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Comparison of Four Different Polymeric Adsorbents as Clean-up Agents for Pesticide Analysis in Tea with LC MS/MS

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Abstract: Previously published studies indicate that tea (*Camellia sinensis*) contains essential oils, flavonoids, phenolics, lipids, natural pigments, sugars, and oligosaccharides. These essential biomolecules in *Camellia sinensis* cause serious problems in the determination of pesticide residues. High amount of co extractives can exhibit chromatographic characteristics similar to some pesticides, which may cause serious matrix effects and significant interference in mass spectrometry analysis. In this study, we compared four polymeric resins as clean-up sorbents for the determination of 216 pesticide residues in tea by a high performance liquid chromatography triple quadrupole mass spectrometry. styrene-divynilbenzene (Diaion HP20), Polyamide 6, Polyvinylpolypyrrolidone (PPVP), and Amberlite XAD 7 were used as clean-up sorbents instead of PSA. However,to evaluate the effectiveness of the adsorbents, recovery studies were carried out using these adsorbents. In addition, GC-MS analysis was also performed to see the ability of these adsorbents to remove co-extracts. According to the recovery results, when the acceptable limit was accepted as 60-140%, it was determined that the resin that gave the best results with 170 pesticides was polyamide. Diaion was the second resin with 166 pesticides, while XAD, PSA which was used as control group and PPVP were determined as the third, fourth, and fifth resins with very close values of 159, 155, and 152 pesticides, respectively. According to GC-MS total ion analysis, it was observed that PSA gave the chromatogram with the least co- extract, while it was observed that PSA was the worst adsorbent in removing caffeine, one of the main bioactive compounds in tea. XAD-7 and Polyamide were found to be the best adsorbents in removing caffeine.

Keywords: Pesticide**,** LC-MS/MS**,** Tea, Adsorption, QuEChERS, clean-up.

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1. INTRODUCTION

Pesticides are widely used in agriculture to protect the products from harmful pests and diseases. Besides its positive effects, pesticide residue can be hazardous to human health. For this reason, many countries have applied monitoring programs to control pesticide residues in edible products. Pesticide residues can easily be found in tea due to their widespread usage in order to kill pests and to eliminate weeds and diseases during the tea cultivation (1). Tea is one of the most widely consumed beverages for centuries. Tea contains essential oils, flavonoids, phenolics, lipids, natural pigments, sugars, and oligosaccharides (2). Therefore, tea is an important source of antioxidants and its health-promoting effects have been widely investigated. Antioxidant effect of tea mainly comes from polyphenols such as flavonols (quercetin, kaempferol, myricetin), flavan-3-ols (catechins and theaflavins), and alkaloids (caffeine and theaflavins), gallic acid derivatives, hydroxycinammate quinic esters (caffeoylquinic acids) (3, 4). On the other hand, these essential characteristic compounds of tea cause serious problems for determination of pesticide residues in tea. A high amount of co-extractives can exhibit chromatographic characteristics similar to some pesticides, which may cause serious matrix effects and significant interference in mass spectrometric analysis (2). In the mass spectrometer, these polyphenols compete with the target analytes for access to the droplet

surface prior to gas phase emission which may suppress or enhance the ionization of target compounds, and affect the detection results (5). Since the target analytes occur at low concentrations and belong to a wide range of chemical classes, it is critical that isolation of pesticide residues in acceptable recovery range while minimizing co extractives and matrix effects.

In the literature, there are previously published methods for determination of pesticide residues in tea. These methods usually include solid phase extraction (6-8) and dispersive solid phase extraction (QuEChERS) (9, 10). In time, the QuEChERS methods has been most widely used method for determination of pesticide residues in food samples. Furthermore, this method has become a standard test method of AOAC 2007.01. Despite the fact that this method has been developed in the determination of pesticide residues in fruits and vegetables, with slight modifications it can be used for other food matrices. The method includes extraction of pesticide with acetonitrile, and the raw extract is cleaned up with dispersive solid phase extraction (SPE) by mixing with magnesium sulfate and primary secondary amine (PSA) to remove water and undesired co-extractives. PSA is the most commonly used sorbents in QuEChERS methods and its main function is to remove co-extracted constituents such as fatty acids, sugars, and ionic lipids. Another sorbent option is known as C18. The C18 has a nonpolar nature which is useful in removing fat and wax content of the matrix. Although PSA and C18 are widely used as dispersive solid phase extraction sorbents, some novel sorbents have been used as alternatives to cope with complex matrixes. Li et al (2013), developed a novel magnetic SPE method based on magnetic cobalt ferrite-filled carbon nanotubes to determine organochlorine pesticides in tea and honey samples (1). Liu et al (2014), have used graphene with PSA and graphitized carbon black as dispersive solid phase extraction sorbent for the clean-up of tea samples (11). Hou et al (2013), have developed a modified QuEChERS method using multi-walled carbon nanotubes as a dispersive solid phase extraction sorbent for the analysis of 78 pesticides in tea (12). Rejczak and Tuzimski (2017) have used zirconium(IV) oxide (ZrO_2)-based sorbents and PSA as dispersive solid phase extraction clean up material for determination of pesticide in milk (13). Li et al. (2013) have used PPVP, PSA and GCB as clean-up sorbents to remove co-eluting matrix components for the determination of 16 pesticide residues in tea (14). Sun et al. (2022) used a combined sorbent package consisting of MWNTs-OH and PSA for the extraction and purification of 57 pesticides to remove the interferences of pigment in *Lonicerae japonicae* flower buds and improve the quantitative accuracy in pesticide residues analysis (15). Zhao and Shi used non-porous boron nitride nanorods (p-BNNRs) as clean-up sorbents to eliminate matrix interference in QuEChERS analysis method for the detection of five neonicotinoid pesticide residues in goji berries (16).

Polyamide is well suited for the separation of natural substances with phenolic and polyphenolic groups. Because of its swelling properties, polyamide has a higher adsorption capacities than most sorbents currently on the market. This swelling property makes it suited for preparative chromatography as well as for the analysis of biological material (separation of undesirable accompanying compounds). Polyamide is commonly used as an adsorbent for the isolation and identification of natural substances with phenolic and polyphenolic functional groups, e.g. anthocyanins, anthoxanthines, anthraquinone derivatives, and flavones.

Diaion (synthetic adsorbent resin) is a macroporous styrenic polymeric bead type resin designed for adsorption/desorption process scale applications. Its matrix provides an aromatic non-polar surface with excellent selectivity for hydrophobic areas of molecules, including biomolecules like antibiotics via low-energy van der Waals interactions. It is remarkable for its wide pore polymeric structure which provides excellent broad spectrum adsorption characteristics.

