOH]} \quad (3)$$

In addition, the complexation between a metal ion and lignin proceeds by Eq. (4):

$$S_iOH + M^{2+} \rightarrow S_iOM^+ + M^+ \quad (4)$$

The resultant surface acidity constants were log $Ka_1 = -5.57$ to -5.20 and log $Ka_2 = -7.51$ to -7.23, respectively, attributable to carboxylic- and phenolic-type surface groups.

The characterization of acidic sites on *Pseudomonas* biomass by Kony et al. [76] was also facilitated by potentiometric analysis. In their work, they assumed that *Pseudomonas aeruginosa* contains three acidic sites, i.e., COOH (S_1), NH_2 (S_2) and PO_4^{3-} and these acidic sites had the capability to bind protons. Eqs. (1) to (3) as shown above were also employed.

2.9 Surface Area Measurements

The surface area of a solid is another important feature required to fully understand and interpret the ion sorption properties of the solid [69, 85]. In general, the surface area was obtained by applying the BET equation in the relative pressure range of 0.05–0.25 to nitrogen sorption data. Almost all previous studies have shown that biomass has low BET surface area as a result of either low porosity or surface smoothness [69, 72, 82, 85, 97, 124]. For this reason, the physical sorption does not seem to play a significant role in biosorption processes.

3 Influence of Biosorption Conditions on the removal of Heavy Metals

The investigation of the factors affecting the efficiency of heavy metal biosorption is of great interest for the industrial community. The efficiency is strongly influenced by the physico-chemical characteristics of the solutions, e.g., pH, temperature, initial concentration, etc. A large portion of biosorption studies has been devoted to investigating this relationship. Table 3 summarizes the findings of the key investigations. This section is intended to give a brief discussion on these parameters.

3.1 Influence of pH

The solution pH is a crucial factor in heavy metals biosorption. The pH value significantly influences the dissociation site on the surface of the biomass and the solution chemistry of the heavy metals, e.g., hydrolysis, complexation by organic and/or inorganic ligands, redox reactions, and precipitation, as well as the speciation and biosorption availability for heavy metals [33, 57, 72, 76, 104, 113, 124–129]. In a particular pH range, most metal sorption is enhanced with pH, increasing to a certain value followed by a reduction on further pH increase.

In principle, the dependence of metal uptake on pH can be associated with both the surface functional groups on the biomass' cell walls as well as the metal chemistry of the solution [113]. The pH value of the medium affects the equilibrium of the system [125] in accordance with Eqs. (1) or (2), so that the pH can be written as Eq. (5):

$$pH = pKa - \log\frac{[AH]}{[A^-]} \quad (5)$$

When the pH value is lower than the pKa, the equilibrium shifts to the left (refer to Eq. (1)), protons are consumed and the pH rises until its value approaches the pKa. The opposite trend happens if the pH value is higher than the pKa [125].

The investigation of Pb(II), Cu(II), Cd(II), Zn(II), and Ni(II) sorption by *Sargassum* sp. and *Padina* sp. (brown macroalgae), *Ulva* sp. (a green macroalga), and *Gracillaria* sp. (a red macroalga) was carried out in the pH range of 2.0–6.0 [13]. The improved metal sorption with higher pH was attributable to the increase in the amount of ligands for metal ion binding. Moreover, at low pH, competition occurs between protons and metal ions, leading to less metal uptake. Similar tendency were also recognized in heavy metal biosorption by algae, e.g., biosorption of Cr(III) by the green algae *Spirogyra* sp. [130]; Cd(II) by *Corallina officinalis*, *Porphyra columbina* and *Codium fragile* [73]; Cu(II) and Pb(II) by *Cladophora fascicularis* [62, 63]; Pb(II) by *Spi-*

Table 3. Data on the biosorption of heavy metals using different biosorbents.

Biosorbent	Metal	Operating Conditions[a]			q_{max}[b], (mg g^{-1})	References
		pH	T, (°C)	C_o, (mg L^{-1})		
Acid treated *Sphaeroplea*	Ni(II)	4.0–6.0	33	50–500	244.85	[81]
Algae	Cu(II)				216.535	
Acinetobacter sp.	Cr(VI)	3, 5, 7, 9	30	2000	NA	[93]
Activated sludge	Cd(II)	2.0	25	10–150	28	[126]
	Cu(II)				19.05	
	Ni(II)				8.85	
	Pb(II)				142.83	
	Zn(II)				15.6	
Activated sludge	Cd(II)	4.0	25	10–1000	NA	[154]
	Cu(II)					
	Zn(II)					
	Ni(II)					
Aerobic granules	Cd(II)	6.0 ± 0.5	25	100	NA	[49]
	Cu(II)					
	Ni(II)					
Almond shells	Cr(VI)	1.0–10.0	30	20–1000	NA	[155]
Alternaria	Cd(II)	5.0	25	2, 4, 6, 8	NA	[156]
	Ni(II)					
	Cr(II)					
	Cu(II)					
	Co(II)					
	Zn(II)					
	Pb(II)					
Arca shell	Pb(II)	1.0–7.0	25 ± 2	10–500	NA	[11]
	Cu(II)					
	Ni(II)					
	Co(II)					
	Cs(I)					
Arundo donax	Cd(II)	5.8 + 0.1	28 + 1	0.04–0.09	NA	[73]
	Ni(II)					
Ascophyllum nodosum	Cd(II)	1.0–6.0	NA	10–150	87.7	[125]
	Ni(II)				43.3	
	Zn(II)				42.0	
	Cu(II)				58.8	
	Pb(II)				178.6	
Asparagpsis armata	Cd(II)	1.0–6.0	NA	10–150	32.3	[125]
	Ni(II)				17.1	
	Zn(II)				21.6	
	Cu(II)				21.3	
	Pb(II)				63.7	
Aspergillus	Cd(II)	5.0	25	2, 4, 6, 8	NA	[156]
	Ni(II)					
	Cr(II)					
	Cu(II)					
	Co(II)					
	Zn(II)					
	Pb(II)					
Aspergillus Niger	Cr(VI)	1.0–10	25	30	NA	[134]
Aspergillus Niger	Mn(II)	2.0–11.0	NA	25–200	NA	[157]
Aspergillus Niger	Co(II)	1.0–6.0	20–35	25–250	NA	[158]
	Pb(II)					
Aspergillus niger	Cr(VI)	2.0–8.0	5 + 2	10	14.5	[51]
			15 + 2		15.2	
			22 + 2		10.6	
			30 + 2		11.1	
Aspergillus niger	Cr(VI)	6.0	30	500	NA	[111]
Aspergillus niger	Cu(II)	2.0–8.0	NA	10–100	NA	[159]
Aspergillus Sydoni	Cr(VI)	1.0–10	25	30	NA	[134]
Australian Marine algae	Pb(II)	1.0	21 ± 2	0.4–4.5	4.14	[160]
DP95Ca		2.0			157.32	
		3.0			267.03	
		4.0			304.29	
		5.0			320.85	

Table 3. Continued.