Polyvinylpolypyrrolidone (PVPP) is a resinous polymer that acts similarly to proteinaceous fining agents. It is particularly useful in the selective removal of flavans and mono- and dimeric phenolics. As such, PVPP has particular value in diminishing undesirable bitter taste. For this reason, it is usually added relatively early in maturation. It is also efficient in preventing oxidative browning and removing its brown by-products from white wines. It functions well at cool temperatures and precipitates spontaneously. Meng et al. (2021), used a d-SPE purification method for the determination of 134 pesticide in tea using a multi-functional filter which consisted of two layers, an upper layer of porous PVPP to absorb polyphenols and a lower layer containing a mixture of PSA, GCB and anhydrous magnesium sulfate, to remove substances such as pigments (17). Guo et al. (2018), develop a method for determination of 20 pesticide residues from polyphenol-rich agricultural samples (tea, apple, broccoli, and shallot) by using PVPP to precipitate polyphenols. They used clean-upcombination of PVPP (150 mg), PSA (50 mg) and GCB (10 mg) in the clean-up step to remove co-extracts (18). XAD adsorbents are very porous spherical polymers based on highly crosslinked, macro-reticular polystyrene, aliphatic, or phenol-formaldehyde condensate polymers. Amberlite XAD-7 is a non-ionic aliphatic acrylic polymer, which derives its adsorptive properties from its macro-reticular structure (containing both a continuous polymer phase and a continuous pore phase), high surface area, and the aliphatic nature of its surface. It is characterized as a hydrophobic adsorbent having a somewhat more hydrophilic structure comparing to

XAD-4. Its macro-reticular structure also gives it excellent physical and thermal stability and it is also stable at all pH range in an aqueous solution. Due to its aliphatic nature amberlite XAD-7 can adsorb non-polar compounds from aqueous systems and can also adsorb polar compounds from non-polar solvents (19,20).

In this study, it was aimed to modify the QuEChERS method by using polymeric adsorbents as a clean-up agent in pesticide analysis in tea. The adsorbents used in this study were used for the first time in the QuEChERS method as a clean up agent in pesticide analysis in tea. In addition, these adsorbents were tested for the first time for the analysis of a high number of pesticides (216) in the analysis of pesticides in tea samples. In this study, we compared four polymeric resins as clean-up sorbents for the determination of 216 pesticide residues in tea by high performance liquid chromatography triple quadrupole mass spectrometry. We used Diaion, Polyamide, PPVP, and XAD 7 as clean-up sorbents instead of PSA. Since tea includes a high amount of phenolic compounds which can cause interference in determination of pesticide residue, these polymeric resins may more effectively remove co-extracts from tea sample. In addition, to evaluate the effectiveness of adsorbents, recovery studies were carried out using these adsorbents and GC-MS analysis was carried out to evaluate the ability of these adsorbents to remove co-extracts.

2. EXPERIMENTAL SECTION

2.1. Chemicals

Acetonitrille, magnesium sulfate, sodium acetate, Dianon, PPVP, XAD7 and Polyamide were used (Sigma Aldrich, and Dr. Erhenstorfer, Germany). Pesticide standards used in this study were given in Table 2. Individual standard solutions 1000 mg/L were prepared in acetonitrile and further dilutions were made with acetonitrile. Black tea samples were purchased from a local market and were checked for existence of pesticides.

2.2. Extraction and Clean-up

The extraction was carried out according to BS EN 15662 “Foods of plant origin”. Multimethod was used for the determination of pesticide residues using GC- and LC-based analysis followed by acetonitrile extraction/partitioning and clean-up by dispersive SPE called “Modular QuEChERS-method”. A 2 g tea sample was weighed into 50 mL polypropylene centrifuge tube and 10 mL deionized water was added. After mixing and allowed to soak for 10 mins, 10 mL of acetonitrile was added and shaken vigorously for 15 mins using a shaker. Buffer salt mixtures (4 g of anhydrous magnesium sulfate, 1 g of sodium chloride, 1 g of trisodium citrate dihydrate, and 0.5 g of disodium hydrogen citrate sesquihydrate) was added and immediately shaken vigorously for 1 min by hand and centrifuged for 5 min at 4000 rpm. After centrifugation, 6 mL of the supernatant was taken into a 15-mL polypropylene tube, 450 mg sorbent and 900 mg magnesium sulfate were added and agitated for 1 minute.

In the clean-up step four polymeric resins namely, Dianon, Polyamide, PPVP and XAD-7 were used. PSA was used for comparison with the standard method. To avoid possible deviation which may come from the extraction process, spiking of standard pesticide solution to the samples were made after the extraction step and just before the clean-up process. After spiking of pesticide standard solutions, Dianon, Polyamide, PPVP, XAD-7 and PSA were added with magnesium sulfate as clean up reagent as described BS EN 15662 method. For each resin, two different concentrations and 6 replicates were performed. After centrifuging at 4000 rpm for 5 mins 1 mL supernatant were taken for LC-MS/MS analysis (API 4000 Q-TRAP).

2.3. LC-MS/MS analysis

For the liquid chromatographic analysis Shimadzu HPLC (UFLC LC-20AD) system was used. The chromatographic separation was achieved with inertsil 100 mm x 2,1 mm column with 3 µm particle size. The mobile phase A contained methanol/water (2+8, v/v) with 5 mmol/L ammonium formate and mobile phase B contained methanol/water (9+1, v/v) with 5 mmol/L ammonium formate. The gradient program was given at Table 1. A 10 µL of the sample was injected at a flow rate of 0.3 mL at 40 °C.

Table 1: LC flow program.

Time	%B
0 min	0
11 min	100
23 min	100
25 min	0
36 min	0

Determination of pesticides was achieved by Applied bio-system triple quadrupole mass spectrometer was operated in multiple reactions monitoring (MRM). The mass spectrometer ion source parameters were: curtain gas, ion source gas, temperature, and ion spray voltage were set to 20 mL/min, 50 mL/min, 550 °C, and 5500 V, respectively. Pesticide and their transitions ions used for the quantification, collision energy (CE), and de-clustering voltage (DP) are listed in Table 2.

Table 2: LC-MS/MS parameters of the pesticides.