Biosorbent	Metal	Operating Conditions[a]			q_{max}[b], (mg g^{-1})	References
		pH	T, (°C)	C_o,(mg L^{-1})		
Australian Marine algae DP95Ca	Cu(II)	1.0	21 ± 2	0.4 – 4.5	2.54	[160]
		2.0			11.43	
		3.0			62.865	
		4.0			76.835	
		5.0			82.55	
Australian Marine algae ER95Ca	Pb(II)	1.0	21 ± 2	0.4 – 4.5	10.35	[160]
		2.0			86.94	
		3.0			204.93	
		4.0			242.19	
		5.0			260.82	
Australian Marine algae ER95Ca	Cu(II)	1.0	21 ± 2	0.4 – 4.5	4.445	[160]
		2.0			28.575	
		3.0			60.325	
		4.0			67.31	
		5.0			70.485	
Bacillus cereus	Pb(II)	5.5	25	5 – 100	36.71	[52]
	Cu(II)				50.32	
Bacillus jeotgali	Cd(II)	4.0 – 7.0	25	35	37.3	[161]
			30		47.5	
			35		57.9	
Bacillus jeotgali	Zn(II)	4.0 – 7.0	25	75	105.2	[161]
			30		222.2	
Bacillus licheniformis	Cr(VI)	2.0 – 6.0	25, 37, 50	20 – 300	69.35	[162]
Bertholettia excelsa	Cd(II)	5.8 + 0.1	28 + 1	0.04 – 0.09	NA	[73]
	Ni(II)					
Brewery waste	Pb(II)	4.0	30	33.1 – 1656	85.49	[110]
	Ag(I)			17.3 – 864	42.77	
	Sr(II)			14.1 – 704	72.29	
	Cs(I)			21.3 – 1064	10.11	
Cactus leaves	Cr(VI)	1.0 – 10.0	30	20 – 1000	NA	[155]
Cassia fistula	Ni(II)	3.0 – 8.0	30	25 – 800	188.40	[55]
Cephalosporium aphidicola	Pb(II)	1.0 – 6.0	20 – 40	100 – 400	92.322	[58]
Cladophora fascicularis	Co(II)	2.0 – 6.0	15, 25, 35, 45	11.8 – 236	NA	[115]
Chlamydomonas reinhardtii	Hg(II)	2.0 – 7.0	25	20 – 400	122.61	[59]
	Cd(II)				77.625	
	Pb(II)				146.97	
Chlorella miniata	Cr(VI)	0 – 4.0	25	50, 100 200	NA	[60]
Chlorella Vulgaris	Co(II)	4.0 – 5.0	25	5 – 300	NA	[163]
Chlorella vulgaris	Cd(II)	4.0	25	25 – 150	58.4	[164]
	Ni(II)	4.5			86.6	
Chlorella vulgaris	Cr(VI)	1.0 – 5.5	25	25 – 250	NA	[8]
Chondrus crispus	Cd(II)	1.0 – 6.0	NA	10 – 150	75.2	[125]
	Ni(II)				37.2	
	Zn(II)				45.7	
	Cu(II)				40.5	
	Pb(II)				204.1	
Chroococcus sp.	Cr(VI)	1.0 – 5.0	26	5 – 20	21.36	[135]
Chryseomonas luteola TEM 05 cells	Cr(VI)	6.0	25	1.92	NA	[165]
	Cd(II)			0.89		
	Co(II)			1.69		
Cladonia rangiformis hoffin	Cu(II)	2.0 – 5.0	15	10 – 100	7.6923	[166]
Cladophora fascicularis	Cu(II)	2.0 – 6.0	15 – 45	12.7 – 254	NA	[62
Coconut copra meal	Cd(II)	3.0 – 7.0	26	10.5 – 201	4.92	[140]
			28		4.68	
			50		2.66	
			60		2.01	
Coconut copra meal	Cd(II)	3.53, 4.06, 4.52, 5.04, 5.53	24	100 – 120	NA	[148]
Codium fragile	Cd(II)	5.8 + 0.1	28 + 1	0.04 – 0.09	NA	[73]
	Ni(II)					

Table 3. Continued.

Biosorbent	Metal	Operating Conditions[a]			q_{max}[b], (mg g^{-1})	References
		pH	T, (°C)	C_o, (mg L^{-1})		
Codium vermilara	Cd(II)	1.0 – 6.0	NA	10 – 150	21.8	[125]
	Ni(II)				13.2	
	Zn(II)				23.8	
	Cu(II)				16.9	
	Pb(II)				63.3	
Corallina officinalis	Cd(II)	5.8 + 0.1	28 + 1	0.04 – 0.09	NA	[73]
	Ni(II)					
Cotton cellulose	B(III)	6.0	NA	5 – 500	6.8780	[64]
		6.5			13.0550	
		7.0			15.4080	
		7.5			17.7940	
		8.0			41.4940	
Crab shell	Cu(II)	3.5 – 6.0	NA	500 – 2000	243.9	[167]
	Co(II)				322.6	
Cupriavidus taiwanensis	Pb(II)	NA	37	100 – 1500	50.01	[168]
	Cu(II)				19.0	
	Cd(II)				19.6	
Dried activated sludge	Cr(VI)	1.0 – 6.0	25	25 – 500	NA	[169]
	Ni(II)					
Eichhornia crassipes	Cr(VI)	1.0	25	10 – 100	NA	[68]
Enteromorpha prolifera	Ni(II)	2.0 – 5.0	20	50 – 150	55.55	[143]
			25		58.82	
			30		65.36	
Escherichia coli	Ni(II)	NA	35 – 37	50 – 400	NA	[170]
	Cd(II)					
Eucalyptus bark	Cd(II)	2.0 – 5.0	20	25 – 300	20.58	[129]
			30		22.52	
			40		25.25	
			50		29.67	
Exhausted coffee	Cu(II)	5.2	20 ± 1	5 – 300	11.60	[171]
	Ni(II)				7.25	
Fucus spiralis	Cd(II)	1.0 – 6.0	NA	10 – 150	114.9	[125]
	Ni(II)				50.0	
	Zn(II)				53.2	
	Cu(II)				70.9	
	Pb(II)				204.1	
Fusarium	Cd(II)	5.0	25	2, 4, 6, 8	NA	[156]
	Ni(II)					
	Cr(II)					
	Cu(II)					
	Co(II)					
	Zn(II)					
	Pb(II)					
Fungi from serpentine soil of Andaman	Co(II)	2.0 – 9.0	30	0.5 – 4.0	NA	[172
Geotrichum	Cd(II)	5.0	25	2, 4, 6, 8	NA	[156]
	Ni(II)					
	Cr(II)					
	Cu(II)					
	Co(II)					
	Zn(II)					
	Pb(II)					
Grape stalk	Cu(II)	5.2	20 ± 1	5 – 300	42.92	[171]
	Ni(II)				38.31	
Green coconut shell	Cr(VI)	1.0 – 10.0	27	20 – 100	NA	[106]
	As(V)					
	Cd(II)					
	Cr(III)					
Green coconut shell powder	Cd(II)	4.0 – 9.0	27	20	NA	[132]
Green taro (*Colocasia esculenta*)	Cr(III)	4.5 – 5.5	30	10 – 150	6.072	[70]
	Cr(VI)				1.418	
Hazelnut shell	Ni(II)	3.0 – 8.0	20 – 40	15 – 200	NA	[137]
Hybrid biosorbent	Cd(II)	2.0 – 8.0	25 ± 2	10 – 500	141.32 ± 3.25	[173]

Table 3. Continued.

Biosorbent	Metal	Operating Conditions[a]			q_{max}[b], (mg g^{-1})	References
		pH	T, (°C)	C_o, (mg L^{-1})		
Hydrilla verticillata	Cd(II)	1, 3, 5, 7, 9	25 + 2	1, 10, 100	15	[174]
Ilex paraguaiensis	Cd(II)	5.8 + 0.1	28 + 1	0.04 – 0.09	NA	[73]
	Ni(II)					
Lignin	Pb(II)	5.5	20	0.2 – 2.5	1293.75	[72]
	Cu(II)				22.86	
	Cd(II)				25.43	
	Zn(II)				11.18	
	Ni(II)				6.018	
Live and dead *spirulina*	Cd(II)	6.0 ± 0.5	35 – 38	2000 – 20000	NA	[66]
Maize bran	Cr(VI)	1.4 – 8.0	20 – 40	20 – 300	NA	[136]
Mangrove leaves (*Rhizophora mangle* L)	Cr(III)	4.5 – 5.5	30	10 – 150	6.544	[70]
	Cr(VI)				0.342	
Marrubium globosum	Co(II)	5.5	25	50	NA	[87]
Mimosa pudica without inoculatttion	Pb(II)	NA	37	100 – 1500	26.1	[168]
	Cu(II)				22.7	
	Cd(II)				25.3	
Mirabilis jalapa	Cd(II)	5.8 + 0.1	28 + 1	0.04 – 0.09	NA	[73]
	Ni(II)					
Modified yeast cell	Hg(II)	2.0 – 7.0	4 – 35	25 – 200	114.6	[92]
Moringa oleifera	As(III)	2.0 – 12.5	NA	1 – 100	NA	[97]
	As(V)					
NaOH treated Sour orange residue	Cu(II)	4.5	28	300	52.08	[80
NaOH Untreated Sour Orange residue	Cu(II)	4.5	28	300	23.47	[80]
Nemspora crassa	Pb(II)	4.0 ± 0.1	25	5 – 300	43.29	74]
	Cu(II)	5.0 ± 0.1			5.55	
Nostoc calcicola	Cr(VI)	1.0 – 5.0	26	5 – 20	12.23	[135]
Oil palm fiber	Cr(VI)	1.5 – 5.0	28 ± 1	20 – 200	NA	[99]
Olive cake	Cr(VI)	1.0 – 10.0	30	20 – 1000	NA	[155]
Olive Cake	Cd(II)	2.0 – 11.0	28	100	65.359	[128]
			35		60.606	
			45		44.444	
Orange peel	Pb(II)	1.0 – 7.0	NA	103.5 – 2070	NA	[175]
Palm tree leaves	Zn(II)	5.0 – 5.8	25	20 – 300	14.7	[176]
Penicillium	Cd(II)	5.0	25	2, 4, 6, 8	NA	[156]
	Ni(II)					
	Cr(II)					
	Cu(II)					
	Co(II)					
	Zn(II)					
	Pb(II)					
Palm kernel fiber	Pb(II)	3.0 – 8.0	36 ± 3	120	NA	[177]
Penicillium janthinellum	Cr(VI)	1.0 – 10	25	30	NA	[134]
Phanerochaete chrysosporium	Cd(II)	2.0 – 8.0	25 ± 2	10 – 500	68.61 ± 2.47	[173]
Pine needles	Cr(VI)	1.0 – 10.0	30	20 – 1000	NA	[155]
Populus tremula	Cu(II)	4.5	25 – 60	30 – 200	NA	[14]
Pseudomonas aeruginosa	Cr(III)	NA	25	0 – 5	NA	[77]
	Cr(VI)					
Quercus ithaburensis	Cr(VI)	2.0 – 6.0	24, 45, 60	100, 200, 300, 400	NA	[78]
Reed mat (*Cannonois Vvirgata*)	Cr(III)	4.5 – 5.5	30	10 – 150	7.184	[70]
	Cr(VI)				1.662	
Rice bran	Zn(II)	3.0 – 5.0	30	40 – 160	14.17	[178]
			40		14.84	
			50		18.31	
Rhizopus arrhizus	Pb(II)	2.0 – 5.0	20 – 45	5 – 15	2.643	[179]
Rhizopus arrhizus	Cr(VI)	1.3	30	50 – 200	NA	[180]
Rhizopus arrhizus	Cr(VI)	4.0	25	25 – 250	NA	[181]
	Cu(II)			25 – 300		
Rhodococcus opacus	Pb(II)	5.0 ± 0.2	28 ± 1	15 – 200	94.185	[19]
	Cr(III)	6.0 ± 0.2			73.008	
	Co(II)	6.0 ± 0.2			29.854	
Saccharomyces cerevisiae	Cr(VI)	1.0 – 6.0	NA	25 – 200	384.61	[182]
Saccharomyces cerevisiae	Mn(II)	2.0 – 11.0	NA	25 – 200	NA	[157]