Pesticide	Polarity	Q1 mass	Q3 mass	DP (v)	CE (v)
2 4 D	ESI -	219.0	160.9	20	15
2.4.5-T	ESI -	253.0	195	40	10
Acephate	ESI +	184.1	124.9	10	25
Acetamiprid	ESI +	223.0	126	61	27
Aclonifen	ESI +	265.0	182.1	55	40
Alachlor	ESI +	270.1	238.1	30	15
Atrazine	ESI +	216.1	174.0	71	25
Azoxystrobin	ESI +	404.1	371.9	36	20
Benalaxyl	ESI +	326.2	148.2	26	25
Benfluralin	ESI +	336.0	57	30	10
Bentazon	ESI -	239.1	132	51	30
Bifenazate	ESI +	299.0	253	40	10
Bitertanol	ESI +	338.2	70	5	25
Boscalid	ESI +	343.0	307	71	25
Bromacil	ESI +	261.0	205	21	20
Bromophos Ethyl	ESI +	394.9	338.7	51	25
Bromoxynil	ESI -	273.9	79	46	35
Bromuconazole	ESI +	378.0	159	46	35
Bupirimate	ESI +	317.1	166.1	31	33
Buprofezin	ESI +	306.2	201.2	6	15
Butacarboxim Sulfoxide	ESI +	207.1	131.9	41	10
Cadusafos	ESI +	271.1	159	66	20
Carbaryl	ESI +	202.1	144.9	66	15
Carbendazim	ESI +	192.1	160	56	25
Carbofuran	ESI +	222.1	165.1	46	10
Carbosulfan	ESI +	381.2	118.1	36	25
Carboxin	ESI +	236.1	142.9	26	21
Chlorfenvinphos	ESI +	358.9	155	36	20
Chlorfluazuron	ESI +	539.9	158	70	25
Chloridazon	ESI +	222	92.2	91	35
Chloroxuron	ESI +	291.1	72	51	40
Chlorpropham	ESI +	214	172	25	10
Chlorpyrifos	ESI +	349.9	96.9	21	41
Chlorpyrifos-Methyl	ESI +	321.9	125.1	25	27
Chlorsulfuron	ESI +	358	141	50	25
Chlorthamid	ESI +	205.9	118.9	35	55
Cinidon-Ethyl	ESI +	411.1	348	40	30
Clofentezine	ESI +	303.1	102.1	55	45
Cyazofamid	ESI +	325	108	36	20
Cyclanilide	ESI -	272	159.9	55	30
Cycloate	ESI +	216.1	154.3	56	10
Cymoxanil	ESI +	199.1	128	61	10
Cyproconazole	ESI +	292.1	70.2	15	35
Cyprodinil	ESI +	226.1	76.9	81	65
Deltamethrin	ESI +	522.9	280.7	16	25
Demeton S Methyl	ESI +	248	89.1	6	17
Demeton S Methyl Sulfoxide	ESI +	247	169	10	15
Desmedipham	ESI +	318.1	182.2	31	20
Di-Allate	ESI +	270	86.1	41	23
Diazinon	ESI +	305.1	169.1	20	30
Dichlofluanid	ESI +	350	223.9	20	40
Dichlorprop-P	ESI -	233.0	161	20	15
Dichlorvos	ESI +	220.9	127.1	71	27
Difenoconazole	ESI +	406.1	250.9	41	35
Dimethenamide	ESI +	276.1	244.1	11	20
Dimethoate	ESI +	230	125	31	10
Dimethomorph	ESI +	388.1	301.1	45	30

Pesticide	Polarity	Q1 mass	Q3 mass	DP (v)	CE (v)
Dimoxytrobin	ESI +	327	116	30	10
Diniconazole	ESI +	326	70	55	45
Dinobutan	ESI +	327	215	45	10
Dinoterb	ESI -	239.1	176	30	50
Diphenylamine	ESI +	170.1	93.1	66	35
Disulfoton	ESI +	275	89.2	10	10
Disulfoton Sulfone	ESI +	307	153	50	10
Disulfoton Sulfoxide	ESI +	291	213	30	10
Ditalimfos	ESI +	300	130	35	10
Dithianion	ESI +	296	264	50	25
Diuron	ESI +	233	72	65	30
Epoxiconazole	ESI +	330.1	121	36	25
Eptc	ESI +	190.1	128.1	46	15
Esfenvalerat	ESI +	437.1	125	25	50
Ethiofencarb	ESI +	226.1	107.2	41	20
Ethion	ESI +	385	199.1	15	20
Ethirimol	ESI +	210.2	98.1	86	35
Ethofumesate	ESI +	304.1	121.1	35	25
Ethoprophos	ESI +	243	131	20	30
Ethoxyquin	ESI +	218.2	160.2	66	45
Etoxzole	ESI +	360.2	141	65	40
Etrimfos	ESI +	293.1	125	25	35
Famoxodane	ESI +	392.2	238	16	25
Fenamidone	ESI +	312.1	92.2	40	35
Fenamiphos	ESI +	304.1	217.1	40	30
Fenarimol	ESI +	331	81	45	45
Fenazaquin	ESI +	307.2	161.2	51	30
Fenbuconazole	ESI +	337.1	125.1	41	40
Fenhexamid	ESI +	302.1	97.2	90	35
Fenitrothion	ESI +	278.1	125	41	30
Fenoxaprop-Ethyl	ESI +	362.1	288.1	45	23
Fenoxycarb	ESI +	302.1	88	66	30
Fenpropatrin	ESI +	350.2	125.1	41	20
Fenpropimorph	ESI +	304.3	147.1	45	40
Fenthion	ESI +	279.1	169.1	20	25
Fenvalerate	ESI +	437.1	125	35	55
Flazasulfuron	ESI +	408.1	182.1	40	25
Fluazifop-P-Butyl	ESI +	384.1	282.1	50	27
Fludioxinil	ESI -	247	125.9	56	40
Flufenacet	ESI +	364.1	194.2	10	17
Flufenoxuron	ESI +	489	158.1	85	30
Fluopicolide	ESI +	383	109	35	10
Flurochloridone	ESI +	312	291.9	60	30
Flurtamone	ESI +	334.1	247.1	50	30
Flusilazole	ESI +	316.1	247.1	36	25
Flutolanil	ESI +	324.1	262.1	86	25
Foramsulfuron	ESI +	453.1	182.2	50	25
Fosthiasate	ESI +	284	104.1	61	27
Furathiocarb	ESI +	383.2	195	50	23
Heptenophos	ESI +	251	127	35	20
Hexaconazole	ESI +	314.1	70.1	35	40
Hexythiazox	ESI +	353.1	227.9	65	20
Imazalil	ESI +	297	158.9	25	30
Imazamox	ESI +	306	246	30	10
Indoxacarb	ESI +	528.1	203	75	50
Iprodione	ESI -	328	141.1	5	10
Iprovalicarb	ESI +	321.2	119	46	23
Isoproturon	ESI +	207.1	165.2	46	20
İmazaquin	ESI +	312.1	199.1	45	35