Table 3. Continued.

Biosorbent	Metal	Operating Conditions[a]			q_{max}[a], (mg g^{-1})	References
		pH	T, (°C)	C_o, (mg L^{-1})		
Saccharomyces cerevisiae	Cd(II)	7.3	25	1.12–22.4	NA	[183]
Saccharomyces cerevisiae	Zn(II)	7.3	25	0.65–13	NA	[183]
Sargassum glaucescens	Pb(II)	5.0	20 ± 2	1	NA	[184]
	Cd(II)					
Sphaeroplea Algae	Ni(II)	4.0–6.0	33	50–500	200.6	[81]
	Cu(II)				140.335	
Sphaerotilus natans	Co(II)	3.0–6.0	NA	NA	NA	[185]
	Cd(II)					
Spirulina platensis	Cr(VI)	1.0–5.5	25	25–250	NA	[8]
Spirogyra insignis	Cd(II)	1.0–6.0	NA	10–150	22.9	[125]
	Ni(II)				17.5	
	Zn(II)				21.1	
	Cu(II)				19.3	
	Pb(II)				51.5	
Spirogyra sp	Cu(II)	2.5–5.0	NA	50–250	133.3	[186]
Streptomyces rimosus	Cu(II)	5.0	25	100	NA	[187]
	Zn(II)					
	Cr(VI)					
Tea factory waste	Cr(VI)	2.0–5.0	25, 45, 60	50–400	54.65	[133]
Tea factory waste	Ni(II)	2.0–5.0	NA	50–200	NA	[188]
Tea waste	Cu(II)	2.0–7.0	22 ± 2	25–200	NA	[189]
	Pb(II)					
Termitomyces clypeatus	Cr(VI)	3.0	30	10–1000	NA	[85]
Trichoderma	Cd(II)	5.0	25	2, 4, 6, 8	NA	[156]
	Ni(II)					
	Cr(II)					
	Cu(II)					
	Co(II)					
	Zn(II)					
	Pb(II)					
Ulva lactuca	Pb(II)	2.0–8.0	20–50	10–400	34.7	[131]
	Cd(II)				29.2	
Water hyacinth (*Eichornia crassipes*)	Cr(III)	4.5–5.5	30	10–150	6.614	[70]
	Cr(VI)				0.342	
Water lily flower (*Nymphaea* sp.)	Cr(III)	4.5–5.5	30	10–150	6.112	[70]
	Cr(VI)				5.110	

[a] NA: Not available.

rogyra sp. [82]; Cr(III) by *Chlorella miniata* [91]; Cu(II), Cd(II), Pb(II), and Zn(II) by *Caulerpa lentillifera* [57]; Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) by *Codium vermilara*, *Spirogyra insignis*, *Asparagopsis armata*, *Chondrus crispus*, *Fucus spiralis* and *Ascophyllum nodosum* [125] and also Pb(II) and Cd(II) by *Ulta lactuca* [131].

Anber and Matouq [128] looked at the pH effect on metal uptake in the adsorption process of heavy metals using agricultural waste, e.g. olive cake. Upon increasing the pH from 2 to 6, the removal efficiency of Cd(II) increased from 42 to 66%. Practically speaking, at low pH, the concentration of H^+ ions was high, and hence, Cd(II) ions must compete with H^+ ions in order to attach to the surface functional groups of the olive cake. With the pH rise, fewer H^+ ions exist, and consequently, Cd ions have a better chance to bind to free binding sites. Later, when the pH enters basic conditions (Eqs. (6–8)), the formation of $Cd(OH)_3^-$ takes place due to the dissolution of $Cd(OH)_2$ and as a result, the adsorption rate decreases.

$$Cd^{2+} + H_2O \rightleftharpoons Cd(OH)^+ + H^+ pK_1 = 9 \quad (6)$$

$$Cd^{2+} + 2H_2O \rightleftharpoons Cd(OH)_2 + 2H^+ pK_1 = 19.1 \quad (7)$$

$$Cd^{2+} + 3H_2O \rightleftharpoons Cd(OH)_3^- + 3H^+ pK_1 = 30.3 \quad (8)$$

The removal of cadmium by green coconut shell powder was also shown to be pH dependent. At pH 4, the removal efficiency is only 69%. By increasing the pH to 7, the percentage removal rises to 98% [132]. The efficiency value then stays steady at pH 7 to 9 while higher pH brings about the precipitation of Cd(II) ions to $Cd(OH)_2$ as indicated by Eq. (7). Tea factory waste has also been utilized as a heavy metal adsorbent by Malkoc and Nuhoglu [84, 133]. The maximum adsorption performance for Ni(II) ions was found at a pH of 4 [84], followed by a significant decrease after the pH value is adjusted to 2.

In contrast the opposite trend can also exist, e.g., in Cr(VI) adsorption on fungal biomass. Low pH values favor this system [134]. In acidic solution, i.e., pH range 2.0–6.0, the chromium ions exist in the form of $HCrO_4^-$ and $Cr_2O_7^{2-}$ so that their equilibrium relations can be written as Eqs. (9) and (10):

$$H_2Cr_2O_7 \longrightarrow 2H^+ + Cr_2O_7^{2-} \quad (9)$$

$$H_2CrO_4 \rightleftharpoons H^+ + HCrO_4^- \quad (10)$$

However, in alkaline pH, the equilibrium relation differs as represented by Eqs. (11) and (12):

$$Cr_2O_7^{2-} + OH^- \rightarrow HCrO_4^- + CrO_4^{2-} \quad (11)$$

$$HCrO_4^- + OH^- \rightarrow CrO_4^{2-} + H_2O \quad (12)$$

The most plausible answer behind the high adsorption capacity at low pH values is the presence of excess H^+ ions that are able to neutralize the negatively charged adsorbent surface, and thereby, reduce the hindrance for diffusion of dichromate ions [134]. Similar tendencies were also noticed in the adsorption of chromium ions from solutions by diverse biosorbents [54, 61, 68, 78, 79, 85, 98, 99, 114, 132, 133, 135, 136].

3.2 Influence of Temperature

Depending on the structure and surface functional groups of a biosorbent, temperature has an impact on the adsorption capacity, to a certain extent. It is well known that a temperature change alters the adsorption equilibrium in a specific way determined by the exothermic or endothermic nature of a process. Quite a number of biosorption studies have been performed concerning the effect of temperature on isotherms, metal uptake and also with respect to biosorption thermodynamics parameters [14, 17, 78, 82, 114, 122, 128, 129, 133, 136 – 143].

The impact of temperature on the adsorption isotherm of cupric and cadmium ions by corncob particles at a certain pH was explored by Shen and Duvnjak [138]. They found that the uptake of ions increased with higher temperature. A more enhanced level of uptake in parallel with a temperature rise resembles the nature of a chemisorption mechanism (endothermic process). These trends were also spotted by other research groups [114, 122, 133, 141, 142]. In contrast, Padmavathy [144] obtained the opposite behavior for the temperature effect on adsorption capacity. In his study, higher temperature leads to a lower adsorption capacity of baker's yeast.

For engineering practice, enthalpy, entropy and Gibbs free energy factors generally need to be determined so that the spontaneity of the process can be inferred [140, 141, 144]. These thermodynamic properties, i.e., enthalpy, entropy and Gibbs free energy of adsorption can be estimated using equilibrium constants as a function of temperature [141]. The Gibbs free energy change, ΔG°, which is normally considered as a spontaneity indicator of a chemical reaction can also serve as a criterion for spontaneity in biosorption processes [140]. The relation between Gibbs free energy change and temperature, T, as well as biosorption equilibrium constant, K_a, is given by Eq. (13):

$$\Delta G^\circ = -RT \ln K_a \quad (13)$$

A negative Gibbs free energy value indicates the feasibility and spontaneous nature of the biosorption process [2, 14, 79, 92, 100, 128, 129, 131, 133, 136, 140, 145].

Likewise, the enthalpy, ΔH°, and entropy, ΔS°, changes for the biosorption process can be estimated from biosorption equilibrium constants as a function of temperature via the Van't Hoff equation, Eq. (14):

$$\ln K_a = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (14)$$

A positive ΔH° value signifies the endothermicity of a process [2, 14, 62, 63, 79, 92, 129, 136, 146], while exothermic processes usually has negative ΔH° value [100, 128]. On the other hand, a positive ΔS° value denotes the increased randomness at the solid-solution interface during the biosorption process [2, 79, 92, 128, 136, 140, 146], whereas negative ΔS° values represent the opposite phenomenon (decreased randomness) [100].

3.3 Effect of Ionic Strength

Industrial wastewater often contains other than heavy metal ions, e.g., Na^+, K^+, Mg^{2+}, and Ca^{2+}, which may interfere with heavy metal ion uptake by biomass. The ionic strength as indicated by the presence of light metals in solution is an important variable that plays a role in the aqueous phase equilibrium. Miscellaneous inorganic chemicals, e.g., NaCl, $NaNO_3$, KCl, $MgCl_2$, $CaCl_2$, etc., have been employed to elucidate the effect of ionic strength on heavy metal uptake. As a general trend, the metal uptake is found to decrease with increasing ionic strength of the aqueous solution as a result of more electrostatic attraction and metal activity change [11, 62, 63, 72, 76, 102, 124, 129, 147 – 150].

3.4 Effect of Initial Concentration

The initial heavy metal concentration can alter the metal removal efficiency through a combination of factors, i.e., the availability of specific surface functional groups and the ability of surface functional groups to bind metal ions (especially at high concentrations). The initial concentration acts as a driving force to overcome mass transfer resistance for metal ion transport between the solution and the surface of the biomass. Several studies that sought to clarify the effect of initial heavy metal concentration on metal uptake by biosorbent have been undertaken [2, 11, 13, 14, 19, 50, 79, 83, 92, 98 – 101, 103, 114, 129, 130, 133 – 136, 142, 148, 149, 151]. Taty-Costodes et al. [101] found that the initial ion concentration exhibits quite an interesting effect on the equilibrium sorption capacity of the *Pinus sylvestris* for Cd(II) and Pb(II). At a fixed biosorbent dose, pH and temperature, the equilibrium sorption capacity improved with higher initial ion concentration. The ion removal was highly concentration dependent. The increase in the biosorbent's loading capacity as a function of metal ion concentration was believed to be due to a high driving force for mass transfer. In agreement with this, a more concentrated solution should display better adsorption performance. In their experiment, for most cases with low initial ion concentration, the sorption capacity or metal uptake was enhanced with higher initial ion concentrations. However, the opposite phenomenon occurred when starting with high initial ion concentration. The authors argued that this opposite tendency was caused by saturation of the available active sites on surface functional groups, thus preventing further metal ion uptake.

3.5 Effect of Adsorbent Dosage

The amount of biomass in the solution also affects the specific metal uptake. By increasing the adsorbent dose, the adsorption efficiency increases even though the amount adsorbed per unit mass decreases. In principle, with more adsorbent present, the available adsorption sites or functional groups also increase. In turn, the amount of adsorbed heavy metal ions is increased, which brought about an improved adsorption efficiency [2, 11, 14, 19, 24, 58, 68, 79, 83, 98, 99, 104, 125, 128 – 131, 140, 146, 147].