Pesticide	Polarity	Q1 mass	Q3 mass	DP (v)	CE (v)
İmidachloprid	ESI +	256.1	175	45	25
İoxynil	ESI -	369.8	126.8	45	35
İsoxaben	ESI +	333	150	40	30
Lambda Cyhalothrin	ESI +	467.1	225	16	23
Malathion	ESI +	331	99	17	30
Mcpa	ESI -	199	140.8	45	20
Mecarbam	ESI +	330	227	25	15
Mecoprop-P	ESI -	213	140.7	50	15
Mepanipyrim	ESI +	224.1	77	41	10
Mesosulfuron Methyl	ESI +	504.1	182.1	60	33
Metalaxyl-M	ESI +	280.1	220	45	19
Metazachlor	ESI +	278.1	210.1	5	15
Methacrifos	ESI +	241	209.1	31	15
Methamidophos	ESI +	142	124.9	25	20
Metolachlor	ESI +	284	252	25	30
Metosulam	ESI +	418	175.1	26	25
Metribuzin	ESI +	215.1	187.2	61	25
Mevinphos	ESI +	225	193.1	30	10
Molinate	ESI +	188.1	83.2	20	25
Monocroptos	ESI +	224.1	127	46	21
Monolinuron	ESI +	215.1	125.9	51	25
Monuron	ESI +	199.1	72	51	29
Myclobutanil	ESI +	289.1	70.1	35	30
Nuarimol	ESI +	315	81.1	40	40
Omethoate	ESI +	214.1	109	46	35
Oxadiargyl	ESI +	341	223	25	10
Oxadiazon	ESI +	362.1	220	40	30
Oxadixyl	ESI +	279.1	219.2	45	25
Oxamyl	ESI +	237.1	90	20	15
Oxasulfuron	ESI +	407.1	150.1	55	25
Oxycarboxin	ESI +	268	175.1	35	20
Oxyflourfen	ESI +	379	316	20	25
Penconazole	ESI +	284.1	158.9	41	40
Pendimethalin	ESI +	282.1	212.2	5	15
Permethrin	ESI +	408.1	153.1	30	25
Pethoxamid	ESI +	296	250	15	10
Phenmedipham	ESI +	301.1	136.1	56	25
Phenthoate	ESI +	321	163.1	36	17
Phorate	ESI +	278.1	74.9	5	23
Phosalon	ESI +	367.9	182	50	20
Phosmet	ESI +	317.9	160.1	30	20
Phosphamidon	ESI +	300	127.1	35	25
Picloram	ESI -	240.9	196.9	66	15
Picolinafen	ESI +	377.1	145	56	70
Primicarb	ESI +	239.1	72.1	15	30
Primiphos-Methyl	ESI +	306.1	164.1	25	30
Prochloraz	ESI +	376	308	15	15
Profenofos	ESI +	372.9	302.9	55	25
Prometyrn	ESI +	242.1	158.1	30	30
Propamocarb Hydrochloride	ESI +	189.2	102	51	10
Propanil	ESI +	218	162	56	10
Propargite	ESI +	368.1	175.1	5	20
Propham	ESI +	180.1	138.1	31	10
Propiconazole	ESI +	342.1	69.1	45	33
Propyzamide	ESI +	256	173.1	35	30
Prothiophos	ESI +	344.9	240.9	40	27
Pymetrozine	ESI +	218.1	105	76	10
Pyraclostrobin-	ESI +	388.1	194	5	20
Pyrazophos	ESI +	374.1	222.1	60	30

Pesticide	Polarity	Q1 mass	Q3 mass	DP (v)	CE (v)
Pyridaben	ESI +	365.1	309.1	26	20
Pyridaphention	ESI +	341	189	45	30
Pyridate	ESI +	379.1	207.1	5	20
Pyrimethanil	ESI +	200.1	106.9	50	30
Pyriproxyfen	ESI +	322.1	96.2	15	20
Quinalphos	ESI +	299	163	20	30
Quinoxyfen	ESI +	307.9	162	20	60
Quizalofop Ethyl	ESI +	373.1	298.9	70	25
Resmethrin	ESI +	356.2	171.2	20	20
Rimsulfuron	ESI +	432.1	182	46	30
Simazine	ESI +	202.1	132.2	66	10
Spiroxamine	ESI +	298.3	144.2	40	30
Sulfosulfuron	ESI +	471.1	261	10	25
Taufluvalinate	ESI +	520.1	208.1	30	23
Tebuconazole	ESI +	308.1	70	20	40
Tepp	ESI +	291.1	179	45	25
Terbufos	ESI +	289	57.1	30	35
Terbumeton	ESI +	226.1	170.2	25	25
Terbuthylazine	ESI +	230.1	174.1	40	20
Terbutryn	ESI +	242.1	186.1	20	25
Tetrachlorvinphos	ESI +	366.9	127.1	46	21
Thiacloprid	ESI +	253	126	81	30
Thiamethoxam	ESI +	292	211	50	15
Thiamethoxam	ESI +	292	211	40	25
Thifensulfuron Methyl	ESI +	388	167	35	20
Thiodicarb	ESI +	355	88	26	20
Thiophanate Methyl	ESI +	343	151	26	25
Tolclophos-Methyl	ESI +	301	175	46	35
Tolylfluanid	ESI +	364	237.9	6	20
Triadimefon	ESI +	294	197.2	36	20
Triadimenol	ESI +	296.1	70.1	10	20
Tri-Allate	ESI +	304	142.9	40	35
Triasulfuron	ESI +	402.1	167.1	46	25
Triazophos	ESI +	314	119.1	36	50
Tribenuron Methyl	ESI +	396.1	155	50	20
Trichlorfon	ESI +	274	108.9	10	30
Tridemorph	ESI +	298.3	116.1	55	30
Trifloxystrobin	ESI +	409.1	186.1	10	25
Triflumizole	ESI +	346	278	10	15
Triticonazole	ESI +	318.1	70.2	35	35
Zoxamide	ESI +	336	159	40	15