4 Biosorption Mechanism

Biosorption applications have derived their usefulness through the metal binding capacities of various biological materials. Biosorption is made possible by the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical uptake pathways. Due to the interaction of several factors on specific biosorbents, it is almost impossible to propose a general mechanism. Although several metal-binding mechanisms have been put forward, e.g., chemisorption by ion exchange, coordination and/or chelation, complexation, physical adsorption, etc., the actual mechanism of metal biosorption is still not fully understood [33].

4.1 Chemisorption Mechanism

Ion exchange is a reversible chemical reaction where an ion within a solution is replaced by a similarly charged ion attached onto an immobile solid particle [91]. In general, the ion exchange mechanism can be represented by Eq. (15):

$$M^{X+} + X(HY) \rightarrow XH^{+} + MY_X \tag{15}$$

where HY corresponds to the number of acid sites on the solid surface, M^{X+} is metal ion, and MY_X is the sorbed M^{X+}. By considering Eq. (15) as shown above, the ion-exchange equilibrium constant can be determined by Eq. (16):

$$K_{ie}^{H} = \frac{[H^+]^X[MY_X]}{[M^{X+}][HY]^X} \tag{16}$$

Romero et al. [145] claimed that cadmium biosorption on dealginated seaweed waste followed an ion exchange mechanism. They investigated the cadmium ion binding process using several techniques such as potentiometric titration, FT-IR spectroscopy, calcium displacement and esterification. The resultant ion exchange constant for the adsorption in their study was $0.329 \cdot 10^{-6}$ [145].

Tan and Cheng [146] examined the mechanism involved for the removal of five heavy metals, i.e., Cu(II), Ni(II), Zn(II), Pb(II), and Cr(III), by *Penicillium chrysogenum* using a series of batch experiments. Ion exchange was claimed as the dominant mechanism. Akar et al. [104] probed the interaction between Pb(II) ions and the fungus *Aspergillus parasitus*. They stated that this biosorption process could be expressed by ion exchange or complexation. Ion exchange was later ruled out as the most plausible mechanism by data for the adsorption energy value, *E*, obtained from the D-R isotherm model. The yeast *Rhodotorula glutinis* was tested for its capability to remove Pb(II) from aqueous solution by Cho and Kim [147]. The Pb(II) removal mechanism by *R. glutinis* involved direct biosorptive interaction with the biomass through ion exchange and precipitation by phosphate released from the biomass. The interaction between Pb(II) ions and the functional groups on the surface of the fungus *Aspergillus parasiticus*'s cell wall is also believed to occur by a combination of ion exchange and complexation processes [104].

Ofomaja and Ho [148] highlighted the role of ion exchange in the biosorption of cadmium ions onto copra meal. They performed their experiments at different initial cadmium concentrations and pH values. Increasing the initial cadmium concentration leads to a reduction of the final pH value. This phenomenon occurred due to the replacement of H^+ ions on functional groups by cadmium ions in the bulk solution. They generated a plot of initial cadmium ion concentration vs. H^+ ions, with the aim of obtaining the connection between initial cadmium ion concentration and the amount of H^+ ions released into solution. A simple correlation of $C_0 = 50.6\,\Delta H^+ - 9.85$ was determined, from which the ion exchange rate with respect to initial cadmium concentration was 50.6 mg/g mM of proton concentration.

Ahmady-Asbchin et al. [69] noticed that in the biosorption of copper ions on *Fucus serratus*, the bond between the copper ions and the surface functional groups of the biomass formed as soon as calcium ions were released from the surface. This ion exchange process is one of the most well-known surface reactions, which represents a great degree of complexity, primarily due to its multi-species nature. By employing Eqs. (15) and (16), the authors proposed that the ion-exchange reaction proceeds according to Eq. (17):

$$\overline{FS - M^{2-}} + [Cu^{2-}]_{solution} \rightarrow \overline{FS - Cu^{2-}} + [M^{2-}]_{solution} \tag{17}$$

while the apparent selectivity constant is believed to be given by Eq. (18):

$$K^{Cu^{2-}/M^{2-}} = \frac{\overline{FS - Cu^{2+}}}{\overline{FS - M^{2+}}} \times \frac{[M^{2+}]}{[Cu^{2-}]} \tag{18}$$

The apparent selectivity constants obtained from their experimental data were 3.37 ± 1.10 and 3.88 ± 1.43 for calcium and magnesium, respectively. A slightly higher value for magnesium as compared to calcium denoted the fact that it was easier to substitute the magnesium ions on the surface of *Fucus serratus* by Cu(II) ion than calcium ions.

Chen and Wang [110] investigated the interaction between zinc and *Saccharomyces cerevisiae* by employing a combination of SEM-EDX and XAFS methods. The existence of both covalent and ionic bonds between Zn(II) and the available functional groups on a yeast cell surface was verified by displacement of H^+, K^+, Mg^{2+}, Ca^{2+}, and Na^+ ions during zinc uptake. The release of K^+, Mg^{2+}, Ca^{2+}, and Na^+ from the biosorbent during heavy metal ion attachment was taken as evidence that ion exchange was the dominant mechanism. The existence of an ion-exchange mechanism during Pb(II), Ni(II), Cu(II), and Cd(II) biosorption by olive stone waste was reported by Fiol et al. [124]. They spotted a significant release of Ca^{2+}, Mg^{2+}, and K^+ from the biosorbent immediately after the uptake of Pb(II), Ni(II), Cu(II), and Cd(II). Ion-exchange processes were also suggested as the main biosorption mechanism by other research groups [49, 71, 90, 101, 148, 155].

Metal sequestration during biosorption adheres to complex mechanisms that mainly include ionic interactions, formation of complexes between metal cations and ligands contained within the cell wall biopolymer structure and precipitation on the cell wall matrix. Raize et al. [90] proposed biosorption mechanisms of different heavy metals by brown marine macroalgae. In their study, Cd(II) ions were attached to chemical groups containing oxygen, carbon, nitrogen and sulfur. In addition, the binding process did not alter the magnesium and calcium concentration in solution, which indicates that ion exchange might not be the main mechanism for Cd(II) biosorption on the brown marine macroalgae *Sargassum vulgaris*. A similar phenomenon was also observed for lead, but in this experiment, the binding process was also accompanied by a significant decrease in calcium and magnesium concentration, which denotes the existence and major role of combined chelation and ion-exchange mechanisms [90].