2.4. Recovery

To evaluate the effectiveness of the sorbent, pesticide standard solutions tea samples were spiked at two different concentration levels, viz. 10 and 100 µg/kg and analyzed with the method which was described in sample preparation above. Standard solutions were added just before the clean-up step to eliminate possible deviation coming from extraction step. Four different sorbents, namely Dianon, Polyamide, PPVP, and XAD, were used as clean-up sorbents and PSA was used as the control group. Pesticide standard solutions were added to the samples at 10 and 100 µg/kg levels. After analyzing samples with LC-MS/MS, recovery% values were calculated according to Equation 1.

$$Recovery\,(\%) = \left(\frac{C_1}{C_2}\right) \times 100 \quad \text{(Eq. 1)}$$

2.5. Matrix Effect

In order to see the effectiveness of these 4 different adsorbents in eliminating the co-extracts, the blank tea extracts, which were clean-up with these adsorbents, were analyzed by GC-MS. GC-MS analyses were carried out in total ion mode to see the composition of co-extracts. GC/MS analyses were carried out using a capillary HP-50 column (50% phenyl-methyl polysiloxane, with 30 m length, 0.25 ID and 0.25 µm film thickness). Oven program of gas chromatography are given in Table 3.

Table 3: Gas Chromatography Oven Program.

Initial Temp.(°C)	Rate (°C/Min)	Last Temp.(°C)	Hold (min)
50	-	50	4
50	5	260	4

3. RESULTS AND DISCUSSION

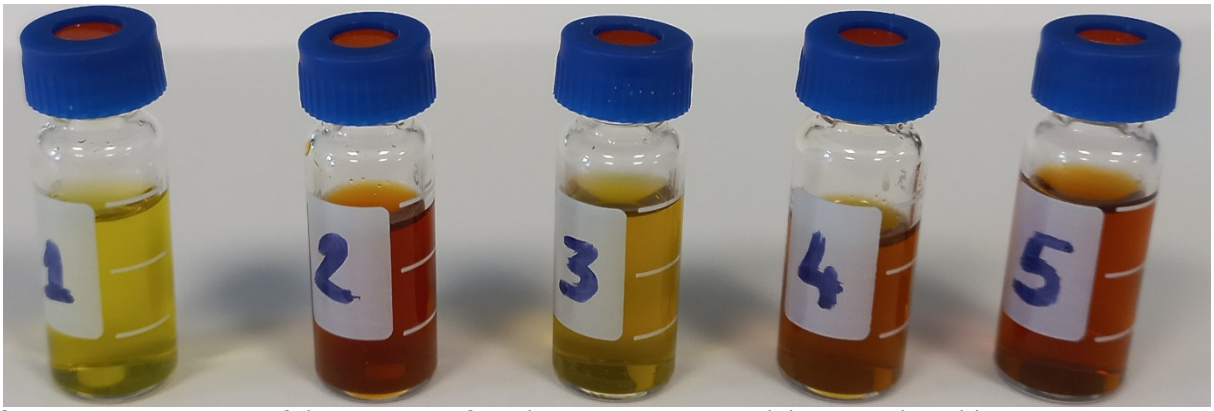

Figure 1: Appearance of the extracts after clean-up 1: PSA, 2: Diaion, 3: Polyamide, 4: PPVP, 5: XAD 7.

After clean-up process, samples were analyzed with LC-MS/MS. In the spiking solution, 216 pesticides were included. After clean up process appearance of the tea extracts were shown in Figure 1. It was observed that both PSA and polyamide could better in removing the color of the tea extract than the rest of the sorbents. For the determination of these 216 pesticides matrix, matched calibrations were used. Matrix matched calibrations were prepared for each resin with using the same resin. Recovery studies were performed with each resin in six replicates at 10 and 100 µg/kg. The recovery values for each pesticide were given in Table 4. Also, the recovery ratios for each resins were summarized in Table 5 and Figure 2. For both concentration levels, similar recovery results were obtained.

Table 4: Recovery ratios for each resins.

Recovery%	PSA	Diaion	Polyamide	PPVP	XAD
<60	41	12	23	17	22
60 - 80	9	9	9	4	4
80 - 120	135	130	84	86	99
120 - 140	11	27	77	62	56
>140	20	38	23	47	35
Total	216	216	216	216	216

According to the recovery results, it was observed that the PSA was the best with 135 pesticides in the generally accepted range of 80-120%. After PSA, Diaion was determined as the second with 130 pesticides in the range of 80-120%. Polyamide and PPVP were at the bottom with 84 and 86 pesticides, respectively, in the range of 80 - 120%, while XAD differentiated with 99 pesticides both from PSA and Diaion, and from Polyamide and PPVP. On the other hand, if we select the acceptable limit as 60-140%, polyamide was determined as the resin that gave the best results with 170 pesticides. While Diaion was the second resin with 166 pesticides, XAD, PSA and PPVP were determined as the third, fourth and fifth resins with very close values 159, 155 and 152 pesticides, respectively. It is noteworthy that PSA is determined as the third resin when the acceptable range is referred to as 60-140%. Another remarkable point is that 41 pesticides give a recovery value of less than 60% when PSA was used as clean-up resin. These results are compatible with previously published reports indicative of recoveries of some pesticides were adversely affected by PSA (21). Especially pesticides those containing the P=O group tend to be adsorbed to PSA. On the other hand, 12 pesticides gave a recovery value of less than 60% when Diaion was used as clean-up resin. Although polymeric adsorbents are widely used in the purification of bioactive compounds from tea, they have not been used as a stand-alone cleaning agent in pesticide analysis before. However, some studies have been conducted in which PVPP is used as a clean-up agent in combination with different adsorbents. Jiao and et al. (2016) have developed a

method for the determination of eight pesticide residues with LC–MS/MS, combining a QuEChERS method using PVPP and GCB clean-up with a dilution factor of 400 method in order to diminish the complex and varied matrix interference due to co-extracted from tea. They found average recoveries of eight neonicotinoid insecticides ranged from 66.3 to 108.0% (22). Cao et al. (2015) have developed a method based on matrix solid phase dispersion for the determination and the quantification of 16 pesticides in various tea samples by using PVPP (750 mg), PSA (1 g) and GCB (50 mg) as clean-up sorbent. The recoveries of this method at three spiked concentration levels ranged from 87.7 to 99.6% (14). Hou et al.(2022) developed a method to scan for 134 pesticide residues in tea was developed that employs a novel Multi-Functional Filter (MFF) contained a mixture of 50 mg of PSA, 10 mg of GCB, 150 mg of porous PVPP, and 150 mg of anhydrous $MgSO_4$. They calculated recoveries at two spiked levels (50, 100 µg/kg) ranged between 66.83–118.33%. They reported that purification through the multi-function filter (MFF-3-Layered) reduced the matrix effect more than purification via the modified QuEChERS method (17). Although polymeric adsorbents were used in combination with other adsorbents in these studies, similar results were obtained in our study when they were used alone.

In order to evaluate the clean up efficiency of the adsorbent, gas chromatography mass spectrometry analyses were carried out. Blank tea extracts were analyzed with GC-MS after clean up with these adsorbents. Total ion chromatograms of each extracts were taken to evaluate removal efficiency of co-extracts. Chromatograms were given in Figure 3. As a result of GC MS analysis, it was observed that PSA gave the chromatogram with the least amount of co-extracts. On the other hand, it was observed that PSA was the worst adsorbent in removing caffeine, which is one of the main bioactive compound in tea. XAD-7 and polyamide were found to be the best adsorbents in removing caffeine. PSA was, as expected, very effective in removing the fatty acids. While no fatty acids were found in the extracts cleaned with PSA, fatty acids were detected in the extracts cleaned with other adsorbents. PPVP was found to be insufficient in removing both caffeine and fatty acids.

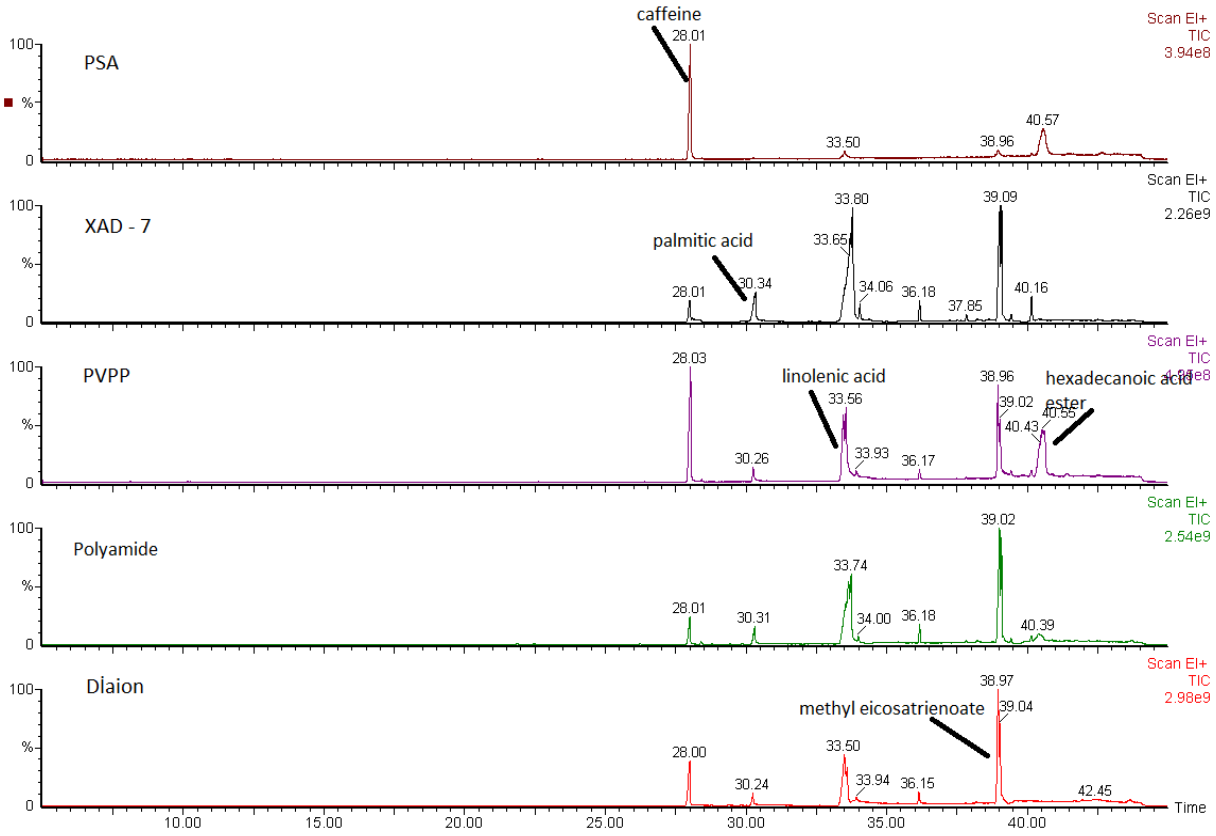

Figure 2: GC-MS chromatogram of tea extracts after clean up.

Table 5: Recovery values of the pesticides.

	Recovery %				
Pesticide	**Dianon**	**PPVP**	**PSA**	**PA**	**XAD**
2 4 D	<0.01	289	40.85	308	<0.01
2.4.5-T	117	68	<0.01	64	105