Another frequently encountered metal binding mechanism is chelation. Chelation can be properly defined as a firm binding of a

metal ion with an organic molecule (ligand) to form a ring structure. As mentioned before, various functional groups including carboxylate, hydroxyl, sulfate, phosphate amides, and amino groups can be considered responsible for metal sorption. Among these groups, the amino group is the most effective for removing heavy metals, since it does not merely chelate cationic metal ions but also adsorbs anionic metal species through electrostatic interaction or hydrogen bonding [149]. In order to clarify the sorption mechanisms of Cr(VI) anions on modified *Penicillium chrysogenum*, Deng and Ting [149] studied Cr(VI) speciation and *Penicillium chrysogenum* surface properties at different pH values. At values of pH less than 10.4, the amino groups on the surface of *Penicillium chrysogenum* are protonated and adsorb anionic hexavalent chromium via electrostatic attractions, as shown by Eq. (19):

$$-NH_3^+ + (HVCr)M \rightarrow NH_3^+ \ldots (HVCr)M^- \quad (19)$$

where $(HVCr)^{M-}$ represents anionic hexavalent chromium. In addition, in the pH range of 2.4 to 10.5, both Cr(VI) and Cr(III) are present on the surface of the biomass, suggesting that anionic hexavalent chromium ions were reduced to Cr(III) during the sorption process. In turn, the resultant Cr(III) species may then be chelated by the amine groups [149].

Panda et al. [150] also reported the significant role of amine groups in Ni(II) binding. The chelation of transition Ni(II) took place through dative bonds with the lone pair of electrons within nitrogen present in the $-NH_2$ groups of *Lathyrus sativus*. Figure 5 shows a schematic diagram of chelation and cation exchange mechanism, as proposed by Panda et al. [150]. Furthermore, the importance of various functional groups on the surface of the biomass, e.g., amino, phosphate, hydroxyl and carboxyl groups, was demonstrated by chemical modification. A reduction in adsorption capacity was observed upon modifying these chemical functional groups. The contribution of amine groups in the Cu(II) adsorption by *Mucor rouxii* was verified by Majumdar et al. [108]. Altun and Pehlivan [151] revealed that chelation and ion-exchange were mainly behind Cu(II) adsorption from aqueous solutions by walnut, hazelnut, and almond shells. These combination (chelation and ion exchange) mechanisms were also verified for Cr(VI) adsorption on modified red pine saw dust [152].

Guo et al. [72] put forward a nonelectrostatic surface complexation model to describe the mechanism of biosorption of several heavy metals on lignin. They used Eqs. (20) to (23) to explain the complexation of a metal ion with lignin:

$$S_1OH + M^{2+} \Leftrightarrow S_1OM^+ + H^+ \quad (20)$$

Their model was based on the formation of 1:1 and 1:2 complexes for each type of site, i.e., carboxylic and phenolic groups, to match the experimental data for the adsorption of Pb(II), Cu(II), Ni(II), Cd(II), and Zn(II):

$$2\,S_1OH + M^{2+} \Leftrightarrow (S_1O)_2M + 2H^+ \quad (21)$$

$$S_1OH + S_2OH \Leftrightarrow (S_1O)(S_2O)M + 2H^+ \quad (22)$$

$$(S_1OH) + M^{2+} + H_2O \Leftrightarrow S_1OMOH + 2H^+ \quad (23)$$

At low pH, the metals predominantly exist as free ions in the aqueous state. As the pH increases, the concentration of free metal ions decreases and the carboxylic-type sites contribute significantly

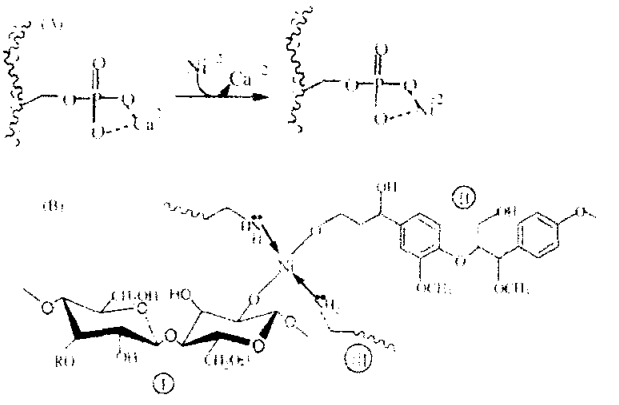

Figure 5. Adsorption mechanism of Ni(II) with HLS biomass: (a) Cation exchange between Ca(II) and Ni(II); (b) Chelation of Ni(II). (I) denotes cellulosic moieties, (II) lignin moieties and (III) protein moieties of HLS biomass (Taken from [150]).

to the binding actions by forming monodentate complexes, i.e., S_1OM^+. Metal adsorption onto phenolic-type sites is seen at higher pH values. Concurrent with the constant pH increase, the concentration of free metal ions in the aqueous phase decreases, and monodentate complexes, i.e., S_1OM^+, are converted into bidentate complexes, i.e., $(S_1O)(S_2O)M$ [72].

In the adsorption mechanism study of Hg(II) on *Aspergillus versicolor* biomass [127], the effect of amino, carboxyl and hydroxyl groups on the adsorption process were apparent. The coupling of electrostatic and complexation reactions was evident. At low pH values, the binding of Hg(II) ions with surface amino groups follows Eq. (24):

$$R-NH_2 + Hg(II)X \rightarrow R-NH_2Hg(II)X \quad (24)$$

while carboxyl and hydroxyl groups proceed according to Eqs. (25) and (26):

$$R'-O^- + Hg(II)X \Leftrightarrow R'-O^-\,Hg(II)X \quad (25)$$

$$R'-COO^- + Hg(II)X \Leftrightarrow R'-COO^-\,Hg(II)X \quad (26)$$

At low pH, the coulombic repulsion between Hg(II) and the positively charged functional groups lead to a reduction of mercury uptake. Enhanced mercury adsorption beyond pH 3.5 was attributed to the formation of negatively charged carboxyl and hydroxyl groups with strong affinities for positively charged or neutral mercury species (shown in Eqs. (25) and (26)) due to electrostatic interaction [127].