Pesticide	Recovery % Dianon	PPVP	PSA	PA	XAD
Acephate	204.5	114.5	76.5	102	103.5
Acetamiprid	62	157.5	367.5	114	129.5
Aclonifen	95.5	186.5	<0.01	128	40.95
Alachlor	110.5	125.5	100	119.5	124.5
Atrazine	112.5	107.5	99.5	103.5	124
Azoxystrobin	319.5	171	391	415	426.5
Benalaxyl	107.5	117.5	97	128	117
Benfluralin	510	458	<0.01	<0.01	<0.01
Bentazon	113.5	54.5	83.5	100.5	108.5
Bifenazate	130.5	132.5	113	70	114.5
Bitertanol	98	106	92.5	132	115
Boscalid	93.5	134	96	117.5	139.5
Bromacil Pztf	94	119	122.5	98	78
Bromophos Ethyl	151.5	100	90	123.5	116
Bromoxynil	99.5	48.05	40.55	90	106.5
Bromuconazole	43.85	107.5	105	<0.01	111
Bupirimate	103.5	133	100.5	128.5	113
Buprofezin	89	112	92.5	112.5	115.5
Butacarboxim Sulfoxide	112.5	129	90.5	116.5	129.5
Cadusafos	119	125.5	101	138.5	146.5
Carbaryl	130	102.5	117	117.5	110
Carbendazim	131	118	208.5	186.5	89
Carbofuran	112	129	116	123	130.5
Carbosulfan	<0.01	105	101.5	88.5	187
Carboxin	101	110.5	99	113.5	109.5
Chlorfenvinphos	99.5	120.5	108	121.5	116
Chlorfluazuron	54.5	129	101	117.5	102
Chloridazon	89.5	91	71	185.5	140
Chloroxuron	106	119.5	102	120.5	104
Chlorpropham	126	139.5	131	<0.01	156
Chlorpyrifos	103	123.5	<0.01	145	119.5
Chlorpyrifos-Methyl	123	123	116	137.5	130
Chlorsulfuron	119	<0.01	22.3	126	123.5
Chlorthamid	286.5	<0.01	70.5	41.8	122.5
Cinidon-Ethyl	110.5	114	103	115.5	124.5
Clofentezine	48.25	128	89.5	117	112.5
Cyazofamid	127.5	130	108	120	127.5
Cyclanilide	113.5	42.9	19.75	63.5	95.5
Cycloate	100.5	119	102.5	127	130.5
Cymoxanil	119.5	66.5	108.5	138.5	84.5
Cyproconazole	128	114	111	108.5	141
Cyprodinil	90	117	99.5	142.5	127.5
Deltamethrin	75.5	90.5	110	137.5	123.5
Demeton S Methyl	228.5	1725	<0.01	148	237
Demeton S Methyl Sulfoxide	105	<0.01	<0.01	140	153.5
Desmedipham	106.5	110.5	106.5	113.5	110
Di-Allate	100	112.5	103	124	107.5
Diazinon	106.5	123.5	102	125	115
Dichlofluanid	404.5	405.5	128	<0.01	415
Dichlorprop-P	115	85.5	10.75	86	94.5
Dichlorvos	203.5	161	<0.01	75.5	207
Difenoconazole	94	115	92	124	118.5
Dimethenamide	113.5	116	100	115.5	116.5
Dimethoate	65.5	132	96	113.5	58
Dimethomorph	112	120.5	102	116.5	110
Dimoxytrobin	277	350	415	160	302.5
Diniconazole	105.5	102.5	89	119.5	114
Dinobutan	433	500	<0.01	<0.01	<0.01

Pesticide	Recovery % Dianon	PPVP	PSA	PA	XAD
Dinoterb	106	97.5	75	112.5	107
Diphenylamine	106	113.5	127	122.5	113.5
Disulfoton	465.5	494.5	<0.01	<0.01	431.5
Disulfoton Sulfone	150.5	158.5	115.5	129.5	144.5
Disulfoton Sulfoxide	<0.01	<0.01	<0.01	153.5	<0.01
Ditalimfos	111.5	127	93.5	122.5	122.5
Dithianion	95.5	1155	104	72	35.35
Diuron	113	115	107	103.5	113
Epoxiconazole	181	190	124.5	<0.01	193
Eptc	110.5	121.5	152.5	139	115.5
Esfenvalerat	137	170.5	<0.01	104	105.5
Ethiofencarb	126.5	120.5	102	119.5	123.5
Ethion	<0.01	<0.01	300.5	<0.01	61
Ethirimol	91.5	131	106	112.5	136.5
Ethofumesate	137.5	144	<0.01	117.5	152.5
Ethoprophos	166.5	720	94	91	<0.01
Ethoxyquin	100.5	114	97.5	110.5	100
Etoxzole	87.5	130.5	93	126.5	116
Etrimfos	108	146.5	105.5	126.5	129.5
Famoxodane	138	178	474.5	325	389.5
Fenamidone	111.5	127	101.5	116.5	121
Fenamiphos	118	114.5	101.5	119.5	117.5
Fenarimol	113.5	107	116	104	116
Fenazaquin	315	321.5	<0.01	<0.01	446
Fenbuconazole	104	129.5	106.5	118.5	121
Fenhexamid	119.5	111.5	94.5	115.5	128.5
Fenitrothion	226	319	100	<0.01	435
Fenoxaprop-Ethyl	98	117.5	99	119	118
Fenoxycarb	115.5	135.5	109.5	122.5	149.5
Fenpropatrin	109.5	145	112.5	127	131.5
Fenpropimorph	110	119	99	115.5	113
Fenthion	111	181	<0.01	133	<0.01
Fenvalerate	137	170.5	145.5	104	105.5
Flazasulfuron	119.5	103.5	37.5	106	109
Fluazifop-P-Butyl	122.5	118.5	97.5	123	117.5
Fludioxinil	118	111.5	107	110.5	108.5
Flufenacet	113	123	103.5	122	128.5
Flufenoxuron	112.5	129	104	120	105.5
Fluopicolide	116	121	112	119	118
Flurochloridone	117.5	113.5	114.5	128.5	120
Flurtamone	389.5	<0.01	349	<0.01	89.5
Flusilazole	113.5	113	103.5	120.5	119.5
Flutolanil	119.5	111	108	118.5	127.5
Foramsulfuron	144.5	94	<0.01	<0.01	57.5
Fosthiasate	114.5	127	111.5	110	112
Furathiocarb	101.5	118.5	98	126	116
Heptenophos	116	185.5	158.5	96.5	133.5
Hexaconazole	116.5	103.5	105.5	108.5	122.5
Hexythiazox	74	131	95.5	126	113.5
Imazalil	106	103.5	80.5	140	117
Imazamox	<0.01	98	2.79	61	4.74
Indoxacarb	117	103.5	109.5	154.5	180
Iprodione	134.5	233	102	113.5	74
Iprovalicarb	117.5	123.5	100.5	117.5	115.5
Isoproturon	113.5	113.5	109.5	116	127.5
İmazaquin	296	<0.01	123	<0.01	965
İmidachloprid	133.5	115	96	126.5	79.5
İoxynil	109	36.45	53	78.5	110

	Recovery %				
Pesticide	**Dianon**	**PPVP**	**PSA**	**PA**	**XAD**
Isoxaben	111	130.5	102.5	113	103
Lambda Cyhalothrin	89	111.5	121.5	126	159.5
Malathion	162.5	144	100.5	<0.01	121.5
Mcpa	120.5	74.5	9.45	76	90.5
Mecarbam	119.5	123	100	124	127
Mecoprop-P	110	102	9.35	91	95
Mepanipyrim	118	128	92.5	111	105
Mesosulfuron Methyl	141.5	126	71	133.5	80.5
Metalaxyl-M	114.5	123.5	109	122.5	114.5
Metazachlor	112.5	116.5	105.5	115	124
Methacrifos	148.5	173	164	137	166
Methamidophos	158.5	221	78.5	176.5	107.5
Metolachlor	<0.01	<0.01	41.75	245	<0.01
Metosulam	106	126	36.5	128	117.5
Metribuzin	70	177.5	109	75.5	101.5
Mevinphos	91.5	63.5	645	116.5	<0.01
Molinate	97.5	121.5	101.5	120.5	117.5
Monocroptos	125	123.5	102.5	119	118
Monolinuron	106.5	125	115.5	119.5	115.5
Monuron	110	107.5	107.5	126	120.5
Myclobutanil	472	468	114	1445	122.5
Nuarimol	79.5	103	104	119.5	115.5
Omethoate	107.5	155.5	84	120.5	97.5
Oxadiargyl	239	163.5	141.5	197	99
Oxadiazon	96.5	107.5	103.5	129.5	124.5
Oxadixyl	119	108.5	106.5	128.5	112.5
Oxamyl	92	117.5	125	107	108.5
Oxasulfuron	114.5	109	54.5	117.5	103
Oxycarboxin	135.5	84.5	101	131	147.5
Oxyflourfen	99	<0.01	116.5	525	164.5
Penconazole	104	126.5	113	123.5	116
Pendimethalin	87	115	0.04105	112	0.112
Permethrin	82	106	42.35	142.5	0.635
Pethoxamid	31.7	400	163	<0.01	27.6
Phenmedipham	104.5	110.5	105.5	116	110.5
Phenthoate	159	117.5	113	144	125
Phorate	104	127	98	122.5	117
Phosalon	116	116	115.5	113.5	130.5
Phosmet	106.5	116	99.5	128	115.5
Phosphamidon	95.5	117.5	105.5	132	58
Picloram	145.5	153	82.5	165	132
Picolinafen	99	117	104	123	114.5
Primicarb	109	125	102	124.5	128.5
Primiphos-Methyl	99.5	131.5	99	123.5	120
Prochloraz	107.5	116.5	94.5	122.5	108.5
Profenofos	83	126.5	101.5	116	137
Prometyrn	109	125.5	98	125	117
Propamocarb Hydrochloride	113	124.5	63	138	99.5
Propanil	88.5	145.5	92	113.5	124.5
Propargite	103	127	<0.01	114.5	124.5
Propham	118	125	129	120	145.5
Propiconazole	112.5	109.5	102.5	102.5	133.5
Propyzamide	129	107.5	101.5	107	154
Prothiophos	455.5	570	<0.01	138.5	111
Pymetrozine	6.3	181.5	<0.01	7800	126
Pyraclostrobin-	198	183	145.5	133.5	224
Pyrazophos	107	113.5	105	129.5	130.5
Pyridaben	87	104.5	124.5	115.5	101.5

	Recovery %				
Pesticide	**Dianon**	**PPVP**	**PSA**	**PA**	**XAD**
Pyridaphention	107	120	113.5	115.5	119.5
Pyridate	81.5	96	57	116	97.5
Pyrimethanil	107.5	120.5	104	124	112.5
Pyriproxyfen	80	118.5	101.5	122	113.5
Quinalphos	103.5	121.5	104.5	129	110
Quinoxyfen	64	107	113.5	145	<0.01
Quizalofop Ethyl	89.5	119.5	98	126.5	129.5
Resmethrin	84	98	74	90	98.5
Rimsulfuron	123	119	30.8	131.5	112.5
Simazine	440	321	359	427	360
Spiroxamine	109	98	92	115.5	114
Sulfosulfuron	385	<0.01	53.5	<0.01	417
Taufluvalinate	75	117	<0.01	133	123
Tebuconazole	98.5	120.5	107.5	124.5	105.5
Tepp	355	<0.01	430	<0.01	625
Terbufos	108.5	131.5	100	139.5	130.5
Terbumeton	110.5	119.5	105	119	121
Terbuthylazine	113	129.5	101	134	112
Terbutryn	98	124.5	94	123.5	113
Tetrachlorvinphos	125	130	104.5	131	101
Thiacloprid	188	200	77.5	95	166
Thiamethoxam	<0.01	<0.01	<0.01	<0.01	131.5
Thifensulfuron Methyl	132.5	142	43.75	124	<0.01
Thiodicarb	128	129.5	111.5	110	128
Thiomethoxam	309	580	330	<0.01	477.5
Thiophanate Methyl	98.5	423.5	102.5	<0.01	133.5
Tolclophos-Methyl	129.5	119.5	120.5	137	<0.01
Tolylfluanid	122	135.5	105.5	135	123.5
Triadimefon	132	120.5	98.5	119	<0.01
Triadimenol	141.5	122.5	112	124	<0.01
Tri-Allate	78.5	153	106.5	98.5	138
Triasulfuron	119.5	130	58.5	125	124.5
Triazophos	282	261.5	<0.01	<0.01	320
Tribenuron Methyl	111	107	80	98.5	93
Trichlorfon	357.5	462	436.5	615	399.5
Tridemorph	117.5	109	99.5	119.5	115
Trifloxystrobin	114	119	96	119	109.5
Triflumizole	107	121	98.5	127	131.5
Triticonazole	133	111.5	106.5	119.5	128.5
Zoxamide	237	<0.01	333.5	<0.01	350

4. CONCLUSION

In this study, the suitability of 4 polymeric resins, namely; Diaion, Polyamide, PPVP and XAD 7 as a clean-up reagent for determination of pesticide residues in tea. In addition, a clean-up process was performed using PSA to compare with the standard method. In order to evaluate the effectiveness of the sorbents, recovery studies were carried out and compared with the recovery study carried out with PSA. According to the recovery results, it was observed that the PSA was the best with 135 pesticides in the generally accepted range of 80-120%. After PSA, Diaion was determined as the second with 130 pesticides in the range of 80-120%. On the other hand, when the acceptable limit was accepted as 60-140%, it was determined that the resin that gave the best results with 170 pesticides was polyamide. Diaion was the second resin with 166 pesticides, while XAD, PSA and PPVP were determined as the third, fourth and fifth resins with very close values of 159, 155 and 152 pesticides, respectively. According to GC-MS total ion analysis of blank tea extracts cleaned with these adsorbents, it was observed that PSA gave the chromatogram with the least co- extract, while it was observed that PSA was the worst adsorbent in removing caffeine, one of the main bioactive compounds in tea. XAD-7 and polyamide were found to be the best adsorbents in removing caffeine. According to result of this study, it was evaluated that the use of polyamide together with PSA as a clean-up reagent for pesticide analysis in tea would be the most effective method for removing both fatty acids and bioactive components in tea.

5. CONFLICT OF INTEREST

Author have no conflict of interest.

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