4.2 Physical Adsorption Mechanism

In physical adsorption, a weak Van der Waals attraction is observed between an adsorbate and a surface. From a thermodynamic point of view, physical adsorption is spontaneous (negative Gibbs energy) and exothermic (negative value of ΔH°). Physical adsorption normally does not play an important part in biosorption processes. However, in several rare biosorption cases, physical adsorption can actually be dominant, e.g., in Cd(II) adsorption by olive cake [128] and Cu(II) adsorption on rubber leaf powder [100].

5 Competitive Metal Biosorption

In most cases, biosorption is utilized for wastewater treatment where more than one type of metal ion is encountered. The removal of one metal ion may be influenced by the presence of other metal ions [19, 141]. Chemical interactions between different species and with the biomass may take place, resulting in competition for the adsorption sites on the surface [19]. As a result, the uptake of metal ions in a competitive adsorption process would be less than that for individual adsorption [103, 138, 157].

Shen and Duvnjak [138] conducted an investigation into competitive adsorption between copper and cadmium ions on corncob particles. Their results showed that the uptake of metal ions in the presence of other competing metal ions was only slightly lower than their individual adsorption at similar operating conditions. In addition, the metal with the smaller ionic diameter, i.e., copper ions, can be adsorbed to a greater extent from the mixture than the ions with larger ionic diameter, i.e., cadmium ions. Since they have lower molecular weight and ionic diameter, the cupric ions have a higher diffusion velocity on the surface and a greater availability to pores in corncob particles as compared to cadmium ions. Furthermore, copper ions have one unpaired electron leading to better attraction with the electric field originating from the adsorbent, while the electrons in cadmium ions are paired [138].

The physico-chemical properties of the metallic species have also been shown to be factors in the binding of metal ions on biomaterials [19]. Due to the chemical interactions between metal ion species in multicomponent mixtures, the component that has higher affinity will readily be adsorbed onto the available adsorption sites, e.g., in the cases of Pb(II), Cr(III), and Cu(II) biosorption by *Rhodococcus opacus*, the metal removal increases with higher affinity, in decreasing order according to Pb(II) > Cu(II) > Cr(III). A biosorption experiment for a binary mixture showed that the presence of copper in the solution resulted in a significant suppression of lead uptake, while the presence of chromium has a less significant effect on lead biosorption [19].

6 Control of Biomass Adsorption Capacity

Pretreatment and modification of biomass using physical or chemical methods can be performed with the aim of enhancing the capability and efficiency of biomass adsorption. The effect of pretreatments on the biosorption capability of biomass varies largely according to the biomass and heavy metal ions chosen [11, 53, 54, 71, 86, 87, 90, 92, 101, 103, 105, 116, 117, 130, 134, 155, 156, 158–160]. In the following paragraphs, the application of several aspects of modification or pretreatment to control the adsorption capability of biomass is discussed.

Surface chemistry modification on *Sargassum* biomass has been carried out using an extraction method followed by soaking in hydrochloric acid solution, which leads to lower metal binding capacities for several heavy metals [90]. In *Sargassum*, the cell wall contains large amounts of alginic acid and sulfated polysaccharides. High concentrations of carboxyl and sulfonate groups exist within these polysaccharides, which are believed to be useful for the uptake of metal cations. During the extraction process, several parts of these polysaccharides were removed, and as a result, the total number of binding sites was lower. The presence of less binding sites results in decreased metal uptake. Panda et al. [105] also reported a similar negative effect towards heavy metal uptake upon surface modification.

Deng et al. [153] carried out surface modification on fungal biomass, *Penicillium chrysogenum*, using polyethylenimine (PEI). This process created long chains of PEI on the surface of the biomass, which provided extra amine sites for metal adsorption, and thus, enhanced the sorption capacity. The as-modified biosorbent was shown to be promising for Cr(VI) removal from aqueous solution due to the protonation of the amino groups on the biomass' surface. After modification with PEI, a 7.2 fold increase in sorption capacity for Cr(VI) was observed [153]. An enhanced adsorption capacity as a result of surface modification was also observed by other research groups [53, 54, 71, 86, 87, 92, 95, 116, 117, 130, 155].

7 Conclusions

Miscellaneous low-cost sources of biomass have been utilized as effective biosorbents for heavy metal removal from wastewater. Diverse techniques exist for the characterization of biosorbents, although a combination of these techniques is commonly required to obtain a complete description of the structure and surface functional groups. Several factors, e.g., pH, temperature, ionic strength, and initial concentration including biosorbent dose, affect the biosorption to various extents. Depending on the interplay of these factors and to a greater extent, specific biosorbent characteristics, diverse metal-binding mechanisms can take place during biosorption processes, e.g., chemisorption by ion exchange, coordination and/or chelation, complexation, as well as physical adsorption. Furthermore, with the presence of other competing metal ions, chemical interactions between the metals of interest and these other metals and biomass can occur, leading to a competition for the adsorption sites on the surface. As a final note, chemical modification of biosorbents has been applied successfully in some cases to improve the adsorption capacity and removal efficiency. To this end, further work is required in this field.

Symbols used

K_{al} [–] equilibrium constant
K_b [–] equilibrium constant
ΔG° [kJ mol^{-1}] Gibbs free energy
ΔH° [kJ mol^{-1}] enthalpy
ΔS° [J mol^{-1}] entropy
R [J K mol^{-1}] gas constant, (8.314 J K mol^{-1})
T [K] temperature
K_{IE}^{H} [–] ion-exchange equilibrium constant

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Review: The review covers most studies published between 2000 and 2008 that centered on the capabilities of biosorbents and the mechanisms involved for the extraction of metal ions from solutions. The characteristics of biosorbents are detailed followed by the presentation of biosorption mechanisms for the removal of a variety of metals on diverse types of biosorbents. The influence of different process parameters on the biosorbent capacity are also discussed.- which was composed of a CN column

Recent Progress on Biosorption of Heavy Metals from Liquids Using Low Cost Biosorbents: Characterization, Biosorption Parameters and Mechanism Studies

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